

# Multiple Metal–Carbon Bonds. 7.<sup>1</sup> Preparation and Characterization of $Ta(\eta^5-C_5H_5)_2(CH_2)(CH_3)$ , a Study of Its Decomposition, and Some Simple Reactions

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**Abstract:** Two moles of thallium cyclopentadienide react with  $MMe_3Cl_2$  to give  $MCp_2Me_3$  ( $M = Nb$  or  $Ta$ ). Trityl tetrafluoroborate attacks the central methyl group in  $TaCp_2Me_3$  selectively to give  $Ph_3CMe$  and  $[TaCp_2Me_2]^+BF_4^-$ .  $Me_3P=CH_2$  (and other bases) deprotonate  $[TaCp_2Me_2]^+BF_4^-$  to give  $TaCp_2(CH_2)(CH_3)$ ;  $k_H/k_D$  for this reaction is  $3.4 \pm 0.3$ . The methylene ligand in pseudotetrahedral  $TaCp_2(CH_2)(CH_3)$  is oriented perpendicular to the C–Ta–C plane and does not rotate readily on the <sup>1</sup>H NMR time scale ( $\Delta G^\ddagger \geq 20$  kcal mol<sup>-1</sup>) for the same reason that ethylene in  $TaCp_2(CH_2CH_2)(CH_3)$  does not rotate readily on the chemical time scale; there is no  $\pi$  orbital perpendicular to the one used to  $\pi$  bond to each which can assist this rotation. The methylene carbon atom is nucleophilic;  $TaCp_2(CH_2)(CH_3)$  reacts with  $AlMe_3$ ,  $Me_3SiBr$ , and  $CH_3I$  to give  $TaCp_2(CH_2AlMe_3)(CH_3)$ ,  $[TaCp_2(CH_2SiMe_3)(CH_3)]^+Br^-$ , and  $TaCp_2(CH_2CH_2)I$ , respectively.  $TaCp_2(CH_2AlMe_3)(CH_3)$  also forms in the reaction between  $TaCp_2Me_3$  and  $AlMe_3$ , and loses  $AlMe_3$  to bases such as  $NEt_3$ .  $TaCp_2(CH_2)(CH_3)$  decomposes at a rate which is second order in Ta ( $k_{30^\circ C} = 3 \pm 1 \times 10^{-5}$  l mol<sup>-1</sup> s<sup>-1</sup>). In the presence of  $PMe_3$  the decomposition rate is again second order in Ta ( $k_{30^\circ C} = 3.1 \pm 0.3 \times 10^{-5}$  l mol<sup>-1</sup> s<sup>-1</sup>;  $k_{60^\circ C} = 5.4 \pm 0.4 \times 10^{-4}$  l mol<sup>-1</sup> s<sup>-1</sup>) and zero order in  $PMe_3$ . The products of the decomposition in the absence of L ( $L = C_2D_4$ , CO,  $PMe_3$ ) are  $TaCp_2(CH_2CH_2)(CH_3)$  (0.5 per Ta) and a complex mixture of unidentified diamagnetic species; no methane evolves. In the presence of L they are  $TaCp_2(CH_2CH_2)(CH_3)$  (0.5 per Ta) and  $TaCp_2(L)(CH_3)$  (0.5 per Ta).  $TaCp_2(CH_2)(CH_3)$  reacts with neat  $Me_3P=CH_2$  at a rate which is pseudo-first-order in Ta ( $k_{22^\circ C} = 8.2 \pm 0.3 \times 10^{-6}$  s<sup>-1</sup>) to give  $TaCp_2(CH_2CH_2)(CH_3)$  and  $PMe_3$ .

## Introduction

A major discovery in organo-transition metal chemistry in the past decade is the class of "carbene" complexes "stabilized" by at least one heteroatom (usually O, N, or S) bound directly to the carbene's  $\alpha$ -carbon atom.<sup>3</sup> "Unstabilized carbene complexes", or what might better be called alkylidene complexes,<sup>4</sup> however, were virtually unknown before 1973<sup>5</sup> when Casey<sup>6</sup> prepared  $(CO)_5WC(C_6H_5)_2$  and Giering<sup>7a</sup> isolated  $Fe(\eta^5-C_5H_5)(CO)_2(\text{benzocyclobutenylidene})$ .<sup>7b</sup> A few other examples of disubstituted methylene complexes have been reported since then.<sup>8</sup>

A monosubstituted methylene complex was discovered in 1974<sup>9</sup> by a reaction which might be viewed as deprotonation of a primary alkyl's  $\alpha$ -carbon atom.<sup>10</sup> This set the stage for preparation of an unsubstituted methylene complex,  $Ta(\eta^5-C_5H_5)_2(CH_2)(CH_3)$ ,<sup>11</sup> shortly thereafter. This is the first isolable transition metal methylene complex. In this paper we report the full details of its preparation, how it decomposes, and how it reacts with selected electrophiles, nucleophiles, and  $\pi$ -acid ligands like CO,  $PMe_3$ , and ethylene.

## Results

**Preparation of Methyl Complexes.**  $TaMe_3Cl_2$  was first prepared in 1964 by reacting 1.5 mol of  $ZnMe_2$  with sublimed  $TaCl_5$  in pentane.<sup>12</sup> A somewhat more convenient, high-yield method of preparing  $TaMe_3Cl_2$  from  $ZnMe_2$  in ether (which is prepared as needed from  $ZnCl_2$  and  $LiMe$ ) is reported here. This volatile, monomeric, pale yellow, pyrophoric compound is slightly unstable thermally but has been well characterized and used by several workers in the past few years to prepare Ta complexes such as  $TaMe_5$ ,<sup>13</sup>  $Ta(\eta^8-C_8H_8)Me_3$ ,<sup>14</sup> or  $Ta(\text{acac})_2Me_3$ .<sup>15</sup> It also reacts smoothly and rapidly with 1 mol of  $TiC_5H_5$  to give orange  $TaCpMe_3Cl$ .<sup>16</sup>  $TaCpMe_3Cl$  is significantly more stable thermally than  $TaMe_3Cl_2$  though not indefinitely at 25 °C under  $N_2$ ; it is best stored at -30 °C. Its <sup>1</sup>H NMR spectrum in  $C_6D_6$  shows only one peak for the three methyl groups. Therefore, if its structure is tetragonal pyramidal with an  $\eta^5-C_5H_5$  ligand at the apex, a common geometry for monocyclopentadienyl complexes,<sup>17</sup> then it must be fluxional in solution at 25 °C.<sup>18</sup>

A second cyclopentadienyl group can be added to  $TaCpMe_3Cl$  to give  $TaCp_2Me_3$  using  $TiC_5H_5$  in toluene or lithium or sodium cyclopentadienide in THF at -78 °C.  $TaCp_2Me_3$  and  $Ta(\eta^5-C_5H_4Me)_2Me_3$  can also be prepared directly from  $TaMe_3Cl_2$  (though considerably less cleanly) using lithium or sodium reagents.  $TaCp_2Me_3$  is also not indefinitely stable at 25 °C under  $N_2$ . On heating in vacuo it begins to sublime slowly, then turns pale purple and suddenly decomposes, giving only methane (1.5–2.0 mol) and a paramagnetic red oil. On heating a 250-mg sample of  $TaCp_2(CD_3)_3$  in 5 mL of  $C_6D_6$  at 125 °C for 16 h 1.8 mol per Ta of methane evolved which was almost all  $CD_3H$  (10%  $CD_4$ , 87%  $CD_3H$ , ~0%  $CD_2H_2$ , 2%  $CDH_3$ , ~0%  $CH_4$ ); clearly the Cp rings are the primary source of hydrogen atoms in this decomposition.  $TaCp_2Me_3$  is slightly soluble in pentane and very soluble in aromatic hydrocarbons; the compounds containing one or two  $\eta^5-C_5H_4Me$  rings are significantly more soluble but not noticeably more or less stable thermally.

The <sup>1</sup>H NMR spectrum of  $TaCp_2Me_3$  shows three singlets in the ratio 10:6:3. Almost certainly, therefore, and by analogy with compounds such as  $NbCp_2(C_2H_4)(C_2H_5)$ ,<sup>19</sup> whose structure is known,<sup>20</sup>  $TaCp_2Me_3$  and related biscyclopentadienyl compounds are members of the family containing the "bent" biscyclopentadienyl unit.  $TaCp_2Me_3$  is the only example of a  $MCp_2L_3$  complex except for the well-known trihydrides of the type  $[MCp_2H_3]^{n+}$ .<sup>21</sup> The structures of  $NbCp_2H_3$  and  $TaCp_2H_3$  are known;<sup>22</sup> the three hydrides (two "outside", one "inside") lie in a plane perpendicular to the (Cp centroid)–Nb–(Cp centroid) plane. The three methyl groups in  $TaCp_2Me_3$  therefore most likely lie in a similar plane. The two outside methyl groups can be distinguished from the inside methyl group; the outside methyl resonance (at  $\tau$  9.69) is found *downfield* (by ~0.1 ppm) of the inside methyl resonance.

$TaCp_2Me_3$  reacts readily with  $Br_2$  in  $CH_2Cl_2$ . Slow addition of 1 mol of  $Br_2$  at 0 °C gives an ivory precipitate which analyzes as  $TaCp_2Me_2Br$ ; it is nearly insoluble in common solvents and was not characterized. Part of the yellow product obtained on adding 2–4 mol of  $Br_2$  is not soluble in acetonitrile. It is a brilliant yellow powder which reacts with 3 equiv of methyl-lithium in ether to give  $TaCp_2Me_3$  and is therefore postulated to be  $TaCp_2Br_3$ . Of greatest interest to us here are the aceto-

**Table I.**<sup>a</sup> Reaction of "[TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)(CD<sub>3</sub>)]" with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup>

Sample	(CH <sub>3</sub> ) <sub>0</sub> , <sup>b</sup> %	(CH <sub>3</sub> ) <sub>1</sub> , <sup>b</sup> %	Ph <sub>3</sub> CCD <sub>3</sub> , %	Ph <sub>3</sub> CCH <sub>3</sub> , %
A	85	15	84 (83 <sup>c</sup> )	16 (17 <sup>c</sup> )
B	77	23	89	11
C	79	21	78 <sup>c</sup>	22 <sup>c</sup>

<sup>a</sup> All results were obtained by <sup>1</sup>H NMR integration at 60 (A), 90 (B), or 220 MHz (C) or by mass spectroscopy (as noted). Samples A, B, and C were prepared from different samples of [TaCp<sub>2</sub>(CH<sub>3</sub>)(Br)]<sup>+</sup>Br<sup>-</sup>. <sup>b</sup> (CH<sub>3</sub>)<sub>0</sub> corresponds to the percentage TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)(CD<sub>3</sub>),<sup>23</sup> (CH<sub>3</sub>)<sub>1</sub> to the percentage TaCp<sub>2</sub>(CD<sub>3</sub>)(CH<sub>3</sub>)(CD<sub>3</sub>)<sup>23</sup> in the mixture (see text and Experimental Section). <sup>c</sup> Determined by mass spectroscopy.

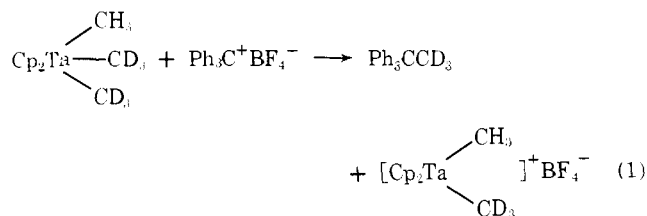
nitrile-soluble yellow and orange products obtained when 2–3 mol of Br<sub>2</sub> is added at 0 °C.

The yellow and orange products are difficult to separate but the more soluble orange product sometimes can be obtained pure as plates; it analyzes as TaCp<sub>2</sub>MeBr<sub>4</sub> and is postulated to be salt [TaCp<sub>2</sub>(Me)(Br)]<sup>+</sup>Br<sub>3</sub><sup>-</sup>. Its <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN (τ 3.25 (10), 9.05 (3)) is identical with that of the yellow product, and to [TaCp<sub>2</sub>(Me)(Br)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> prepared from [TaCp<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (vide infra) and Br<sub>2</sub>. The yellow product is therefore postulated to be [TaCp<sub>2</sub>(Me)(Br)]<sup>+</sup>Br<sup>-</sup>; it can be converted to the BF<sub>4</sub><sup>-</sup> salt using Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> in dichloromethane or TlBF<sub>4</sub> in acetonitrile.

[TaCp<sub>2</sub>(CH<sub>3</sub>)(Br)]<sup>+</sup>Br<sup>-</sup> reacts smoothly with 2 mol of LiCD<sub>3</sub> in diethyl ether to give TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)<sub>2</sub>. Its <sup>1</sup>H NMR spectrum clearly shows (by integration) that the major component (ca. 80%) is TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)(CD<sub>3</sub>), that is, one in which CH<sub>3</sub> is bound at an outside position; ca. 20% is TaCp<sub>2</sub>(CD<sub>3</sub>)(CH<sub>3</sub>)(CD<sub>3</sub>).<sup>23</sup> It would seem likely, therefore, that the first mole of LiCD<sub>3</sub> gives largely "[TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)]<sup>+</sup>Br<sup>-</sup>" which need not necessarily become neutral TaCp<sub>2</sub>(CH<sub>3</sub>)(Br)(CD<sub>3</sub>) before the second mole of LiCD<sub>3</sub> attacks almost exclusively at the central position.

TaCp<sub>2</sub>Me<sub>3</sub> reacts smoothly with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> to give a sparingly soluble yellow precipitate and triphenylmethylmethane in high yield. The yellow precipitate dissolves in acetonitrile to give solutions whose equivalent conductance is in the range expected for a monocationic salt. It crystallizes on addition of ether as pale yellow needles. Its <sup>1</sup>H NMR spectrum shows two sharp singlets in the ratio of 10 (τ 3.45) to 6 (τ 9.45). It is therefore formulated as [TaCp<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>. A similar reaction starting with TaCp(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)Me<sub>3</sub> or Ta(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>Me<sub>3</sub> gives analogous, more soluble, pale yellow, crystalline, cationic complexes.

The organic product of the reaction of TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)(CD<sub>3</sub>) with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> is Ph<sub>3</sub>CCD<sub>3</sub> (Table I). The amount of Ph<sub>3</sub>CCH<sub>3</sub> formed corresponds to the amount of TaCp<sub>2</sub>(CD<sub>3</sub>)(CH<sub>3</sub>)(CD<sub>3</sub>) in the mixture. Therefore, Ph<sub>3</sub>C<sup>+</sup> attacks the central methyl group specifically (eq 1). At no



time is there any indication of H/D scrambling to give any significant amount of CH<sub>2</sub>D or CD<sub>2</sub>H ligands since the <sup>1</sup>H NMR resonances in labeled compounds are sharp singlets and the mass spectrum of triphenylmethylmethane shows parent peaks due only to Ph<sub>3</sub>CCD<sub>3</sub> and Ph<sub>3</sub>CCH<sub>3</sub>. The cationic product in each case is ca. 80% [TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup>

mixed with ca. 20% [TaCp<sub>2</sub>(CD<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> as judged by the high Cp/CH<sub>3</sub> proton ratio (<sup>1</sup>H NMR integration). This result is consistent with the finding above that ca. 80% TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)(CD<sub>3</sub>) results from the reaction of [TaCp<sub>2</sub>(CH<sub>3</sub>)(Br)]<sup>+</sup>Br<sup>-</sup> with 2 mol of LiCD<sub>3</sub>. Loosely stated, the central methyl group appears to be more carbanionic; it enters the coordination sphere last and leaves it first. Interestingly, Tebbe found that the unique hydride in complexes of the type MCp<sub>2</sub>H<sub>3</sub> (M = Nb or Ta) is that to which Lewis acids add, i.e., the central hydride ligand is the most basic.<sup>21b</sup> The results above now allow one to generalize, at least to the analogous trialkyl complexes.

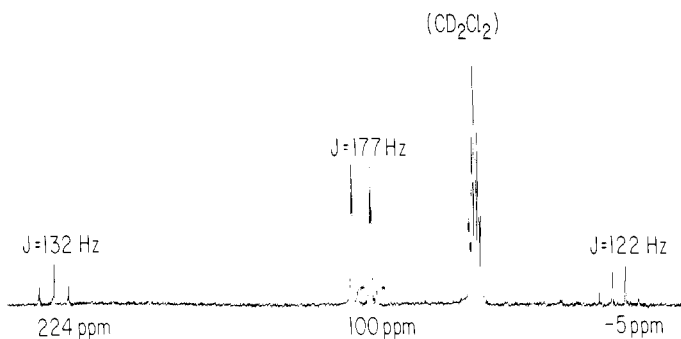
So far the only successful analogous reactions where the metal is Nb is the preparation of NbCp<sub>2</sub>Me<sub>3</sub> from NbMe<sub>3</sub>Cl<sub>2</sub> and 2 mol of TIC<sub>5</sub>H<sub>5</sub> in toluene. NbCp<sub>2</sub>Me<sub>3</sub> is nearly colorless, quite soluble in pentane, and rather unstable at 25 °C, as a solid or in solution. It has therefore been identified only by its <sup>1</sup>H NMR spectrum, which is virtually identical with that of TaCp<sub>2</sub>Me<sub>3</sub>. Since several Ta complexes are themselves not especially stable thermally, one might predict that the corresponding Nb complexes may be more difficult to isolate; they often decompose ca. 50 °C below the approximate decomposition point of the Ta compounds [compare the decomposition temperature of NbMe<sub>5</sub> (ca. -30 °C) with that of TaMe<sub>5</sub> (ca. 25 °C)].<sup>13</sup>

**Preparation of Methylene Complexes.** One might postulate that TaCp<sub>2</sub>Me<sub>3</sub>, like some hypothetical benzyl and neopentyl complexes,<sup>11</sup> could lose methane to give TaCp<sub>2</sub>(CH<sub>2</sub>)(CH<sub>3</sub>). Under the conditions where methane evolves, however, the latter, if formed, must be unstable since more than 1 mol of methane is formed (vide supra). But the cationic complexes, [TaCp<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, which were formed instead of hoped-for [TaCp<sub>2</sub>Me<sub>2</sub>(CH<sub>2</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, are analogous to phosphonium or arsonium salts. They should be fairly acidic and deprotonate easily.

[TaCp<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> is essentially insoluble in THF but dissolves readily on addition of Me<sub>3</sub>P=CH<sub>2</sub>. Removing all solvent and extracting the residue with toluene leaves an essentially quantitative yield of white Me<sub>4</sub>P<sup>+</sup>BF<sub>4</sub><sup>-</sup>. Pale crystals form in the toluene filtrate after adding pentane and cooling. All data presented in the following sections suggest that this neutral complex is the methylene complex, TaCp<sub>2</sub>(CH<sub>2</sub>)(CH<sub>3</sub>). Substituting [TaCp<sub>2</sub>(CD<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> for [TaCp<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> gives TaCp<sub>2</sub>(CD<sub>2</sub>)(CD<sub>3</sub>); no CH<sub>2</sub> is present by <sup>1</sup>H NMR. TaCp(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)(CH<sub>2</sub>)(CH<sub>3</sub>) and Ta(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>3</sub>) can be prepared similarly. An alternative base which can be used with some success is LiN(SiMe<sub>3</sub>)<sub>2</sub>. Li alkyls, in general, give poor yields. TaCp<sub>2</sub>(CH<sub>2</sub>)(CH<sub>3</sub>) is a monomer in benzene. It can be recrystallized easily from toluene by adding pentane, in which it is also somewhat soluble. It decomposes slowly in the solid state at 25 °C (more rapidly in solution in several days) and reacts readily with oxygen or protonic solvents.

The kinetic deuterium isotope effect for the deprotonation reaction can be measured by starting with [TaCp<sub>2</sub>(CH<sub>3</sub>)(CD<sub>3</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (containing ca. 20% [TaCp<sub>2</sub>(CD<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, see Table I) and measuring (by <sup>1</sup>H NMR integration) the ratio of TaCp<sub>2</sub>(CH<sub>2</sub>)(CD<sub>3</sub>) to TaCp<sub>2</sub>(CD<sub>2</sub>)(CH<sub>3</sub>) formed. On reaction with Me<sub>3</sub>P=CH<sub>2</sub> the cation obtained from sample C gave a 33:10 mixture of TaCp<sub>2</sub>(CH<sub>2</sub>)(CD<sub>3</sub>) and TaCp<sub>2</sub>(CD<sub>2</sub>)(CH<sub>3</sub>) (integration done at 220 MHz in frequency sweep mode); therefore, k<sub>H</sub>/k<sub>D</sub> = 3.3. A similar experiment with the cation from sample B gave k<sub>H</sub>/k<sub>D</sub> = 3.5 (integration done at 90 MHz in field sweep mode). Therefore, the error in k<sub>H</sub>/k<sub>D</sub> so determined is estimated to be ±0.3, i.e., k<sub>H</sub>/k<sub>D</sub> = 3.4 ± 0.3. This result may prove important in studies of α-hydrogen atom abstraction reactions which are not strictly deprotonation reactions of the type described here.<sup>9,11</sup>

It is important to note that the ratio of methylene protons



**Figure 1.** The gated decoupled 22.63-MHz  $^{13}\text{C}$  spectrum of  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$  in  $\text{CD}_2\text{Cl}_2$  (\* =  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{CH}_3)$ ).

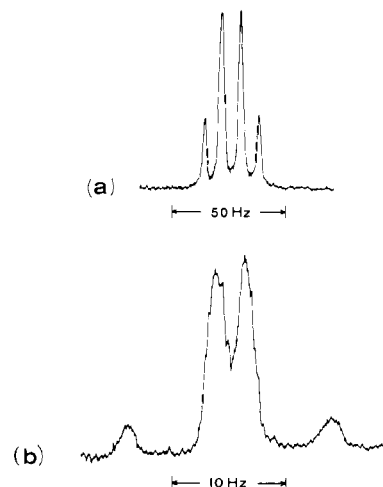
to methyl protons does not change (according to  $^1\text{H}$  NMR) in the above mixtures as the compound decomposes over several days. Therefore, hydrogen (or deuterium) *does not transfer from the methyl to the methylene ligand at a significant rate*. One can estimate that the activation energy for this reaction, if it could be detected before the compound decomposes, must be on the order of or greater than about 20 kcal  $\text{mol}^{-1}$ . Additional evidence that this conclusion is correct is the finding that H and D do not scramble in pure  $\text{TaCp}_2(\text{CH}_2)(\text{CD}_3)$  (prepared from  $\text{TaCp}_2(\text{CD}_2)(\text{CD}_3)$ , vide infra) under conditions where it does not decompose.

**NMR Studies and Infrared Spectra.** The gated decoupled 22.63-MHz  $^{13}\text{C}$  NMR spectrum of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  is shown in Figure 1. The most pertinent feature is the triplet ( $^1J_{\text{CH}} = 132$  Hz) due to the methylene carbon atom 224 ppm downfield of  $\text{Me}_4\text{Si}$ . This is the region in which one might expect to find it since the  $\alpha$ -carbon atom resonance in stabilized carbene complexes is also normally found at low field.<sup>3</sup> The C-H coupling constant is greater than the ca. 125 Hz expected for a tetrahedral carbon atom ( $^1J_{\text{CH}}$  for the methyl group in  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  is  $122 \pm 1$  Hz) though not as large as that found for olefinic carbon atoms (ca. 160 Hz).<sup>24</sup>

The  $^1\text{H}$  NMR spectrum of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  in  $\text{C}_6\text{D}_6$  at 60, 100, or 220 MHz consists of three singlets at  $\tau -0.11$  (2) 4.88 (10), and 10.0 (3) assigned to the  $\text{CH}_2$ , Cp, and  $\text{CH}_3$  protons, respectively. The  $^1\text{H}$  NMR spectrum of  $\text{TaCp}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CH}_2)(\text{CH}_3)$  shows the predicted cyclopentadienyl and methyl peaks but the methylene resonance, which is slightly broadened at 60 MHz, becomes an AB quartet at 220 MHz (Figure 2a) or 100 MHz (Figure 2b) with  $^2J_{\text{H}_A\text{H}_B} = 7.6 \pm 0.1$  Hz.<sup>25</sup> The most reasonable explanation is that  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  is also a member of the "bent" biscyclopentadienyl family and that the  $\text{CH}_2$  ligand in this pseudotetrahedral molecule is oriented perpendicular to the C-Ta-C plane.

The AB patterns at 220 or 100 MHz do not change on warming the sample to 95 °C (Figure 2b), at which temperature decomposition is rapid. A lower limit to  $\Delta G^\ddagger$  for interconverting  $\text{H}_A$  and  $\text{H}_B$  can be conservatively estimated by assuming<sup>26</sup>  $k_c = 2^{-1/2}\pi(\Delta\nu^2 + 6J^2)^{1/2}$  at a coalescence temperature which is 20 °C above the highest attainable, i.e.,  $k_c = 44 \text{ s}^{-1}$  at  $T_c = 388$  K. Therefore,  $\Delta G^\ddagger \geq \text{ca. } 20 \text{ kcal mol}^{-1}$ . The most believable manner in which  $\text{H}_A$  and  $\text{H}_B$  could exchange is by rotation of the methylene ligand 180° about the  $\text{M}=\text{CH}_2$  bond axis. We can postulate then that *the methylene ligand does not rotate readily*, at least on the  $^1\text{H}$  NMR time scale. Note that another possible dynamic process, proton transfer from  $\text{CH}_3$  to  $\text{CH}_2$ , has already been excluded (vide supra).

The infrared spectra of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  and  $\text{TaCp}_2\text{Me}_3$  in Nujol are nearly identical. Only four additional sharp peaks [at 1350 (w), 1130 (w), 785 (m), and 670  $\text{cm}^{-1}$  (m)] are found between 2000 and 600  $\text{cm}^{-1}$  in the spectrum of the methylene complex; the latter two *may* be characteristic of methylene



**Figure 2.** The  $^1\text{H}$  NMR spectrum of the methylene ligand in  $\text{TaCp}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CH}_2)(\text{CH}_3)$  at (a) 220 MHz, 25 °C, and (b) 100 MHz, 95 °C.

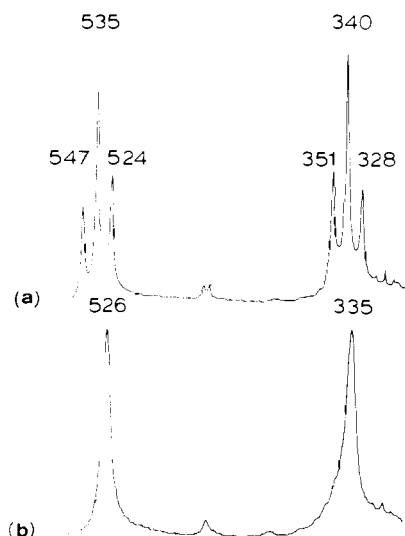
bending and rocking modes (respectively) or possibly a  $\text{Ta}=\text{C}$  stretching mode (or a combination mode with the former), though this proposal remains uncertain at this time for want of additional examples. Three sharp bands at 3120 (w), 3100 (w), and 3080  $\text{cm}^{-1}$  instead of the normally featureless absorption at ca. 3100  $\text{cm}^{-1}$  due to  $\eta^5\text{-C}_5\text{H}_5$  could be ascribed to methylene C-H stretching modes (probably combined with cyclopentadienyl C-H stretching modes), though again any definitive statement must be postponed.

#### Reactions of $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ with Electrophiles.

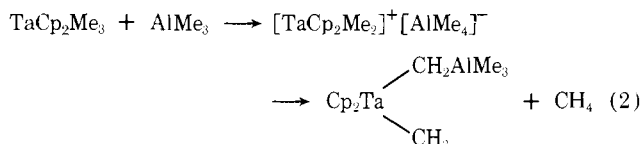
$\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  reacts immediately with 1 mol of  $\text{AlMe}_3$  to form a cream-colored adduct with similar solubility characteristics. Its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show that (in comparison to  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ ) (1) only the methylene  $^1\text{H}$  NMR signal shifts (upfield from  $\tau -0.11$  to 2.32) and (2) the methylene  $^{13}\text{C}$  NMR resonance shifts upfield from 224 to 177 ppm and  $^1J_{\text{CH}}$  decreases from 132 to 124 Hz. Though the range of  $^1J_{\text{CH}}$  for alkylidene ligands is not yet fully known,  $^1J_{\text{CH}}$  for tetrahedral carbon atoms in a methyl group bound to Ta or Al in the compounds discussed here (and others in hand) does not deviate more than  $\pm 3$  Hz from 125 Hz. A decrease in  $^1J_{\text{CH}}$  from 132 to 124 Hz, along with the upfield shift of the methylene carbon and proton resonances, therefore suggest that  $\text{AlMe}_3$  has added to the methylene group. Though conceivably one methyl group could bridge between Al and Ta, it apparently does not, or at least that configuration is not static on the  $^1\text{H}$  NMR time scale. Adding  $\text{Me}_3\text{P}=\text{CH}_2$  or  $\text{Et}_3\text{N}$  to an  $^1\text{H}$  NMR sample of  $\text{TaCp}_2(\text{CH}_2\text{AlMe}_3)(\text{CH}_3)$  generates the spectrum of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  and  $\text{B}\cdot\text{AlMe}_3$  ( $\text{B} = \text{Et}_3\text{N}$  or  $\text{Me}_3\text{P}=\text{CH}_2$ );  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  can be recovered pure by fractional crystallization from pentane in each case. Clearly, therefore, the methylene ligand is nucleophilic; it does not (in contrast to  $(\text{CO})_5\text{W}=\text{CPh}_2$ <sup>27</sup>) form an adduct with  $\text{PMe}_3$ . The  $\text{AlMe}_3$  adduct is probably best described as having a formal positive charge on Ta and a formal negative charge on Al (cf.  $\text{Me}_3\text{PCH}_2\text{AlMe}_3$ <sup>28</sup>).

$\text{TaCp}_2(\text{CH}_2\text{AlMe}_3)(\text{CH}_3)$  may also be formed in good yield in toluene from  $\text{TaCp}_2\text{Me}_3$  and  $\text{AlMe}_3$ . An orange oil, believed to be  $[\text{TaCp}_2\text{Me}_2]^+\text{AlMe}_4^-$  (see Experimental Section), separates rapidly but after several days redissolves as 1 mol of methane evolves. Though the mechanistic details of this reaction have not been explored, it is plausible and tempting to suggest that a methyl group in  $\text{AlMe}_4^-$  is the base which removes a proton from  $[\text{TaCp}_2\text{Me}_2]^+$  to form  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ , methane, and  $\text{AlMe}_3$  (eq 2).

$\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  reacts slowly with  $\text{Me}_3\text{SiBr}$  in dichloromethane to give a pale yellow product which is moderately

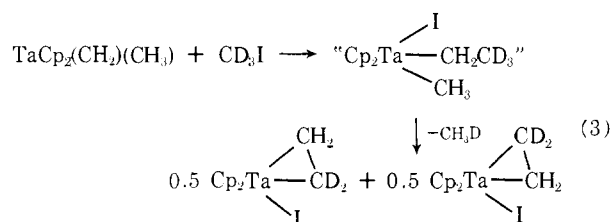


**Figure 3.** The 270-MHz  $^1\text{H}$  NMR spectrum of the ethylene ligand in (a)  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_2\text{H}_4)\text{I}$  and (b) a 1:1 mixture of  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{CD}_2)\text{I}$  and  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CD}_2\text{CH}_2)\text{I}$  (chemical shifts in hertz from  $\text{Me}_4\text{Si}$ ,  $\text{C}_6\text{D}_6$  solvent).

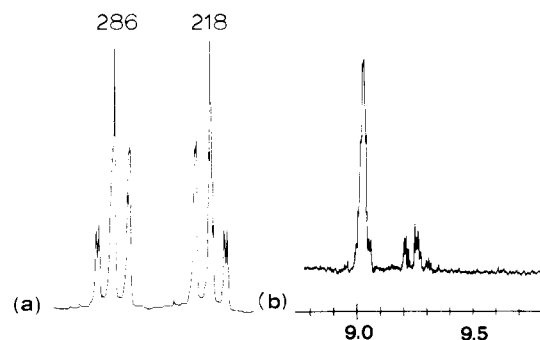


soluble in dichloromethane and acetonitrile but insoluble in nonpolar solvents. It can be recrystallized from acetonitrile in which its equivalent conductance is in the expected range for a monocationic complex. Its  $^1\text{H}$  NMR spectrum in  $\text{CD}_3\text{CN}$  suggests that it is  $[\text{TaCp}_2(\text{CH}_2\text{SiMe}_3)(\text{CH}_3)]^+\text{Br}^-$ . Apparently  $\text{Br}^-$  cannot coordinate to the metal for steric reasons. Like  $[\text{TaCp}_2\text{Me}_2]^+\text{BF}_4^-$ ,  $[\text{TaCp}_2(\text{CH}_2\text{SiMe}_3)(\text{CH}_3)]^+\text{Br}^-$  is insoluble in THF, but dissolves smoothly on addition of  $\text{Me}_3\text{P}=\text{CH}_2$ . The product is  $\text{TaCp}_2(\text{CHSiMe}_3)(\text{CH}_3)$ , the result of removing the more acidic trimethylsilylmethyl  $\alpha$  proton; this complex will be described separately along with other members of this "substituted methylene" class.

$\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  reacts more rapidly with  $\text{CH}_3\text{I}$  in benzene. The solution turns orange as methane (1 mol per Ta) evolves.  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)\text{I}$  is obtained as dark red-orange needles or plates which are moderately soluble in aromatic hydrocarbons, acetonitrile, and dichloromethane (with which it slowly reacts). The  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  shows a singlet due to the cyclopentadienyl protons and an  $\text{A}_2\text{B}_2$  pattern near  $\tau$  8 characteristic of  $\eta^2$ -bonded ethylene in the ratio 10:4 (Figure 3a). We assume that its structure is analogous to that of  $\text{NbCp}_2(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)$ .<sup>20</sup> Substituting  $\text{CD}_3\text{I}$  for  $\text{CH}_3\text{I}$  gives  $\text{CH}_3\text{D}$  and a product whose  $^1\text{H}$  NMR spectrum shows the cyclopentadienyl singlet, but only two broad singlets with total area 2 in place of the  $\text{A}_2\text{B}_2$  pattern, consistent with the product being a 1:1 mixture of  $\text{TaCp}_2(\text{CH}_2\text{CD}_2)\text{I}$  and  $\text{TaCp}_2(\text{CD}_2\text{CH}_2)\text{I}$  (eq 3 and Figure 3b). A small isotope effect



accounts for the slight shift of each  $d_2$ -ethylene  $\text{CH}_2$  resonance in these and other  $\text{CH}_2\text{CD}_2$  complexes to higher field. The



**Figure 4.** The  $^1\text{H}$  NMR spectrum of the ethylene ligand in (a)  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_2\text{H}_4)(\text{CH}_3)$  at 270 MHz (chemical shifts in hertz from  $\text{Me}_4\text{Si}$ ,  $\text{C}_6\text{D}_6$  solvent) and (b) a mixture of 75%  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{CD}_2)(\text{CD}_3)$  and 25%  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{CH}_2)(\text{CD}_3)$  at 220 MHz (chemical shift in  $\tau$ ,  $\text{C}_6\text{D}_6$  solvent).

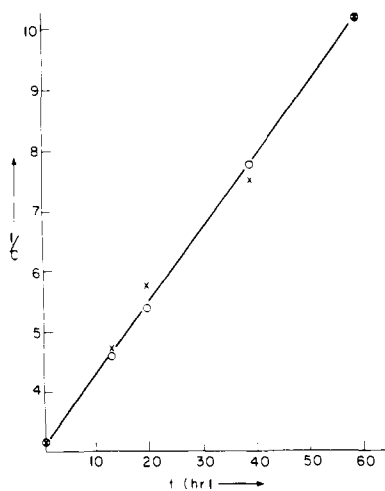
postulated intermediate has not yet been observed by  $^1\text{H}$  NMR. A neutral formulation *may* be sterically allowed but an ionic formulation (or ion pair) is also plausible; the precise stereochemistry and exactly how D finds its way to  $\text{CH}_3$  are therefore uncertain at this time.

$\text{TaCp}_2(\text{CH}_2\text{CH}_2)\text{I}$  reacts with  $\text{KH}$  in THF to give pale yellow  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{H})$  (cf.  $\text{NbCp}_2(\text{CH}_2\text{CH}_2)(\text{H})$ <sup>19</sup>). Its  $^1\text{H}$  NMR spectrum includes resonances due to outside  $\text{CH}_2$  at  $\tau$  9.2, inside  $\text{CH}_2$  at  $\tau$  9.7, and the hydride ligand at  $\tau$  13.4. The hydride resonance is a poor triplet ( $J \approx 2$  Hz) while the outside  $\text{CH}_2$  pattern is much more complex than the inside  $\text{CH}_2$  pattern (which is of the normal  $\text{A}_2\text{B}_2$  type). We propose, therefore, that the hydride is coupled to the outside  $\text{CH}_2$  of the bound ethylene. The isolation of  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{H})$  at least illustrates that  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  is not the favored tautomer.

**Decomposition of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  and Reactions with  $\pi$ -Bonding Ligands.** A saturated  $\text{C}_6\text{D}_6$  solution of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  begins to darken in 1 h and over several days turns an opaque green-brown color. The strongest signals in the  $^1\text{H}$  NMR spectrum of this decomposed sample are those expected for  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{CH}_3)$ . Apparently no product is paramagnetic since all signals are sharp. In a larger scale decomposition reaction only traces of methane evolve and  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{CH}_3)$  can be isolated in 30–40% yield. Its 270-MHz  $^1\text{H}$  NMR spectrum shows the expected  $\text{A}_2\text{B}_2$  pattern due to bound ethylene (Figure 4a) and its  $^{13}\text{C}$  spectrum two triplets at 20.2 and 20.9 ppm downfield from  $\text{Me}_4\text{Si}$  ( $^1J_{\text{CH}} \approx 149$  Hz for each carbon atom; cf. 27.6 and 29.4 ppm,  $^1J_{\text{CH}} = 155$  and 153 Hz, respectively, for ethylene in  $\text{NbCp}_2(\text{CH}_2\text{CH}_2)(\text{CH}_2\text{CH}_3)$ <sup>20</sup>), in addition to the appropriate resonances for  $\eta^5\text{-C}_5\text{H}_5$  and  $\text{CH}_3$  in each case. We can probably safely assume that the NMR signal for the outside ethylene protons in  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{CH}_3)$  occurs downfield of that for the inside protons by analogy with the  $^1\text{H}$  NMR spectrum of  $\text{TaCp}_2\text{Me}_3$ .

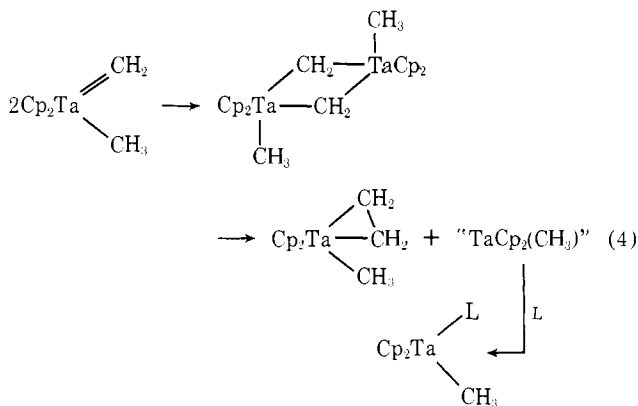
When one allows an equimolar mixture of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  and  $\text{TaCp}_2(\text{CD}_2)(\text{CD}_3)$  to thermally decompose in benzene the isolated ethylene complex is a mixture of  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{R})$ ,  $\text{TaCp}_2(\text{CH}_2\text{CD}_2)(\text{R})$ ,  $\text{TaCp}_2(\text{CD}_2\text{CH}_2)(\text{R})$ , and  $\text{TaCp}_2(\text{CD}_2\text{CD}_2)(\text{R})$  ( $\text{R} = \text{CH}_3$  or  $\text{CD}_3$ ), according to its 270-MHz  $^1\text{H}$  NMR spectrum, which is analogous to that obtained by combining the spectrum in Figure 3a ( $1/2$  the intensity) with that in 3b [see also Figure 4b (discussed in the next section)].

Decomposing  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  under ethylene gives essentially a quantitative yield of  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{CH}_3)$ . Under  $\text{C}_2\text{D}_4$  (1 mol per Ta; total  $P \approx 0.2$  atm) 0.5 mol of pure  $\text{C}_2\text{D}_4$  remains after decomposition is complete. The 270-MHz  $^1\text{H}$  NMR spectrum of the product in the ethylene region is iden-

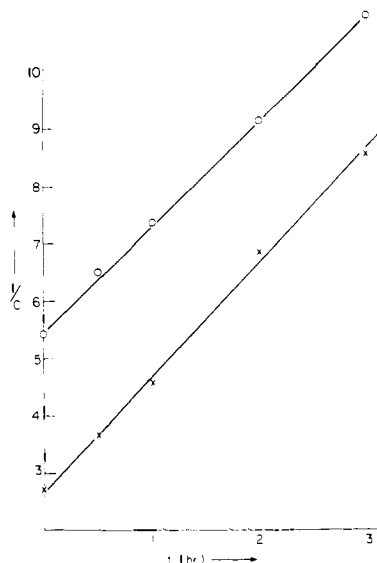


**Figure 5.** A plot of the disappearance of  $Ta(\eta^5-C_5H_5)_2(CH_2)(CH_3)$  in a 0.33 M sample at  $30 \pm 2^\circ C$  in the presence of  $PMe_3$  ( $\times = 0.17 M$ ,  $\circ = 1.7 M$ ) in  $C_6H_6$ .

tical with that of  $TaCp_2(C_2H_4)(CH_3)$  (Figure 4a) except that the resonance due to the ethylene protons is only half as intense. The rest of the spectrum consists of *two* Cp peaks and *two* methyl peaks, 1.5 Hz apart in each case, consistent with a 1:1 mixture of  $TaCp_2(CH_2CH_2)(CH_3)$  and  $TaCp_2(CD_2CD_2)(CH_3)$ . The inverse, decomposition of  $TaCp_2(CD_2)(CD_3)$  under excess  $C_2H_4$  (total  $P \approx 3$  atm), yields a product whose  $^1H$  NMR spectrum shows an ethylene  $A_2B_2$  pattern again essentially identical with that in  $TaCp_2(C_2H_4)(CH_3)$ , but half the intensity.<sup>29</sup> [The peak due to  $CH_xD_{3-x}$  in the starting material (5–10% of one proton) is no larger in the product mixture.] We conclude, therefore, that little or no  $CH_2CD_2$  complex is present in each case, only a 1:1 mixture of  $TaCp_2(C_2H_4)(R)$  and  $TaCp_2(C_2D_4)(R)$  ( $R = CH_3$  or  $CD_3$ ). This result suggests that the  $CH_2=CH_2$  ligand forms by combination of two methylene ligands in separate molecules and that L (e.g.,  $C_2D_4$ ) coordinates to the fragment left after one of the methylene ligands has transferred (eq 4).



In the presence of  $PMe_3$   $TaCp_2(CH_2)(CH_3)$  decomposes to give  $TaCp_2(C_2H_4)(CH_3)$  and  $TaCp_2(PMe_3)(CH_3)$ . The rate at which  $TaCp_2(CH_2)(CH_3)$  disappears can be monitored easily and accurately by  $^1H$  NMR. This rate is *second order* in Ta for a sample 0.33 M in Ta and 0.17 M in  $PMe_3$  in  $C_6H_6$  (Figure 5) at  $30 \pm 2^\circ C$  ( $t_{1/2} = 26$  h,  $k_{30^\circ C} = 3.2 \pm 0.3 \times 10^{-5} L mol^{-1} s^{-1}$ ). Furthermore, a second sample, identical except 1.7 M in  $PMe_3$ , decomposed at an identical rate (Figure 5). Therefore, the reaction is *zero order* in  $PMe_3$ . Figure 6 shows two similar plots of  $1/C$  vs.  $T$  for a sample 0.37 M in Ta (0.50 M in  $PMe_3$ ) and one 0.18 M in Ta (0.50 M in  $PMe_3$ ) in  $C_6H_6$  at  $60^\circ C$ ;  $t_{1/2} = 1.4$  and 2.9 h, respectively, and  $k_{60^\circ C} = 5.4 \pm 0.4 \times 10^{-4} L mol^{-1} s^{-1}$ , again consistent with *bimolecular*



**Figure 6.** A plot of the disappearance of  $Ta(\eta^5-C_5H_5)_2(CH_2)(CH_3)$  in a 0.37 M sample ( $\times$ ) and a 0.18 M sample ( $\circ$ ), each 0.50 M in  $PMe_3$ , in  $C_6H_6$  at  $60^\circ C$ .

decomposition of  $TaCp_2(CH_2)(CH_3)$  to give  $TaCp_2(C_2H_4)(CH_3)$  and a fragment, "TaCp<sub>2</sub>(CH<sub>3</sub>)", which is captured by  $PMe_3$  to give  $TaCp_2(PMe_3)(CH_3)$  (eq 4,  $L = PMe_3$ ).

The decomposition of  $TaCp_2(CH_2)(CH_3)$  in the absence of  $PMe_3$  cannot be followed as accurately by integration (owing to interference by products resulting from "TaCp<sub>2</sub>(CH<sub>3</sub>)", vide infra) but a 0.33 M sample in  $C_6H_6$  decomposed at  $30 \pm 2^\circ C$  at a rate not significantly different ( $k_{30^\circ C} = 3 \pm 1 \times 10^{-5} L mol^{-1} s^{-1}$ ) from that in the presence of  $PMe_3$ .

The decomposition in the presence of  $PMe_2Ph$  proceeds similarly to give an equimolar mixture of  $TaCp_2(C_2H_4)(CH_3)$  and  $TaCp_2(PMe_2Ph)(CH_3)$  and under 2 atm of CO an equimolar mixture of  $TaCp_2(C_2H_4)(CH_3)$  and  $TaCp_2(CO)(CH_3)$  (eq 4;  $L = PMe_2Ph$  and CO, respectively). Both red  $TaCp_2(L)(CH_3)$  ( $L = PMe_3$  or  $PMe_2Ph$ ) and olive-green  $TaCp_2(CO)(CH_3)$  can be separated in good yield from the more soluble  $TaCp_2(C_2H_4)(CH_3)$ . The  $^1H$  NMR and infrared spectra of all are entirely consistent with their formulation (details can be found in the Experimental Section).

The fate of the "TaCp<sub>2</sub>(CH<sub>3</sub>)" fragment in the absence of  $\pi$ -bonding ligands has still not been determined. In a typical decomposition reaction the  $TaCp_2(C_2H_4)(CH_3)$  is removed from the crude solid product mixture by extraction into pentane or hexane. Some of the remaining dark solid (ca. 50% of the starting  $TaCp_2(CH_2)(CH_3)$  by weight) is soluble in toluene and some of that which is not is soluble in tetrahydrofuran. The remainder (ca. 25% of the starting  $TaCp_2(CH_2)(CH_3)$  by weight) is essentially insoluble in THF. The 270-MHz  $^1H$  NMR spectrum of each soluble fraction contains many peaks. Each is apparently a mixture from which no one crystalline product has yet been obtained. It seems plausible that the  $\eta^5-C_5H_5$  rings do not remain intact, e.g., the end products may be related to the titanocenes<sup>30</sup> or niobocene.<sup>31</sup> Since only traces of methane evolve (GLC), "[Ta( $\eta^5-C_5H_5$ )( $\mu-\eta^1, \eta^4-C_5H_4$ )]<sub>2</sub>" must not be a major product (cf. formation of [Th( $\eta^5-C_5H_5$ )<sub>2</sub>( $\mu-\eta^1, \eta^4-C_5H_4$ )]<sub>2</sub> on decomposition of ThCp<sub>3</sub>R<sup>32</sup>).

**Reaction of  $TaCp_2(CH_2)(CH_3)$  with  $Me_3P=CH_2$ .** An  $^1H$  NMR spectrum of  $TaCp_2(CH_2)(CH_3)$  in neat  $Me_3P=CH_2$  is a composite of the two individual spectra. However, over several days at  $25^\circ C$  the starting material disappears and a composite spectrum due to  $TaCp_2(CH_2CH_2)(CH_3)$ ,  $PMe_3$ , and  $Me_3P=CH_2$  appears; the spectrum of an appropriate mixture of these compounds was identical.

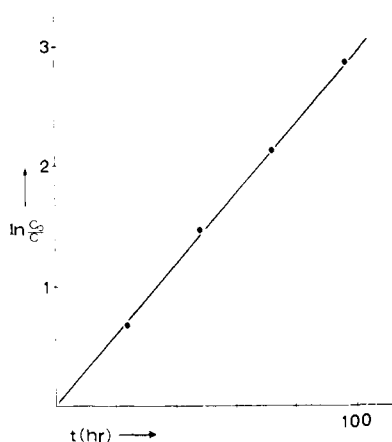
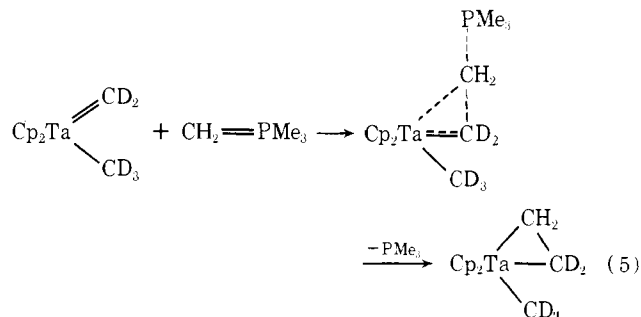


Figure 7. A plot of the disappearance of  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$  (0.33 M) in neat  $\text{Me}_3\text{P}=\text{CH}_2$  at 22 °C.

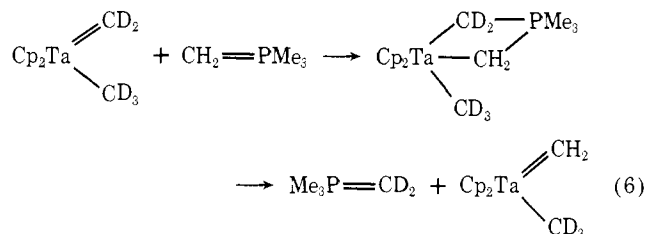
$\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{CH}_3)$  can be isolated quantitatively by removing  $\text{PMe}_3$ ,  $\text{Me}_3\text{P}=\text{CH}_2$ , and solvent in vacuo and is identical with an authentic sample. Formally  $\text{Me}_3\text{P}=\text{CH}_2$  has donated its methylene group to  $\text{Ta}=\text{CH}_2$  where it combines to form an ethylene ligand. This reaction is *pseudo-first-order* in Ta with  $k_{22^\circ\text{C}} = 8.2 \pm 0.3 \times 10^{-6} \text{ s}^{-1}$  (Figure 7).

If only 1 mol of  $\text{Me}_3\text{P}=\text{CH}_2$  per Ta (0.33 M) is used in toluene- $d_8$  as solvent,  $\text{TaCp}_2(\text{PMe}_3)(\text{CH}_3)$  forms in addition to  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{CH}_3)$ . Their ratio is approximately 1:3 (by  $^1\text{H}$  NMR) after the reaction is approximately 90% complete (7 days at 22 °C). Note that the reaction is considerably slower than in neat  $\text{Me}_3\text{P}=\text{CH}_2$  (50% complete in 1 day, 95% complete in 4 days), more on the order of the rate at which  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  decomposes (vide supra). Most likely, therefore,  $\text{TaCp}_2(\text{PMe}_3)(\text{CH}_3)$  forms as a sufficient concentration of  $\text{PMe}_3$  builds up and captures the “ $\text{TaCp}_2(\text{CH}_3)$ ” fragment resulting from reaction of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  with itself. Of course, it is also possible that “ $\text{TaCp}_2(\text{CH}_3)$ ” or  $\text{TaCp}_2(\text{PMe}_3)(\text{CH}_3)$  reacts with  $\text{Me}_3\text{P}=\text{CH}_2$  to form  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ . ( $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{CH}_3)$  is essentially inert toward  $\text{Me}_3\text{P}=\text{CH}_2$ , even neat at 60 °C.) These complications prevent a more accurate determination of the dependence of the rate of the reaction of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  with  $\text{Me}_3\text{P}=\text{CH}_2$  on  $\text{Me}_3\text{P}=\text{CH}_2$  concentration. However, it is reasonable to assume that this dependence is also first order. In that case (assuming that the density of the  $\text{Me}_3\text{P}=\text{CH}_2 \approx 0.8 \text{ g mL}^{-1}$  and  $V \approx 1 \text{ mL}$ ) [ $\text{Me}_3\text{P}=\text{CH}_2] \approx 10 \text{ M}$  and  $k'_{22^\circ\text{C}} \approx 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$  where  $k_{22^\circ\text{C}} = k'_{22^\circ\text{C}}[\text{Me}_3\text{P}=\text{CH}_2]$ . Therefore  $\text{Me}_3\text{P}=\text{CH}_2$  actually reacts a good deal more slowly with  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  (equal concentrations) than  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  reacts with itself (calculated  $k_{22^\circ\text{C}} \approx 1.4 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ ),<sup>33</sup> as the initial observation suggested.

The reaction of  $\text{TaCp}_2(\text{CD}_2)(\text{CD}_3)$  with neat  $\text{Me}_3\text{P}=\text{CH}_2$  provides some details concerning how methylene transfers from P to Ta. After 5 days at 22 °C the reaction was ca. 95% complete. The product is largely (75%)  $\text{TaCp}_2(\text{CH}_2\text{CD}_2)(\text{CD}_3)$ , but little or no  $\text{TaCp}_2(\text{CD}_2\text{CH}_2)(\text{CD}_3)$  is present, according to the 220-MHz  $^1\text{H}$  NMR spectrum (Figure 4b), if we assume that the chemical shift of the outside ethylene protons in coordinated ethylene is greater than that of the inside ethylene protons (cf.  $\text{TaCp}_2\text{Me}_3$ ). Therefore, when  $\text{Me}_3\text{P}=\text{CH}_2$  transfers its methylene it does so selectively from the “outside”, possibly via a transition state as shown in eq 5. But ca. 25% of the product mixture is  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{CD}_3)$  and the remaining 5% of starting material is almost exclusively (90%)  $\text{TaCp}_2(\text{CH}_2)(\text{CD}_3)$  (by  $^1\text{H}$  NMR). Presumably  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{CD}_3)$  arises by reaction of  $\text{TaCp}_2(\text{CH}_2)(\text{CD}_3)$  with  $\text{Me}_3\text{P}=\text{CH}_2$ . But  $\text{TaCp}_2(\text{ethylene})(\text{Me})$  does not react with  $\text{Me}_3\text{P}=\text{CH}_2$  to give  $\text{TaCp}_2(\text{CH}_2)(\text{Me})$  nor can



$\text{TaCp}_2(\text{CH}_2)(\text{CD}_3)$  come from “ $\text{TaCp}_2(\text{CD}_3)$ ” and  $\text{Me}_3\text{P}=\text{CH}_2$  since if  $\text{TaCp}_2(\text{CD}_2)(\text{CD}_3)$  decomposes bimolecularly (to give “ $\text{TaCp}_2(\text{CD}_3)$ ” and  $\text{TaCp}_2(\text{CD}_2\text{CD}_2)(\text{CD}_3)$ ) then some  $\text{TaCp}_2(\text{CD}_2\text{CH}_2)(\text{CD}_3)$  should form by reaction of  $\text{TaCp}_2(\text{CD}_2)(\text{CD}_3)$  with  $\text{TaCp}_2(\text{CH}_2)(\text{CD}_3)$  (vide supra). Therefore,  $\text{TaCp}_2(\text{CH}_2)(\text{CD}_3)$  must form by exchange of  $\text{CD}_2$  (on Ta) with  $\text{CH}_2$  (on P). [ $^1\text{H}$  NMR integration of the Cp vs. the ethylene protons in the product mixture suggests that the appropriate amount of  $\text{CH}_2$  has been incorporated (relative areas 10.0 (defined) to  $2.4 \pm 0.1$ ) but confirmation that  $\text{Me}_3\text{P}=\text{CD}_2$  is formed is virtually impossible owing to intra- and intermolecular H/D scrambling.] Exchange cannot strictly occur from the transition state shown in eq 5 since loss of  $\text{Me}_3\text{P}=\text{CD}_2$  is not microscopically the reverse reaction. Therefore, one must postulate that a second reaction pathway of slightly higher energy leads exclusively to  $\text{CD}_2/\text{CH}_2$  exchange. It is possible that this second pathway consists of the sterically less likely “inside” attack on Ta followed by the energetically favored loss of  $\text{Me}_3\text{P}=\text{CD}_2$  from the “outside” (eq 6), if, of course, “outside” attack is a readily reversible equi-



librium which lies toward  $\text{TaCp}_2(\text{CH}_2)(\text{CD}_3)$  and  $\text{Me}_3\text{P}=\text{CD}_2$  (as the relatively slow rate of the reaction of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  with  $\text{Me}_3\text{P}=\text{CH}_2$  might suggest). Such a postulate does not seem unreasonable since the reaction of  $[\text{TaCp}_2(\text{CH}_3)(\text{Br})]^+\text{Br}^-$  with 2 mol of  $\text{LiCD}_3$  did not give  $\text{TaCp}_2(\text{CH}_3)(\text{CD}_3)(\text{CD}_3)$  exclusively. Both results may be taken as evidence that reactions of these bicyclopentadienyl complexes are not completely specific.

It is interesting to note here that  $\text{TaCp}_2(\text{CH}_2\text{CD}_2)(\text{CD}_3)$  is configurationally stable, that is, ethylene does not “rotate” rapidly on the chemical time scale to give  $\text{TaCp}_2(\text{CD}_2\text{CH}_2)(\text{CD}_3)$ . Presumably there is no orbital of  $\pi$ -type symmetry and appropriate energy perpendicular to the one used to  $\pi$  bond to ethylene in the ethylene-methyl plane which can assist this rotation (see Discussion). Interestingly, this same “missing” orbital is the one needed to  $\pi$  bond to the methylene ligand should it too rotate 90° about its metal bond axis. As argued in a previous section, this rotation is slow, at least on the  $^1\text{H}$  NMR time scale ( $\Delta G^\ddagger \geq 20 \text{ kcal mol}^{-1}$ , conservatively estimated).

The main point to be stressed in this section, however, is that  $\text{Me}_3\text{P}=\text{CH}_2$  reacts with  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  in a manner similar to that in which  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  reacts with itself. This finding further strengthens the argument that  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  is “ylidic”, i.e., the methylene ligand is a good nucleophile and presumably, therefore, negatively polarized relative to Ta.

## Discussion

Terminal methylene complexes have been postulated in the Cu-catalyzed decompositions of diazomethane,<sup>34</sup> in decompositions of methyl complexes,<sup>13,35</sup> in olefin metathesis reactions,<sup>36</sup> in reactions of  $\alpha$ -halo- or  $\alpha$ -alkoxymethyl complexes,<sup>37</sup> and in reactions of cyclopropanes with a W-based olefin metathesis catalyst.<sup>38</sup> In most cases, however, "carbenoid" intermediates cannot be excluded as the reactive intermediate. Diazomethane has been the most popular methylene source in attempts to prepare isolable methylene complexes.<sup>39</sup> Only recently, however, has this method been successful to the extent that bridging methylene complexes have been isolated.<sup>40,41</sup>

The reaction of  $TaCp_2Me_3$  with  $Ph_3C^+BF_4^-$  might be expected to give  $[TaCp_2Me_2(CH_2)]^+BF_4^-$  and  $Ph_3CH$  (cf. the preparation of  $[FeCp(CO)_2(benzocyclobutenylidene)]^+$ , ref 7). The fact that  $[TaCp_2Me_2]^+BF_4^-$  is formed instead was surprising at the time since there are few examples of electrophilic attack on an alkyl ligand at the  $\alpha$ -carbon atom by  $Ph_3C^+$  to give  $Ph_3CR$ . This may be largely because most alkyl ligands contain more readily removed  $\beta$ -hydrogen atoms (see, however, ref 7). It seems less surprising now that  $[TaCp_2Me_2(CH_2)]^+$  does not form since it is difficult to see how  $CH_2$  could be  $\pi$  bonded to Ta(V) (vide infra); the positive charge would have to be localized on the methylene carbon atom.

How this reaction can occur in such a crowded environment is still unclear. It does not seem too unreasonable to postulate that  $Ph_3C^+$  attacks the central Me group on the face opposite Ta; how the methyl-CPh<sub>3</sub> bond could form under these circumstances, however, is not obvious. More complex schemes are possible, for example, one involving electron transfer to give  $[TaCp_2Me_3]^+$  followed by loss of the central Me group as a radical and capture by  $Ph_3C\cdot$  to give  $Ph_3CMe$ .<sup>42</sup> If this reaction is attempted with less crowded Ta(V) alkyl complexes, e.g.,  $Ta(CH_2CMe_3)_3Me_2$ ,  $Ph_3CMe$  is formed but only neutral complexes containing fluoride bound to the metal could be found.<sup>43</sup>  $[TaCp_2Me_2]^+$  does not abstract fluoride from  $BF_4^-$ , most likely because  $BF_4^-$  cannot contact the metal easily in this crowded environment.

Steric crowding in  $[TaCp_2Me_2]^+BF_4^-$  almost certainly also is one reason why  $Me_3P=CH_2$  does not attack the metal but removes what must be a relatively accessible and fairly acidic proton instead. (A quantitative measure of the acidity of this proton is not yet available.) Of course, the overall result would be identical if  $Me_3P=CH_2$  did attack the metal, methylene were transferred, and  $Me_4P^+BF_4^-$  were lost. However, the preparation of  $TaCp_2(CD_2)(CD_3)$  from  $[TaCp_2(CD_3)_2]^+$  and  $Me_3P=CH_2$  and the successful preparation of  $TaCp_2(CH_2)(CH_3)$  using  $LiN(SiMe_3)_2$  clearly rule out this possibility.

The fact that  $TaCp_2(CH_2AlMe_3)(CH_3)$  forms from  $TaCp_2Me_3$  and  $AlMe_3$  seems important for several reasons. First, it demonstrates that an alkylidene complex can form from an aluminum alkyl (aluminum alkyls are common "cocatalysts" in olefin metathesis systems<sup>36</sup>). Secondly, this alkylidene is nucleophilic, now believed to be a likely type in at least some olefin metathesis systems.<sup>44</sup> Thirdly, this alkylidene is "protected" against bimolecular decomposition (for steric as well as electronic reasons; vide infra) by coordination of a fairly labile Lewis acid,  $AlMe_3$ . In general, however, reactions of such "carbenoid" species may not be significantly different from those of the "unprotected", or true, alkylidene ligand where relatively nonbulky substrates, e.g., linear olefins, are concerned. Therefore, such adducts could be the most important component of a metathesis system.<sup>45</sup>

There appear to be two main reasons why  $TaCp_2(CH_2)(CH_3)$  is a stable, isolable species. The first is that other ligands are innocuous, i.e., there is no evidence that either  $\eta^5-C_5H_5$  or

$CH_3$  interacts in any way with the methylene ligand. One possible interaction, H transfer from  $CH_3$  to  $CH_2$ , is nondestructive, of course, and has been observed in other systems,<sup>46</sup> but apparently has a higher activation energy than the decomposition reaction in this case. One might expect typical ligands which are not ancillary in other hypothetical cases to be subject to nucleophilic attack by  $^-CH_2$  (e.g., CO, to give ketene complexes<sup>48</sup>) or electrophilic attack by  $^+CH_2$  (e.g.,  $PR_3$ , to give "ylide" complexes<sup>27</sup>). An apparent complication of this type is the "insertion" of methylene into an Ir-Cl bond to give an Ir- $CH_2Cl$  complex.<sup>39</sup>

The second reason why  $TaCp_2(CH_2)(CH_3)$  is stable is that it cannot readily dimerize by a dipolar  $[2 + 2]$  addition of the  $Ta=CH_2$  bond to itself. Such a dimerization should be independent of the polarization of the metal-carbon bond. Indeed,  $(CO)_5CrCOCH_2CH_2CH_2$  does decompose bimolecularly,<sup>49</sup> the olefin favored by combination of two electrophilic carbene fragments is, in fact, always a major decomposition product.<sup>3</sup> Therefore, we might postulate that a likely decomposition pathway for *any* complex containing a carbenelike ligand, however polarized, will be bimolecular, should alternative reactions of the carbenelike ligand with other ligands or other decomposition pathways be unfavorable. Of course, the fact that  $Me_3P=CH_2$  transfers methylene to  $TaCp_2(CH_2)(CH_3)$  to give  $PMe_3$  and  $TaCp_2(C_2H_4)(CH_3)$ , respectively, is yet further evidence that a bimolecular reaction resulting in alkylidene transfer is reasonable.

It would be premature to attempt to rationalize why the  $Ta=CH_2$  bond is polarized  $+/-$ . We might point out that other members of the  $MCp_2(alkylidene)(R)$  family<sup>50</sup> as well as  $M(CH_2CMe_3)_3(CHCMe_3)$ <sup>51</sup> ( $M = Nb$  or  $Ta$ ) and  $TaCpCl_2(CHCMe_3)$ <sup>1</sup> also contain a nucleophilic alkylidene carbon atom. Therefore at present we can only postulate that this polarization is characteristic of any Nb or Ta alkylidene complex in which the metal is in a relatively high formal oxidation state (+3 or +5 depending on one's point of view).

One acceptable description of how methylene bonds to Ta in  $TaCp_2(CH_2)(CH_3)$  consists of treating  $CH_2$  as an  $sp^2$ -hybridized  $2e$  donor with an empty  $2p_z$  orbital. The filled  $sp^2$  orbital donates electron density into an empty  $\sigma$ -type orbital on Ta while a filled  $\pi$ -type orbital on Ta donates electron density back into the empty  $2p_z$  orbital on the methylene ligand. This bonding picture is of course analogous to that which describes how a simple olefin such as ethylene binds to a metal. Therefore, in any given circumstance where both the methylene and the ethylene complexes are known, the  $M=CH_2$  plane in one complex must be perpendicular to the  $MC_2$  plane in the other (compare  $TaCp_2(CH_2)(CH_3)$  with  $TaCp_2(CH_2=CH_2)(CH_3)$ ). However, the *opposite* donor/acceptor picture is equally appropriate. In fact, we propose that neither donor/acceptor bonding scheme alone is generally valid since we believe that it would then be difficult to rationalize different bond polarities. The postulate that an alkylidene will bond orthogonal to an olefin should not be influenced by what description is ultimately chosen.

Some controversy has arisen in the past few years concerning the number and spatial distribution of bonding and nonbonding orbitals in "bent" biscyclopentadienyl complexes.<sup>20,52,53</sup> A molecular orbital approach seems to explain most of the findings. Briefly, two orbitals lying in the plane passing between the two Cp ligands and ca.  $90^\circ$  to one another are used to  $\sigma$  bond to  $CH_2$  (or  $CH_2=CH_2$ ) and  $CH_3$ ; these bonds complete the pseudotetrahedral  $MCp_2L_2$  structure. A  $\pi$ -bonding orbital also lies in this plane. It is this orbital which can overlap with the  $2p_z$  orbital on  $CH_2$  or the  $\pi^*$  orbital on  $CH_2=CH_2$ . Neither  $CH_2$  nor  $CH_2=CH_2$  rotates readily about the metal-ligand bond axis since no  $\pi$  orbital *orthogonal* to this "in-plane"  $\pi$  orbital exists to assist such a rotation. Lauher and Hoffmann<sup>53</sup> have discussed these ideas thoroughly

and have used the hypothetical model,  $[\text{TiCp}_2(\text{CH}_2)(\text{CH}_3)]^-$ , which is isoelectronic with  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  except for filled shells, to confirm them through calculations; they predict  $\Delta G^\ddagger$  for methylene rotation in  $[\text{TiCp}_2(\text{CH}_2)(\text{CH}_3)]^-$  to be ca. 27 kcal mol<sup>-1</sup>. All of the postulates concerning the structure and bonding in  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  have been confirmed by an x-ray structure in which the hydrogen atoms on both  $\text{CH}_2$  and  $\text{CH}_3$  were located.<sup>11</sup>

The <sup>13</sup>C spectrum of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  illustrates that, contrary to the earliest theories,<sup>3</sup> the formal charge on an alkylidene  $\alpha$ -carbon atom is probably not the *major* factor which causes its resonance to occur at low fields. Though  $\text{CH}_2$  is negatively charged in  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  its resonance occurs in the same region (at 228 ppm) as that for  $\text{Ph}_3\text{C}^+$  (at 211 ppm<sup>54</sup>). Phenomenologically it now seems that some multiple bonding between carbon and a transition metal is probably the single most important factor which causes the carbon resonance to occur in the 200–400-ppm range. However, for a series of similar Fischer-type carbene complexes the chemical shift of the carbene carbon atom does appear to depend directly in the expected manner on the electron-donating ability of substituents attached to it.<sup>3,55</sup> Therefore, it is at least not surprising to find that the nucleophilic methylene resonance is found at the high end of this region while the electrophilic alkylidene  $\alpha$ -carbon resonance in  $(\text{CO})_5\text{W}=\text{CPh}_2$  is found at the low end (at 358 ppm). It is not inconsistent, therefore, to find the methylene resonance in  $\text{Me}_3\text{P}=\text{CH}_2$  near  $\text{Me}_4\text{Si}$  (2.3 ppm upfield with  $^1J_{\text{CH}} = 149$  Hz);<sup>56,57</sup> it is nucleophilic and not attached to a transition metal. Clearly, however, more detailed simplistic interpretations of <sup>13</sup>C chemical shifts should receive more scrutiny than they have in the past.<sup>58</sup>

$^1J_{\text{CH}}$  in  $\text{CH}_2$  bound to Ta (132 Hz) is essentially the same as in that bound to As in  $\text{Me}_3\text{As}=\text{CH}_2$  (131 Hz)<sup>56</sup> but significantly smaller than in that bound to P in  $\text{Me}_3\text{P}=\text{CH}_2$  (149 Hz).<sup>56</sup> Since we know that the  $\text{CH}_2$  ligand in  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  is planar<sup>11b</sup> we must conclude that the magnitude of  $^1J_{\text{CH}}$  in a unique situation will probably vary considerably.<sup>24</sup> This is clearly the case for neopentylidene complexes where  $^1J_{\text{CH}}$  varies from 84–90 Hz in some Ta complexes<sup>1,9,10</sup> to 131 Hz in  $\text{NbCp}_2(\text{CHCMe}_3)\text{Cl}$ .<sup>50</sup>

## Experimental Section

All operations were done under  $\text{N}_2$ , either in a Vacuum Atmospheres HE43 glovebox or by Schlenk techniques. All solvents were dried by passing through Linde 4A molecular sieves and were degassed thoroughly with nitrogen. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen.  $\text{TaCl}_5$ ,  $\text{NbCl}_5$ , and  $\text{TiCl}_3$  were sublimed before use.  $\text{Me}_3\text{P}=\text{CH}_2$  was prepared from  $\text{Me}_4\text{P}^+\text{Br}^-$  and  $\text{NaNH}_2$  in THF<sup>59</sup> and isolated by vacuum distillation (bp 60 °C, 100 mm). <sup>1</sup>H NMR spectra were done on Varian, Perkin-Elmer, or Bruker 60-, 90-, 100-, 220-, or 270-MHz spectrometers and <sup>13</sup>C spectra on Bruker 22.63- or 67.89-MHz spectrometers. Analyses were done by Alfred P. Bernhardt Mikroanalytisches Laboratorium.

**1. Preparation of  $\text{TaMe}_3\text{Cl}_2$ .**  $\text{TaMe}_3\text{Cl}_2$  was prepared by stirring 50 g of sublimed  $\text{TaCl}_5$  with 15.5 mL of  $\text{ZnMe}_2$  in 900 mL of pentane at 25 °C for 6 h. The  $\text{ZnCl}_2$  was filtered off, a small sample of filtrate was stripped, and the residue was analyzed by <sup>1</sup>H NMR in order to determine how much additional  $\text{ZnMe}_2$  is needed to convert any  $\text{TaMe}_2\text{Cl}_3$  to  $\text{TaMe}_3\text{Cl}_2$ . After more  $\text{ZnMe}_2$  was added (here 1.15 mL) the mixture was again filtered and the solvent removed in vacuo leaving 34 g of pale yellow  $\text{TaMe}_3\text{Cl}_2$ .

<sup>1</sup>H NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 8.47 (s) [<sup>1</sup>H NMR of  $\text{TaMe}_2\text{Cl}_3$  ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 8.32 (s).] Mol wt (cryoscopy in benzene) 307 (calcd 297).

The following preparation was developed in order to avoid using isolated  $\text{ZnMe}_2$ .  $\text{ZnCl}_2$  (8.57 g, 63 mmol, 1.2  $\times$  theory, dried with  $\text{SOCl}_2$ ) in 50 mL of ether at  $-78$  °C was treated slowly with 113 mL of 0.90 M  $\text{LiMe}$  (105 mmol) and the mixture was warmed to 0 °C. After stirring for 0.5 h the  $\text{ZnMe}_2$  in ether was removed in vacuo and trapped in a flask containing 33 mmol (0.95 of theory) of sublimed  $\text{TaCl}_5$  (11.88 g). This mixture was warmed to room temperature and

stirred for 1–2 h and 52.5 mmol (4.62 g) of dry dioxane was then added dropwise.  $\text{ZnCl}_2$ -dioxane was filtered off and the solvent removed from the filtrate in vacuo leaving a yellow residue which was extracted with 200 mL of pentane. The mixture was filtered and the pentane removed in vacuo leaving 7.67 g of pale yellow  $\text{TaMe}_3\text{Cl}_2$  (80% yield based on  $\text{TaCl}_5$ ).

**2. Preparation of  $\text{TaCpMe}_3\text{Cl}$ .** Solid  $\text{TiCl}_3\text{H}_5$  (4.5 g) was slowly added to a vigorously stirred solution of 5.0 g of  $\text{TaMe}_3\text{Cl}_2$  in 25 mL of toluene. After 1 h the  $\text{TiCl}_3$  was filtered off and the solvent removed in vacuo leaving an orange residue (5.0 g) of essentially pure  $\text{TaCpMe}_3\text{Cl}$ . Orange needles can be obtained easily by adding pentane to a saturated toluene solution followed by standing the partially crystallized product in the mother liquor at  $-40$  °C overnight.  $\text{TaCpMe}_3\text{Cl}$  slowly decomposes in the solid state at 25 °C under nitrogen (weeks or months).

Anal. Calcd for  $\text{TaC}_8\text{H}_{14}\text{Cl}$ : C, 29.42; H, 4.32; Cl, 10.85. Found: C, 29.19; H, 4.11; Cl, 10.69.

<sup>1</sup>H NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 4.45 (s, 5), 8.88 (s, 9).

**3. Preparation of  $\text{TaCp}_2\text{Me}_3$  and  $\text{TaCp}_2(\text{CD}_3)_3$ .**  $\text{TaMe}_3\text{Cl}_2$  (20.0 g) and 36.2 g of  $\text{TiCl}_3\text{H}_5$  were stirred in 200 mL of toluene for 16 h.  $\text{TiCl}_3$  was filtered off and the solution volume reduced in vacuo until a small crop of crystals formed. Three volumes of pentane were added and the solution was chilled at  $-40$  °C for 6 h to give 18.0 g of silvery-white crystals. A second crop of 2.5 g was obtained similarly after reducing the volume of toluene still further; total yield 20.5 g (85%). The solid turns a pale purple color under  $\text{N}_2$  at 25 °C in 24 h, but not at  $-30$  °C.

Anal. Calcd for  $\text{TaC}_{13}\text{H}_{19}$ : C, 43.83; H, 5.38. Found: C, 43.78; H, 5.37.

<sup>1</sup>H NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 5.15 (s, 10, Cp), 9.69 (s, 6, outside Me), 9.79 (s, 3, inside Me).

A 1.30-mmol sample was pyrolyzed by gently heating in an evacuated 100-mL flask. A small amount of white solid sublimed, then it (and that which had not sublimed) turned a pale purple and suddenly decomposed very rapidly to give 1.59 mmol of gas and a benzene-soluble red solid whose <sup>1</sup>H NMR spectrum showed only two very broad peaks, one in the Cp region, one in the Me region. A 1.52-mmol sample gave 2.82 mmol of gas which was shown to be 96%  $\text{CH}_4$  containing traces (ca. 1% each) of  $\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ .

$\text{TaCp}_2(\text{CD}_3)_3$  was prepared similarly. A 250-mg sample in 5 mL of  $\text{C}_6\text{D}_6$  at 125 °C gave off 1.8 mol of methane which was shown by mass spectroscopy to be 10%  $\text{CD}_4$ , 87%  $\text{CD}_3\text{H}$ ,  $\sim 0\%$   $\text{CD}_2\text{H}_2$ , 2%  $\text{CDH}_3$ , and  $\sim 0\%$   $\text{CH}_4$ .

**4. Preparation of  $\text{TaCp}(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Me}_3$ .** A solution of 2.0 g of  $\text{TaCpMe}_3\text{Cl}$  in 25 mL of THF at  $-78$  °C was treated with 0.55 g of  $\text{LiC}_5\text{H}_4\text{Me}$  in 10 mL of THF. The mixture was warmed to room temperature with stirring and all THF removed in vacuo. The residue was extracted with pentane (25 mL) and the  $\text{LiCl}$  removed by filtration. Pentane was removed in vacuo until crystals appeared and the solution was then allowed to stand at  $-30$  °C for 6 h to give 1.40 g (62%) of white, platelike crystals of the product. It was identified by comparison of its <sup>1</sup>H NMR spectrum to that of  $\text{TaCp}_2\text{Me}_3$  and  $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Me}_3$  (see 5).

<sup>1</sup>H NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 5.15 (s, 5, Cp), 5.26 (t, 2,  $J_{\text{HH}'} \approx 3$  Hz,  $\text{C}_5\text{H}_2$  set), 5.47 (t, 2,  $J_{\text{HH}'} \approx 3$  Hz,  $\text{C}_5\text{H}_2'$  set), 8.30 (s, 3,  $\text{C}_5\text{Me}$ ), 9.75 (s, 6, outside Me), 9.87 (s, 3, inside Me).

**5. Preparation of  $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Me}_3$ .** A solution of 3.44 g of  $\text{LiC}_5\text{H}_4\text{Me}$  in 25 mL of THF was added slowly to 5.95 g of  $\text{TaMe}_3\text{Cl}_2$  in THF at  $-78$  °C with stirring. The mixture was warmed to room temperature and all solvent removed in vacuo. The residue was extracted with 500 mL of warm hexane and the mixture was filtered. Crops of silvery-white crystals were filtered off as the solvent was removed in vacuo; total yield 5.9 g (76%).

Anal. Calcd for  $\text{TaC}_{15}\text{H}_{23}$ : C, 46.88; H, 6.03. Found: C, 46.88; H, 5.91.

<sup>1</sup>H NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ , 220 MHz) 5.23 (t, 4,  $J_{\text{HH}'} = 2.6$  Hz,  $\text{C}_5\text{H}_2$  set), 5.48 (t, 4,  $J_{\text{HH}'} = 2.6$  Hz,  $\text{C}_5\text{H}_2'$  set), 8.26 (s, 6,  $\text{C}_5\text{Me}$ ), 9.79 (s, 6, outside Me), 9.92 (s, 3, inside Me).

**6. Preparation of  $[\text{TaCp}_2\text{Me}_2]^+\text{BF}_4^-$ .** A solution of 14.24 g of  $\text{TaCp}_2\text{Me}_3$  in 100 mL of  $\text{CH}_2\text{Cl}_2$  was treated dropwise with 13.20 g of  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  in 100 mL of  $\text{CH}_2\text{Cl}_2$  to give a pale yellow precipitate of  $[\text{TaCp}_2\text{Me}_2]^+\text{BF}_4^-$  (16.5 g, 97%). The product was filtered off and the solvent removed from the filtrate in vacuo. The residue was extracted with pentane. The mixture was filtered and the filtrate was reduced to dryness to give 8.0 g (67%) of  $\text{Ph}_3\text{CMe}$  which was identified by <sup>1</sup>H NMR [ $\tau$  3.00 (br, 15, Ph), 7.98 (s, 3, Me), in  $\text{C}_6\text{D}_6$ ] and mass



spectroscopy. The pale yellow precipitate from above was recrystallized from acetonitrile with ether to give yellow needles from which the last traces of acetonitrile and ether were removed in vacuo.

Anal. Calcd for  $TaC_{12}H_{16}BF_4$ : C, 33.68; H, 3.76. Found: C, 33.66; H, 3.82.

$^1H$  NMR ( $\tau$ ,  $CD_3CN$ ) 3.45 (s, 10, Cp), 9.45 (s, 6,  $CH_3$ ).

The resistance of a solution of 160 mg of the product in 50 mL of acetonitrile was 1000  $\Omega$  ( $\Lambda = 133$ ).

**7. Preparation of  $[TaCp_2(\eta^5-C_5H_4Me)Me_2]^+BF_4^-$ .** A solution of 1.32 g of  $Ph_3C^+BF_4^-$  in 30 mL of  $CH_2Cl_2$  was added to 1.48 g of  $TaCp_2(\eta^5-C_5H_4Me)Me_3$  in 20 mL of  $CH_2Cl_2$  with stirring. The solvent was removed in vacuo until the volume was about 10 mL and 30 mL of ether was added to complete crystallization, yield 1.57 g. Unlike  $[TaCp_2Me_2]^+BF_4^-$ , this material is soluble enough in dichloromethane to obtain an NMR spectrum, which by comparison to that of  $[TaCp_2Me_2]^+BF_4^-$  in  $CD_3CN$  serves to identify it.

$^1H$  NMR ( $\tau$ ,  $CD_2Cl_2$ ) 3.56 (s, 10, Cp), 3.83 (m, 4,  $C_5H_4$ ), 7.56 (s, 3,  $C_5Me$ ), 9.48 (s, 6, TaMe).

**8. Preparation of  $[Ta(\eta^5-C_5H_4Me)_2Me_2]^+BF_4^-$ .** The procedure was identical with that in 7 using 3.86 g of  $Ta(\eta^5-C_5H_4Me)_2Me_3$  and 3.30 g of  $Ph_3C^+BF_4^-$ , yield 4.3 g (93%).

$^1H$  NMR ( $\tau$ ,  $CD_2Cl_2$ , 220 MHz) 3.61 (t, 4,  $J_{HH} = 2.6$  Hz), 3.77 (t, 4,  $J_{HH} = 2.6$  Hz), 7.52 (s, 6,  $C_5Me$ ), 9.54 (s, 6, TaMe).

**9. Preparation of  $TaCp_2Me_2Br$ .**  $Br_2$  (0.45 g) in 10 mL of dichloromethane was added slowly at 0 °C to a solution of 1 g of  $TaCp_2Me_3$  in 25 mL of dichloromethane. The ivory precipitate was filtered, washed with  $2 \times 10$  mL of acetonitrile and 10 mL of ether, and dried in vacuo, yield 0.98 g (83%).

Anal. Calcd for  $TaC_{12}H_{16}Br$ : C, 34.21; H, 3.82. Found: C, 33.49; H, 3.69.

**10. Preparation of  $[TaCp_2(Me)(Br)]^+X^-$  ( $X^- = Br^-, Br_3^-$ ).** Neat  $Br_2$  (0.63 mL) was rapidly added to a solution of 1.89 g of  $TaCp_2Me_3$  in 25 mL of dichloromethane. The dichloromethane was removed in vacuo and 15 mL of acetonitrile added to the residue. Filtration gave 0.91 g of canary yellow  $TaCp_2Br_3$ . Addition of one volume of ether to the filtrate gave 0.3 g of microcrystalline, yellow  $[TaCp_2(Me)(Br)]^+Br^-$ . Further addition of ether followed by cooling at  $-30$  °C gave 0.55 g of orange, crystalline  $[TaCp_2(Me)(Br)]^+Br_3^-$ .

Anal. Calcd for  $TaC_{11}H_{13}Br_4$ : C, 20.45; H, 2.03; Br, 49.52. Found: C, 20.66; H, 2.00; Br, 49.78.

$^1H$  NMR ( $\tau$ ,  $CD_3CN$ ) 3.20 (s, 10, Cp), 9.00 (s, 3, Me).

**11. Preparation of  $[TaCp_2(Me)(Br)]^+BF_4^-$ .** A solution of 0.12 mL of  $Br_2$  in 10 mL of dichloromethane was added dropwise with stirring to 1.0 g of  $[TaCp_2Me_2]^+BF_4^-$  in 20 mL of  $CH_2Cl_2$  at 0 °C. The suspension was warmed to room temperature and stirred for 2 h. The  $CH_2Cl_2$  was removed in vacuo to yield 0.92 g of yellow  $[TaCp_2(Me)(Br)]^+BF_4^-$  (80%). The yellow product may be recrystallized from acetonitrile with ether to give yellow plates or needles. Its  $^1H$  NMR spectrum is identical with that of the  $Br^-$  and  $Br_3^-$  salts (see 10) and its infrared spectrum shows a characteristic strong, broad absorption at  $\nu \approx 1070$   $cm^{-1}$  due to  $BF_4^-$ . It may also be prepared from  $[TaCp_2(Me)(Br)]^+Br^-$  and  $TiBF_4$  in acetonitrile.

**12. Preparation of  $NbCp_2Me_3$  and Identification by  $^1H$  NMR.** Orange  $NbMe_2Cl_3$  was prepared by a procedure analogous to that used to prepare  $TaMe_3Cl_2$  (stirred for 16 h) and converted to yellow  $NbMe_3Cl_2^{12}$  with an additional 0.5 mL of  $ZnMe_2$  in pentane. Solid  $TiCp$  was added to a solution of 0.42 g of  $NbMe_3Cl_2$  in 25 mL of toluene. The white  $TiCl$  was filtered off after 1 h (0.95 g, quantitative) and the solvent almost completely removed from the filtrate in vacuo to give an oil. Addition of a few milliliters of pentane caused pale shimmering crystals to form (0.28 g). An  $^1H$  NMR spectrum in  $C_6D_6$  ( $\tau$  5.27 (10), 9.70 (6), 9.85 (3)) was essentially identical with that of  $TaCp_2Me_3$ .  $NbCp_2Me_3$  readily decomposes near room temperature, as a solid or in solution.

**13. Preparation of  $TaCp_2(CH_2)(CH_3)$  and  $TaCp_2(CD_2)(CD_3)$ .** (a) Using  $Me_3P=CH_2$ . To a suspension of 4.28 g of  $[TaCp_2Me_2]^+BF_4^-$  in 25 mL of THF was added slowly 0.95 g of  $Me_3P=CH_2$  in 10 mL of THF and the mixture was stirred for 15 min. The solvent was removed in vacuo and the residue extracted with toluene leaving an 88% yield (1.75 g) of  $Me_4P^+BF_4^-$  which was identified by comparison of its infrared spectrum with that of an authentic sample. Toluene was removed in vacuo until crystals appeared, then about three volumes of pentane was added and the mixture stood at  $-30$  °C for 1 h. Filtration gave 2.55 g of shimmering greenish-white needles (second crop 0.22 g), total yield 2.77 g (82%). This procedure has been successfully scaled up by a factor of 5.

(b) Using  $LiN(SiMe_3)_2$ . A suspension of 10.58 g of  $[TaCp_2Me_2]^+BF_4^-$  in 200 mL of THF was cooled to  $-78$  °C and a solution of 4.15 g of  $LiN(SiMe_3)_2$  in 50 mL of THF added slowly. The mixture was warmed to room temperature and all the THF was removed in vacuo. The tan solid must be extracted immediately with toluene. The  $LiBF_4$  was filtered off and the filtrate's volume reduced in vacuo until crystals appeared. The product was isolated as in (a), total yield 6.35 g (78%).

(c) From  $TaCp_2(CH_2AlMe_3)(CH_3)$  and Lewis Bases. (i)  $Et_3N$ .  $TaCp_2(CH_2AlMe_3)(CH_3)$  (0.41 g) and 0.1 g of  $Et_3N$  were mixed in 5 mL of ether. Addition of 5 mL of pentane and standing at  $-30$  °C for 1 h gave 0.10 g of  $TaCp_2(CH_2)(CH_3)$ .

(ii)  $Me_3P=CH_2$ .  $TaCp_2(CH_2AlMe_3)(CH_3)$  (0.41 g) and 90 mg of  $Me_3P=CH_2$  were stirred in 5 mL of toluene. The solution was stripped to a thick liquid and 10 mL of pentane was added. The 0.41 g of pale crystals, which were filtered off, are a 1:2 mixture of  $TaCp_2(CH_2)(CH_3)$  and  $Me_3PCH_2AlMe_3$ . [ $^1H$  NMR of the latter ( $\tau$ ,  $C_6D_6$ ) 9.27 (d, 9,  $J_{HP} = 13$  Hz,  $PMe_3$ ), 10.0 (d, 2,  $J_{HP} = 17$  Hz,  $CH_2$ ), 10.43 (s, 9,  $AlMe_3$ ).] The filtrate contains pure  $TaCp_2(CH_2)(CH_3)$  which may be recovered by removing the pentane in vacuo, yield 80 mg.

Anal. Calcd for  $TaC_{12}H_{15}$ : C, 42.37; H, 4.44. Found: C, 42.10; H, 4.44.

$^1H$  NMR ( $\tau$ ,  $C_6D_6$ )  $-0.11$  (s, 2,  $=CH_2$ ), 4.88 (s, 10, Cp), 10.0 (s, 3,  $CH_3$ ).  $^{13}C$  NMR (ppm from  $Me_4Si$ , gated decoupled,  $CD_2Cl_2$ ) 224 (t,  $^1J_{CH} = 132$  Hz,  $CH_2$ ), 100 (d,  $^1J_{CH} = 177$  Hz, Cp),  $-5$  (q,  $^1J_{CH} = 122$  Hz,  $CH_3$ ).

$TaCp_2(CD_2)(CD_3)$  was prepared as in (a). Its  $^1H$  NMR spectrum showed a Cp resonance at  $\tau$  4.88 but only barely detectable resonances at  $\tau -0.11$  or 10.0 at  $10\times$  the amplitude.

**14. Preparation of  $TaCp_2(\eta^5-C_5H_4Me)(CH_2)(CH_3)$ .** A suspension of 0.60 g of  $[TaCp_2(\eta^5-C_5H_4Me)Me_2]^+BF_4^-$  in 4 mL of THF was treated with 0.12 g of  $Me_3P=CH_2$  in 4 mL of THF with stirring as in 13a. The residue was extracted with 25 mL of pentane leaving 0.18 g (75%) of  $Me_4P^+BF_4^-$ . The pentane was removed in vacuo leaving 0.35 g (73%) of fluffy, pale yellow crystals which were identified by comparison of the 220-MHz  $^1H$  NMR with that of  $TaCp_2(CH_2)(CH_3)$ .

$^1H$  NMR ( $\tau$ , toluene- $d_8$ , 220 MHz) 0.02 and 0.10 (AB quartet,  $J_{HH} = 7.6$  Hz,  $CH_2$ ), 4.92 (s, 5, Cp), 4.96 (m, 2,  $C_5H_2$  set), 5.16 (m, 2,  $C_5H_2$  set), 8.01 (s, 3,  $C_5Me$ ), 10.06 (s, 3, TaMe). [The 220-MHz spectrum of  $TaCp_2(CH_2)(CH_3)$  in toluene- $d_8$  shows the  $CH_2$  group as a singlet at  $\tau$  0.0, Cp at  $\tau$  4.96, and Me at  $\tau$  10.04.] (See Figure 2.)

**15. Preparation of  $Ta(\eta^5-C_5H_4Me)_2(CH_2)(CH_3)$ .** The procedure is identical with that for  $TaCp_2(\eta^5-C_5H_4Me)(CH_2)(CH_3)$  using 0.36 g of  $Me_3P=CH_2$  and 1.83 g of  $[Ta(\eta^5-C_5H_4Me)_2Me_2]^+BF_4^-$ , yield 0.95 g (64%) of white crystals.

$^1H$  NMR ( $\tau$ ,  $C_6D_6$ , 220 MHz) 0.03 (s, 2,  $CH_2$ ), 4.19 (m, 2,  $C_5H$ ), 5.14 (m, 6,  $C_5H_3$ ), 7.99 (s, 6,  $C_5Me$ ), 9.99 (s, 3, TaMe).

**16. Preparation of  $TaCp_2(CH_2AlMe_3)(CH_3)$ .** (a) From  $TaCp_2Me_3$  and  $AlMe_3$ .  $AlMe_3$  (0.44 g) in 10 mL of toluene was added to a stirred solution of 2.14 g of  $TaCp_2Me_3$  in 30 mL of toluene. An oily orange layer formed rapidly but after 10 days stirring the solution was again homogeneous. Nearly all the solvent was removed in vacuo and 25 mL of pentane was slowly added to give 2.15 g (87%) of cream-colored  $TaCp_2(CH_2AlMe_3)(CH_3)$ .

If the oily orange layer from above is washed three times with toluene and pentane is then added, 2.05 g of a yellow solid is obtained whose  $^1H$  NMR spectrum in  $CD_2Cl_2$  at  $-80$  °C (100 MHz) shows three broad singlets at  $\tau$  3.4, 9.3, and 10.9 in the ratio of 10:6:12. At room temperature all are quite broad. The yellow solid is believed to be  $[TaCp_2Me_2]^+[AlMe_4]^-$ . In  $CH_2Cl_2$  or acetonitrile it is only  $\sim 1/10$  as good a conductor ( $\Lambda = 10$  for a 110-mg sample in 50 mL of  $CH_2Cl_2$ ;  $\Lambda = 9$  for a 120-mg sample in  $CH_3CN$ ) as  $[TaCp_2Me_2]^+BF_4^-$  in acetonitrile ( $\Lambda = 133$  for a 160-mg sample in 50 mL).

A sample of 1.07 g of  $TaCp_2Me_3$  (3.0 mmol) and 0.22 g of  $AlMe_3$  (3.0 mmol) in toluene were sealed in vacuo in a flask equipped with a break-seal and the mixture was stirred for 4 days at room temperature. The evolved gas was then measured with a Toepler pump (2.1 mmol) and identified by mass spectroscopy; it was essentially pure  $CH_4$  containing only traces of ethylene and ethane.

(b) From  $TaCp_2(CH_2)(CH_3)$  and  $AlMe_3$ .  $AlMe_3$  (0.080 g) and  $TaCp_2(CH_2)(CH_3)$  (0.34 g) were mixed in 5 mL of toluene at 25 °C. Nearly all the toluene was removed and 10 mL of pentane was added. Standing at  $-40$  °C for 3 h gave 0.280 g of product as fluffy, pale

yellow crystals.

Anal. Calcd for  $\text{TaC}_{15}\text{H}_{24}\text{Al}$ : C, 43.70; H, 5.86. Found: C, 43.40; H, 5.73.

$^1\text{H}$  NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 2.32 (s, 2,  $\text{CH}_2$ ), 4.88 (s, 10, Cp), 10.0 (s, 3, TaMe), 10.32 (s, 9, AlMe<sub>3</sub>).  $^{13}\text{C}$  NMR (ppm from Me<sub>4</sub>Si, gated decoupled,  $\text{C}_6\text{D}_6$ ) 177 (t,  $^1J_{\text{CH}} = 124$  Hz, methylene C), 105 (d,  $^1J_{\text{CH}} = 178$  Hz, Cp), 16.5 (q,  $^1J_{\text{CH}} = 123$  Hz, TaMe), -2.6 (broadened q,  $^1J_{\text{CH}} = 109$  Hz, AlMe<sub>3</sub>). The last two peaks were assigned assuming that the broadening is due to the onset of coupling to  $^{27}\text{Al}$ .

**17. Preparation of  $[\text{TaCp}_2(\text{CH}_2\text{SiMe}_3)(\text{CH}_3)]^+\text{Br}^-$ .** Me<sub>3</sub>SiBr (3.06 g) in 10 mL of dichloromethane was added to a solution of 6.80 g of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  in 35 mL of dichloromethane. Pale yellow crystals (3.75 g) were filtered off after 12 h and 3.65 g of additional product on addition of 100 mL of diethyl ether to the filtrate, total yield 7.40 g (75%). The product recrystallizes slowly from dichloromethane on addition of diethyl ether to give ivory microcrystals.

Anal. Calcd for  $\text{TaC}_{15}\text{H}_{24}\text{SiBr}$ : C, 36.52; H, 4.90. Found: C, 36.75; H, 4.84.

$^1\text{H}$  NMR ( $\tau$ ,  $\text{CD}_2\text{Cl}_2$ ) 3.25 (s, 10, Cp), 8.61 (q, 2,  $J \approx 1$  Hz,  $\text{CH}_2$ ), 9.43 (t, 3,  $J \approx 1$  Hz, TaMe), 9.87 (s, 9, SiMe<sub>3</sub>). A 100-mg sample in 50 mL of  $\text{CH}_3\text{CN}$  gave  $\Delta = 102$ .

**18. Preparation of  $\text{TaCp}_2(\text{C}_2\text{H}_4)\text{I}$ .** Methyl iodide (0.19 mL) was added to a solution of 1.02 g of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  in 5 mL of benzene. After 12 h all solvent was removed in vacuo leaving an orange powder (1.13 g) which was recrystallized from a saturated toluene solution as metallic orange needles by cooling to  $-30^\circ\text{C}$ .

Anal. Calcd for  $\text{TaC}_{12}\text{H}_{14}\text{I}$ : C, 30.92; H, 3.03; I, 27.22. Found: C, 31.11; H, 3.00; I, 27.16.

$^1\text{H}$  NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ , 270 MHz) 5.20 (s, 10, Cp), 8.02 (t, 2, outside  $\text{CH}_2$ ), 8.74 (t, 2, inside  $\text{CH}_2$ ); see Figure 3a.

**19. Preparation of  $\text{TaCp}_2(\text{CH}_2\text{CD}_2)\text{I}/\text{TaCp}_2(\text{CD}_2\text{CH}_2)\text{I}$  Mixture.** The reaction between 0.68 g of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  (2.0 mmol) and  $\text{CD}_3\text{I}$  (2.0 mmol) in 5 mL of benzene in an evacuated sealed flask equipped with a break-seal at  $25^\circ\text{C}$  for 16 h gave 2.0 mmol of methane which was shown to consist of 93%  $\text{CH}_3\text{D}$ , 5%  $\text{CH}_4$ , and 2% all others by mass spectroscopy. The  $^1\text{H}$  NMR spectrum of the orange product obtained by removing all volatiles showed a Cp singlet at  $\tau$  5.20 and two broad singlets at  $\tau$  8.05 and 8.76 in the ratio of 10.0 (defined):1.0:1.0 (see Figure 3b).

**20. Preparation of  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{CH}_3)$ .** A 100-mL pressure bottle containing a solution of 1.7 g of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  in 10 mL of benzene was pressurized to 40 psi with ethylene and stirred and heated to  $80^\circ\text{C}$  for 8 h. The solvent was then removed in vacuo and the residue dissolved in 200 mL of hexane. The solution was treated with decolorizing charcoal and filtered. The volume was decreased to 25 mL and this solution stood at  $-30^\circ\text{C}$  for 3 h. Filtration gave 1.2 g (68%) of gold crystals.

Anal. Calcd for  $\text{TaC}_{13}\text{H}_{17}$ : C, 44.08; H, 4.83. Found: C, 43.78; H, 4.81.

$^1\text{H}$  NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ , 220 MHz) 5.55 (s, 10, Cp), 9.02 (2nd order t, 2, outside  $\text{CH}_2$ ), 9.22 (2nd order t, 2, inside  $\text{CH}_2$ ), 9.50 (s, 3,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (ppm from Me<sub>4</sub>Si, gated decoupled,  $\text{C}_6\text{D}_6$ ) 97.6 (d,  $^1J_{\text{CH}} = 177$  Hz, Cp), 20.9 (t,  $^1J_{\text{CH}} = 148$  Hz,  $\text{CH}_2$ ), 20.2 (t,  $^1J_{\text{CH}} = 149$  Hz,  $\text{CH}_2$ ), -5.4 (q,  $^1J_{\text{CH}} = 122$  Hz,  $\text{CH}_3$ ).

**21. Reaction of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  with  $\text{C}_2\text{D}_4$ .**  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  (0.68 g, 2.0 mmol) and 10 mL of benzene were placed in a 250-mL flask equipped with a break-seal.  $\text{C}_2\text{D}_4$  (45 mL at 760 mm, 2.0 mmol) was condensed in and the flask was sealed and heated with stirring to  $80^\circ\text{C}$  for 16 h. The flask was opened and all gas noncondensable at  $-78^\circ$  measured; noncondensables 1.2 mmol; 92%  $\text{C}_2\text{D}_4$ , 4%  $\text{C}_2\text{D}_3\text{H}$ , 4%  $\text{C}_2\text{H}_4$  by mass spectroscopy. Workup as in 20 gave 0.50 g of gold crystals whose  $^1\text{H}$  NMR spectrum was identical with that of  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{CH}_3)$  at 100 MHz except that the relative areas were 10.0 (defined):2.1:2.9. The ethylene pattern at 270 MHz was identical with that in Figure 4a. The Cp singlet and the methyl singlet in  $\text{TaCp}_2(\text{CD}_2\text{CD}_2)(\text{CH}_3)$  are located 1.5 Hz upfield (we propose) of the Cp and methyl singlets in  $\text{TaCp}_2(\text{CH}_2\text{CH}_2)(\text{CH}_3)$ .

**22. Preparation of  $\text{TaCp}_2(\text{PMe}_3)(\text{Me})$  from  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ .** A mixture of 2.04 g of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  and 0.50 g of  $\text{PMe}_3$  in 20 mL of toluene was heated to  $40^\circ\text{C}$  for 5 days. The solution was then filtered and an equal volume of hexane added. Cooling to  $-30^\circ\text{C}$  yielded a red mixture of  $\text{TaCp}_2(\text{PMe}_3)(\text{Me})$  and  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{CH}_3)$  which was similarly recrystallized to give pure  $\text{TaCp}_2(\text{PMe}_3)(\text{Me})$  (31%).

Anal. Calcd for  $\text{TaC}_{14}\text{H}_{22}\text{P}$ : C, 41.80; H, 5.52; P, 7.70. Found: C, 39.92; H, 5.51; P, 8.13.

$^1\text{H}$  NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 5.78 (d, 10,  $J \approx 2$  Hz, Cp), 9.02 (d, 9,  $J = 7$  Hz,  $\text{PMe}_3$ ), 10.50 (d, 3,  $J = 8$  Hz, Me).

**23. Preparation of  $\text{TaCp}_2(\text{PMe}_2\text{Ph})(\text{Me})$  from  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ .** The procedure is identical with that in 22, yield 0.70 g (51%) of metallic red needles or plates.

$^1\text{H}$  NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 2.90 (br m, 5, Ph), 5.90 (d, 10,  $J \approx 2$  Hz, Cp), 8.80 (d, 6,  $J = 7$  Hz,  $\text{PMe}_2$ ), 10.70 (d, 3,  $J = 7$  Hz, Me).

**24. Preparation of  $\text{TaCp}_2(\text{CO})(\text{CH}_3)$  from  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ .** A pressure bottle containing a solution of  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  (1.0 g) in 5 mL of benzene was flushed with CO, then pressurized to 55 psi. The vessel was heated to  $80^\circ\text{C}$  and the solution stirred vigorously for ca. 8 h. All benzene was removed in vacuo leaving a green residue whose  $^1\text{H}$  NMR spectrum showed it to be a 1:1 mixture of  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{CH}_3)$  and  $\text{TaCp}_2(\text{CO})(\text{CH}_3)$ . The latter is slightly less soluble in hexane than the former. If the reaction is repeated in 25 mL of hexane, 0.35 g of pure  $\text{TaCp}_2(\text{CO})(\text{CH}_3)$  crystallizes out during the reaction. It can be recrystallized from minimal benzene by adding pentane and cooling. In the solid state it is bluish-green; its solutions are green.

Anal. Calcd for  $\text{TaC}_{12}\text{H}_{13}\text{O}$ : C, 40.70; H, 3.70. Found: C, 40.40; H, 3.90.

$^1\text{H}$  NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 5.55 (s, 10, Cp), 10.40 (s, 3,  $\text{CH}_3$ ). IR (Nujol,  $\text{cm}^{-1}$ ) 1850 s ( $\nu_{\text{C=O}}$ ).

**25. Preparation of  $\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{H})$ .**  $\text{TaCp}_2(\text{C}_2\text{H}_4)\text{I}$  (0.5 g) and KH (0.050 g) were stirred in THF for 4 days. All solvent was removed and the residue was extracted with 5 mL of benzene. Pentane (20 mL) was added along with decolorizing charcoal and the solution was filtered. All solvent was once again removed in vacuo and the residue taken up in 25 mL of pentane. Pale yellow, fluffy needles formed after removing much of the solvent in vacuo and standing the remaining solution at  $-40^\circ\text{C}$  for 2 h, yield 0.130 g (36%).

$\text{TaCp}_2(\text{C}_2\text{H}_4)(\text{H})$  was identified by  $^1\text{H}$  NMR (cf.  $\text{NbCp}_2(\text{C}_2\text{H}_4)(\text{H})^{19}$ ).  $^1\text{H}$  NMR ( $\tau$ ,  $\text{C}_6\text{D}_6$ ) 5.50 (s, 10, Cp), 9.2 (m, 2, outside  $\text{CH}_2$ ), 9.7 (2nd order t, 2, inside  $\text{CH}_2$ ), 13.4 (poor t, 1,  $J \approx 2$  Hz, hydride).

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