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**MASTER**

PAST RESEARCH SUMMARY

REDUCTION OF CARBON MONOXIDE

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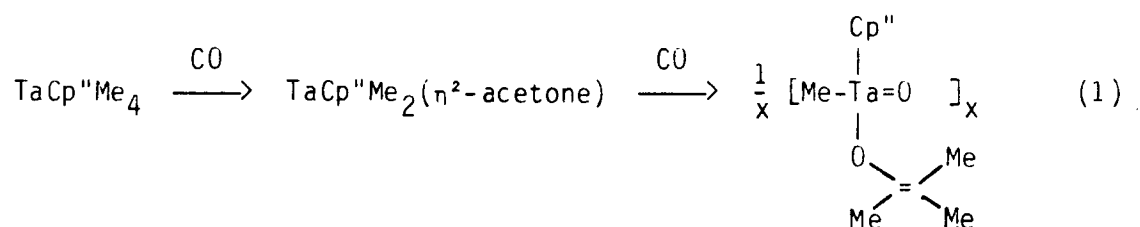
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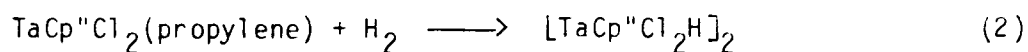
## PAST RESEARCH SUMMARY

The type of hydride complex we set out to prepare was suggested by some early results concerning how CO reacts with  $\text{TaCp}''\text{Me}_4$  ( $\text{Cp}'' = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$ ).<sup>12</sup> We found that an  $\eta^2$ -acetone complex was formed first, followed by a polymeric trimethylenolate complex (equation 1), each in an intramolecular fashion. Therefore we considered preparing  $\text{TaCp}''\text{H}_4$  from  $\text{TaCp}''\text{Me}_4$  and  $\text{H}_2$ . Eventually, we had to admit that whatever the product was, it probably was not



' $\text{TaCp}''\text{H}_4$ '. We then lowered our expectations by attempting to make  $\text{TaCp}''\text{Cl}_2\text{H}_2$ . This goal was more realistic and successful.

We found that  $\text{TaCp}''\text{Cl}_2(\text{propylene})$ , a molecule we discovered and used extensively for studying the selective dimerization of  $\alpha$ -olefins,<sup>13</sup> reacts smoothly with  $\text{H}_2$ , as shown in equation 2. The corresponding  $\text{Cp}'$  complex was

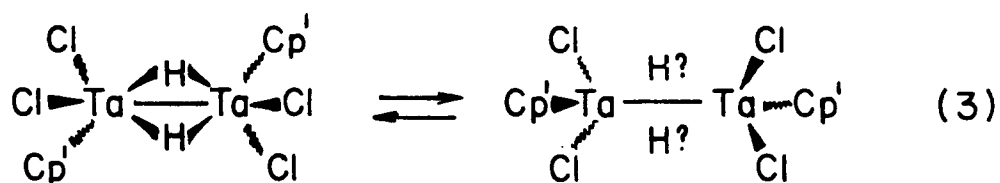


more soluble, and in spite of its having a more complex NMR spectrum, we routinely study it instead of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$ .  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  could also be made from  $\text{TaCp}'\text{Cl}_2\text{Np}_2$  and hydrogen. In each case  $\text{TaCp}'\text{Cl}_2\text{R}(\text{H})$  ( $\text{R} = \text{propyl}$  or  $\text{CH}_2\text{CMe}_3$ ) is an intermediate. The subsequent reaction to form  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  probably does not involve formation of  $\text{TaCp}'\text{Cl}_2\text{H}_2$  as an intermediate.

Upon reacting  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  with alkylating agents monoalkyl derivatives  $\text{Ta}_2\text{Cp}'_2\text{Cl}_3\text{H}_2\text{R}$  are formed. A drawing of the structure of the methyl derivative is shown in Figure 1. We assume the parent complex has an analogous structure shown schematically below the ORTEP drawing, and that the hydrides are present in bridging positions as shown. A preprint of the paper describing this structure and relevant chemistry is provided in Appendix I.

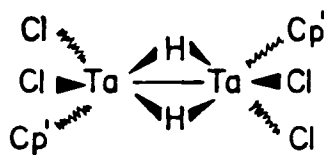
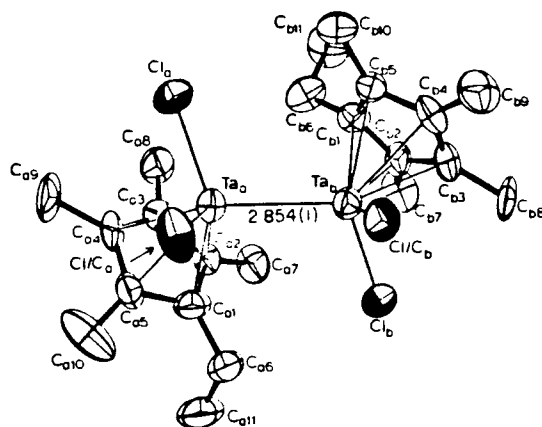
There are several features of these dimeric molecules which I want to summarize here, since they will be useful to us in the next stage where we worry about whether the dimer remains intact when it reacts with CO. All evidence to date suggests that (see Scheme I)

- (i) the dimer does not break into monomers under mild conditions ( $70^\circ$ , 5 hr);
- (ii) intermolecular hydride exchange is not negligible, but it is slow;
- (iii) intermolecular non-ionic halide exchange is fast;
- (iv) the ends of the dimers can rotate partially with respect to one another so as to pass through the structure which is shown in equation 3.

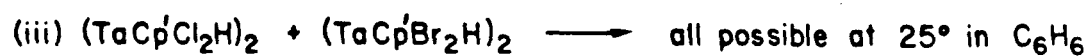
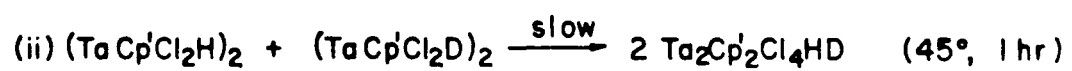
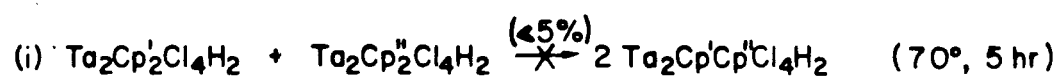


The fourth conclusion follows from observations i, ii, and iii and the fact that only two types of methyl groups are observed in the  $^1\text{H}$  NMR spectrum of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ . We do not know for certain where the hydrides are located in the more symmetric species, nor if their mobility is contingent upon the twisting process.

Figure 1. X-ray Structure of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{Me}(\text{H})_2$   
(C. S. Day)

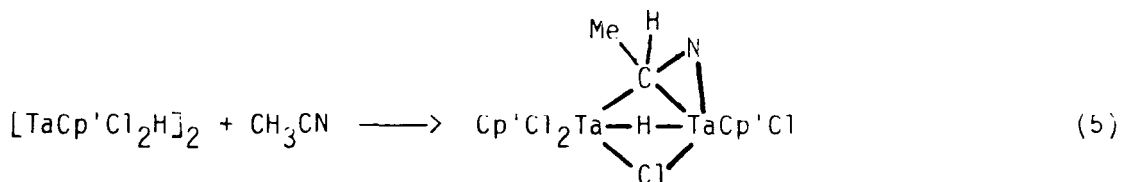
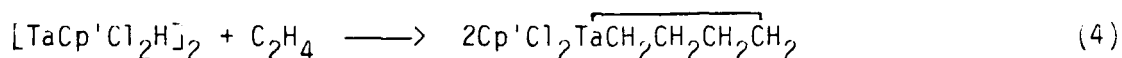


SCHEME I. SOME LABELING STUDIES





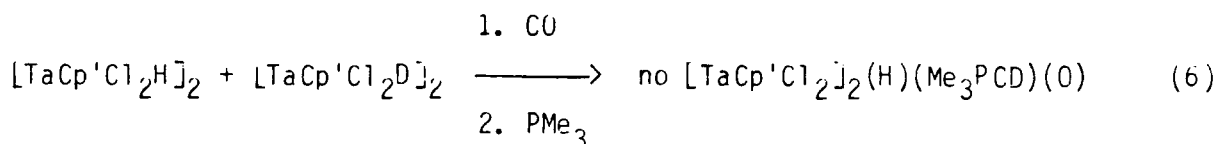
The binuclear tantalum hydride complexes react with carbon monoxide to give a molecule which is, to my knowledge (with the exception of Bercaw's formation of zirconoxy carbene complexes (Scheme II)<sup>14</sup>), the only example of reduction of CO by a transition metal hydride to give a complex containing a CHO ligand. (A preprint is provided in Appendix II. ) Like Bercaw's "zirconoxy carbene", the "formyl hydride" product contains an unusual "formyl" ligand, one which is trapped between two tantalum centers (Figure 2).<sup>15</sup> The metals are now too far apart to form a Ta-Ta bond. Isonitriles react with the dimeric tantalum hydride complex in an analogous fashion to give dimeric formimidoyl complexes. We also know that  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  reacts with ethylene as shown in equation 4, and with acetonitrile as shown in equation 5; these studies will be published later, along with a full account of how  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  reacts with small molecules (see Proposed Research).



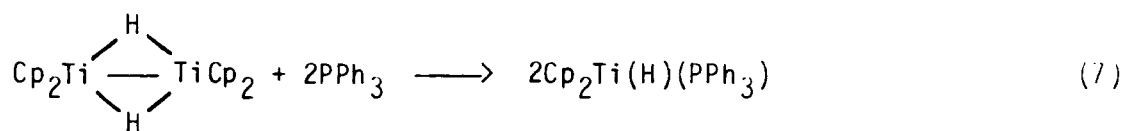
When  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$  is hydrolyzed with aqueous HCl, methanol forms in >90% yield. We have assumed that the oxygen in the methanol is that from the original CO molecule. (We could have postulated that  $\text{H}_2\text{O}$  or OH attacks a  $\mu$ -methylene ligand, but as we shall see shortly, a complex which does contain a  $\mu$ -methylene ligand hydrolyzes to give methane, not methanol.) Methane

(35% yield) can be obtained from  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$  by adding  $\text{AlCl}_3$ . The yield improves significantly ( $\sim 80\%$ ) if molecular hydrogen is present in addition to  $\text{AlCl}_3$ . It seems reasonable to propose that the aluminum coordinates to the oxygen of the  $\mu$ -formyl ligand and assists in breaking the CO bond.

Before we had obtained suitable x-ray quality crystals of  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$ , we attempted to prepare a more crystalline derivative by adding  $\text{PMe}_3$ . Yellow needles were obtained<sup>16</sup> of a compound whose structure is shown in Figure 3.<sup>17</sup> The CH-O bond must break when  $\text{PMe}_3$  attacks the formyl carbon atom to give a  $\mu$ - $\text{Me}_3\text{PCH}$  ligand. The metals, as in  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$ , are still too far apart to be bonded to each other, but they are closer together in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{Me}_3\text{PCH})(\text{O})$  than in  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$  as a result of the CH-O bond cleavage. Besides telling us that "bases" will attack the formyl carbon atom, the favorable characteristics of the  $^1\text{H}$  NMR spectra allowed us to do the experiment shown in equation 6. It proves that the dimeric



hydride does not break into free monomeric units when it reacts with CO. (The possibility that the two hydrides (deuterides) stay with one monomeric metal fragment, but do not scramble, is a possible, but we feel less likely alternative.) We had expected CO to cleave the Ta-Ta bond by comparison with the known reaction shown in equation 7.<sup>18</sup>



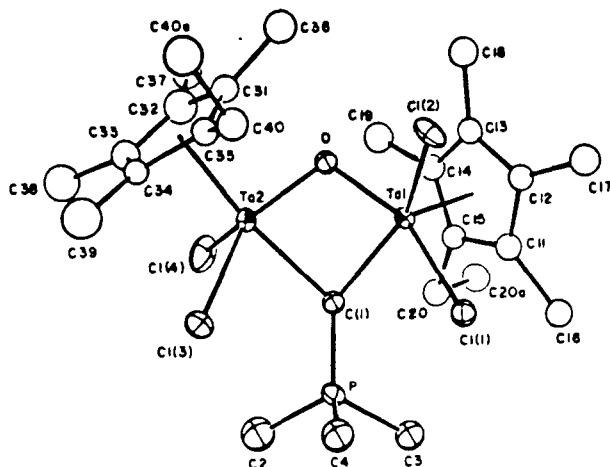


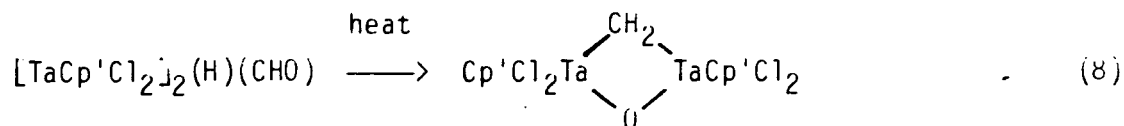
Figure 3. Labeling of atoms in the  $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TaCl}_2]_2(\text{H})(\mu\text{-CHPMe}_3)(\mu\text{-O})$  molecule (ORTEP diagram; 30% probability ellipsoids).

Table . Intramolecular Distances with Esd's for  $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TaCl}_2]_2(\text{H})(\mu\text{-CHPMe}_3)(\mu\text{-O})$

atoms	dist, Å	atoms	dist, Å
(A) Distances from the Tantalum Atoms			
Ta(1)···Ta(2)	2.992 (1)	Ta(2)–Cl(3)	2.405 (5)
Ta(1)–Cl(1)	2.445 (4)	Ta(2)–Cl(4)	2.417 (6)
Ta(1)–Cl(2)	2.437 (5)	Ta(2)–C(1)	2.354 (17)
Ta(1)–C(1)	2.187 (17)	Ta(2)–O	1.958 (11)
Ta(1)–O	1.895 (11)	Ta(2)–C(31)	2.486 (22)
Ta(1)–C(11)	2.531 (20)	Ta(2)–C(32)	2.477 (20)
Ta(1)–C(12)	2.481 (19)	Ta(2)–C(33)	2.532 (21)
Ta(1)–C(13)	2.414 (18)	Ta(2)–C(34)	2.513 (18)
Ta(1)–C(14)	2.476 (20)	Ta(2)–C(35)	2.439 (17)
Ta(1)–C(15)	2.502 (18)	Ta(2)···Cp(2)	2.172
Ta(1)···Cp(1)	2.165		
(B) Distances within the CHPMe <sub>3</sub> Ligand			
P–C(1)	1.751 (19)		
P–C(2)	1.846 (26)		
P–C(3)	1.835 (21)		
P–C(4)	1.838 (22)		
(C) Internal C–C Distances for the $\eta^5\text{-C}_5\text{Me}_4\text{Et}$ Ligands			
C(11)–C(12)	1.452 (27)	C(31)–C(32)	1.448 (31)
C(12)–C(13)	1.422 (27)	C(32)–C(33)	1.442 (31)
C(13)–C(14)	1.416 (27)	C(33)–C(34)	1.392 (29)
C(14)–C(15)	1.439 (27)	C(34)–C(35)	1.446 (26)
C(15)–C(11)	1.394 (27)	C(35)–C(31)	1.420 (28)
(D) External C(sp <sup>3</sup> )–C(sp <sup>3</sup> ) Distances for the $\eta^5\text{-C}_5\text{Me}_4\text{Et}$ Ligands			
C(11)–C(16)	1.549 (28)	C(31)–C(36)	1.531 (33)
C(12)–C(17)	1.536 (29)	C(32)–C(37)	1.512 (29)
C(13)–C(18)	1.545 (30)	C(33)–C(38)	1.557 (33)
C(14)–C(19)	1.536 (30)	C(34)–C(39)	1.534 (31)
C(15)–C(20)	1.535 (28)	C(35)–C(40)	1.472 (26)
(E) External C(sp <sup>3</sup> )–C(sp <sup>3</sup> ) Distances for the $\eta^5\text{-C}_5\text{Me}_4\text{Et}$ Ligands			
C(20)–C(20A)	1.565 (31)	C(40)–C(40A)	1.588 (30)

The question as to how CO reacts with  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  becomes an urgent and especially important one upon consideration of the preliminary results shown in Scheme III. Apparently the  $\pi$ -bonding ligands ( $\text{PMe}_3$  and CO) form analogous paramagnetic dimers. We have obtained one poor quality FT IR spectrum of a sample of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{CO})$  in which what is probably a  $\nu_{\text{CO}}$  band is observed at  $1953 \text{ cm}^{-1}$ ; this must be carefully checked (see Proposed Research). We have also obtained preliminary EPR spectra of the  $\text{PMe}_3$  and CO adducts which suggest that the situation which gives rise to the paramagnetism is not a simple one. Our working hypothesis is that the monocarbonyl adduct is a dimer which consists of weakly interacting  $d^1$  centers bridged by chlorides as shown in Scheme IV; the hydrides should no longer be able to bridge if the Ta-Ta bond is partially broken. All of these results are strictly preliminary and I present them here only in order to illustrate how potentially interesting and important they are.

Another preliminary and interesting result is that when  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$  is heated in the solid state it gives a species which contains a methylene ligand ( $J_{\text{CH}} = 135$ ,  $\delta^{13}\text{C} \sim 130 \text{ ppm}$ ) derived from  $^{13}\text{CO}$ . We suspect that the bridging hydride (a "base") attacks the formyl carbon atom to give a  $\mu$ -methylene  $\mu$ -oxo complex (equation 8). While  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$  hydrolyzes to give methanol (see above), the  $\mu$ -methylene  $\mu$ -oxo complex hydrolyzes to give methane.



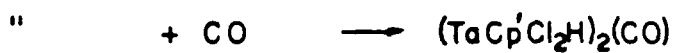
SCHEME III. FORMATION OF ADDUCTS



- (i) green, diamagnetic
- (ii) 5 inequiv. py protons
- (iii) inequiv. hydrides

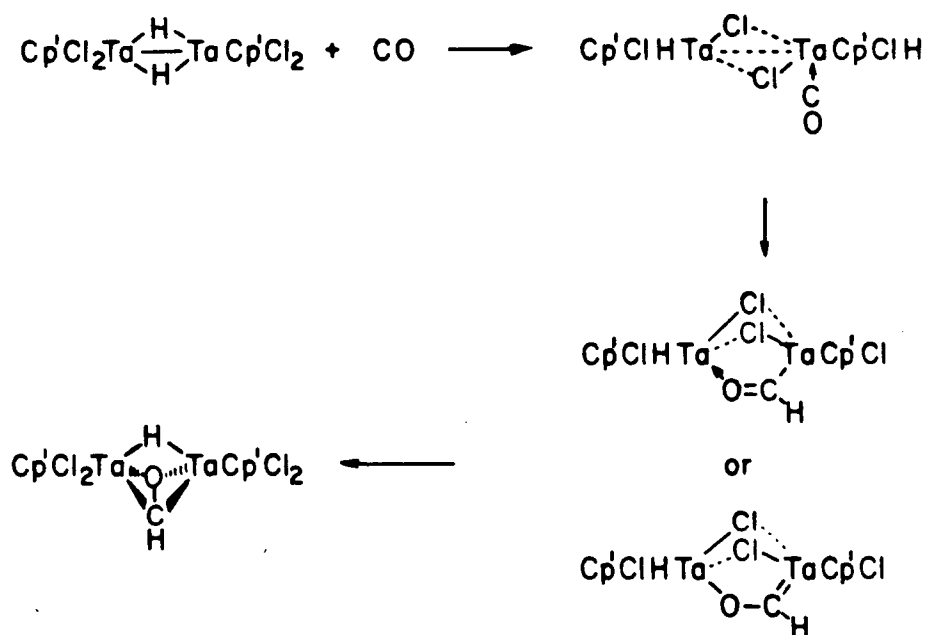


- (i) purple, paramagnetic, dimeric ( $\text{C}_6\text{H}_6$ )
- (ii) decomposes at  $25^\circ$



- (i) purple, paramagnetic (2.3 BM,  $-60^\circ$ )
- (ii) decomposes at  $-30^\circ$  to formyl hydride

SCHEME IV. PROPOSED MECHANISM



We have spent some time exploring analogous niobium chemistry. Some details must still be worked out.  $[\text{NbCp}'\text{Cl}_2\text{H}]_2$  can be prepared readily in a manner analogous to that used to prepare  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ . It is virtually indistinguishable from  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  physically, but its IR and NMR spectra differ from those for the tantalum species; a metal-hydride mode is not found at  $1650\text{ cm}^{-1}$  in the IR spectrum and a hydride resonance is absent in the NMR spectrum.  $[\text{NbCp}'\text{Cl}_2\text{H}]_2$  does not react readily with CO, and when it does, monomeric products such as  $\text{NbCp}'\text{Cl}_2(\text{CO})_2$  result.

I will not include in this summary the many unsuccessful attempts to prepare other tantalum and niobium hydride complexes or derivatives of those we have in hand. The few which apparently were successful need to be verified and clarified before we can report the results confidently. Sometimes a result we have obtained is mentioned in the Proposed Research section simply because it serves to define a new direction or invites proof and elaboration.

SCHEME II. Formation of zirconoxy carbene complexes

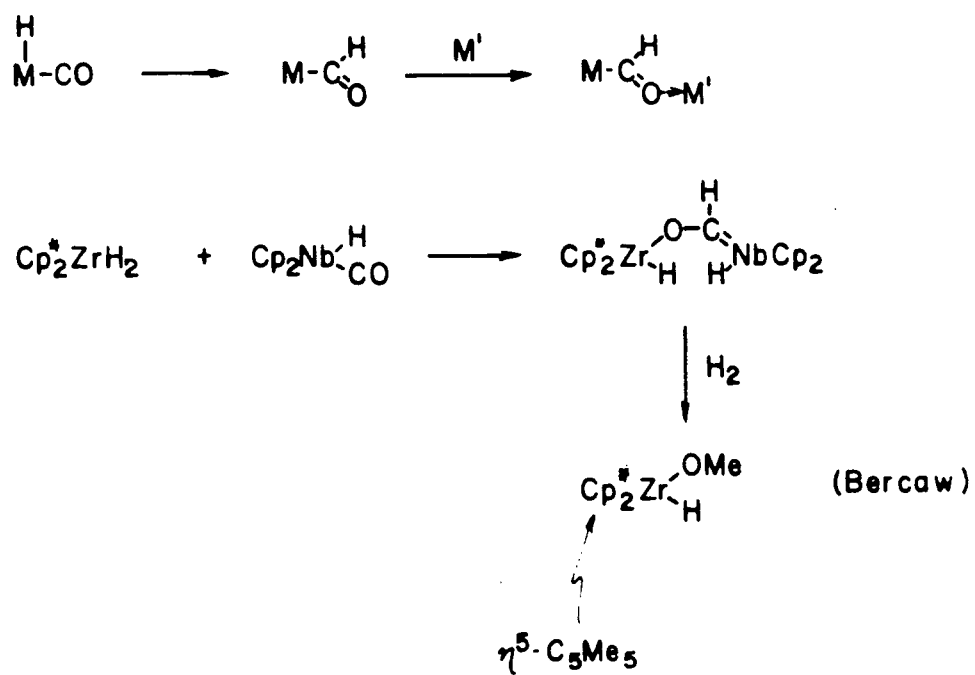
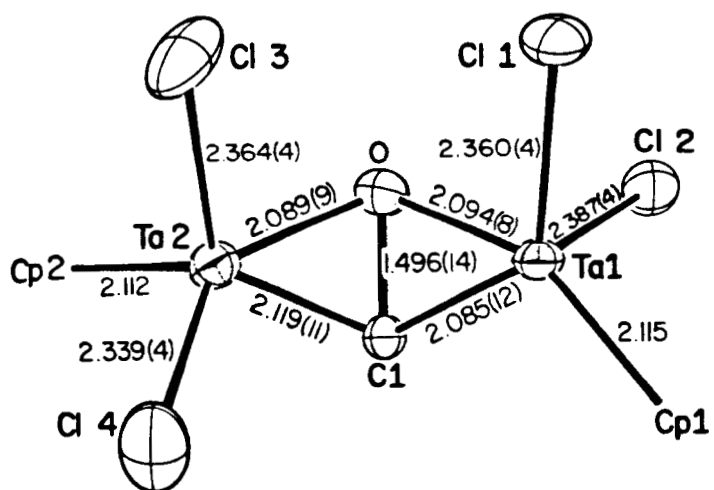
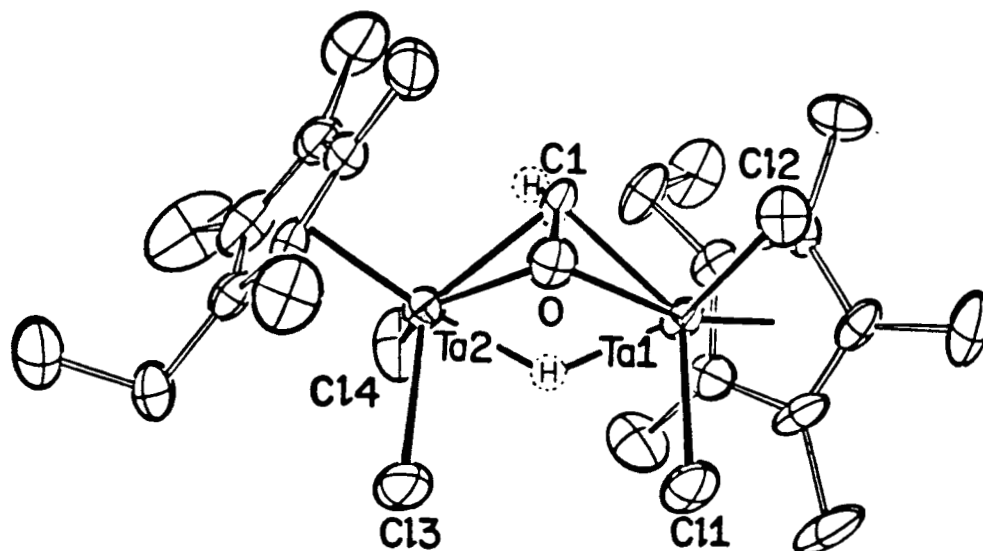




Figure 2. X-ray Structure of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_4(\text{H})(\text{CHO})$

(Churchill & Wasserman)



APPENDIX I

Binuclear Tantalum Hydride Complexes

by

Patricia A. Belmonte, Richard R. Schrock\* and Cynthia S. Day<sup>1</sup>

Contribution from the  
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Massachusetts Institute of Technology  
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## ABSTRACT

Cyclopentadienyl tantalum olefin or dineopentyl complexes react with molecular hydrogen to give binuclear hydride complexes,  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]_2$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ). The dimeric hydride complexes react with alkylating agents to give monoalkyl derivatives ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{SiMe}_3$ ).  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{H}_2(\text{Me})$  crystallizes in the monoclinic space group  $\text{P}2_1/c$  with  $a = 20.084(6)\text{\AA}$ ,  $b = 16.972(4)\text{\AA}$ ,  $c = 15.869(4)\text{\AA}$ , and  $\beta = 96.86(2)^\circ$ . The structure was solved by full-matrix least-squares techniques to R values of  $R_1 = 5.6\%$  and  $R_2 = 7.0\%$  for 6542 absorption-corrected reflections having  $2\theta_{\text{MoK}\alpha} < 55^\circ$  and  $I > 3\sigma(I)$ . There are two independent molecules per asymmetric unit. Each consists of two approximately tetrahedrally coordinated  $\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}(\text{Cl}/\text{C})$  fragments joined by a Ta-Ta bond ( $2.854(1)\text{\AA}$  in molecule 1); the Cl/C terminology signifies that the methyl group is disordered with the chloride ligand with which it is eclipsed. We propose that the hydride ligands are bridging. We have shown that the dimer remains intact throughout (i) a fluxional process in  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{H}_2(\text{R})$  which exchanges the two inequivalent hydrides; (ii) a bimolecular halide exchange process in  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}_2\text{H}]_2$  which is slow on the NMR time scale but fast on the chemical time scale; and (iii) a bimolecular hydride exchange process in  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}_2\text{H}]_2$  which is slow on the chemical time scale. The formation of  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}_2\text{H}]_2$  is believed to involve a complex bimolecular decomposition of intermediate  $\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}_2(\text{H})(\text{R})$  complexes, one of which ( $\text{R} = \text{CH}_2\text{CMe}_3$ ) has been isolated and characterized by IR and NMR methods.

## INTRODUCTION

There are now several homogeneous transition metal systems which will catalyze the reduction of carbon monoxide by molecular hydrogen.<sup>2</sup> In all cases the catalyst contains a Group VIII metal, the reduction products are oxygenates,<sup>3</sup> and with one possible exception,<sup>4</sup> the reductions are not selective for any oxygenate containing one or more C-C bonds.<sup>2,3</sup> Therefore, there is considerable room for improving the known catalyst systems. Studies of stoichiometric "model" reactions between hydride complexes of the earlier transition metals and carbon monoxide might help determine how this can be done.<sup>5</sup> What model studies also do, however, is increase the probability of discovering a catalyst which does not contain a Group VIII metal, one which might reduce carbon monoxide more selectively than known catalysts, or under milder conditions than known catalysts, or both. For these two reasons we became interested in exploring reactions between niobium and tantalum hydride complexes and carbon monoxide.

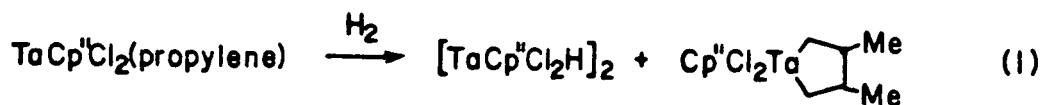
The known niobium and tantalum polyhydride complexes,  $\text{MCp}_3\text{H}_3$ <sup>6</sup> (Cp =  $\eta^5\text{-C}_5\text{H}_5$ ) and  $\text{MH}_5(\text{dmpe})_2$ ,<sup>7</sup> lose one and two equivalents of  $\text{H}_2$  in the presence of CO to give  $\text{MCp}_2(\text{H})(\text{CO})$  and  $\text{M}(\text{H})(\text{dmpe})_2(\text{CO})_2$ , respectively. The monohydride complexes do not reduce CO. Therefore our first task was to prepare new types of hydride complexes. Recently we discovered that  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)\text{Me}_4$  would reduce CO to give an  $\eta^2$ -acetone complex, and that the  $\eta^2$ -acetone complex would react further with CO to give a derivative containing a trimethylenolate ligand.<sup>8</sup> Therefore we felt that  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)\text{H}_4$  or  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\text{H}_2$  might reduce CO. We opted to attempt to make the latter types of molecules since they should be obtained by reacting known monocyclopentadienyl tantalum dialkyl,<sup>9a</sup> alkyldene,<sup>9a</sup> or olefin<sup>9b</sup> complexes with molecular hydrogen. In this paper we

report the results of these reactions, a new class of binuclear tantalum hydride complexes. In subsequent papers we will report how these new tantalum complexes react with small molecules, including carbon monoxide, and how the analogous chemistry of niobium compares with that of tantalum.

## RESULTS

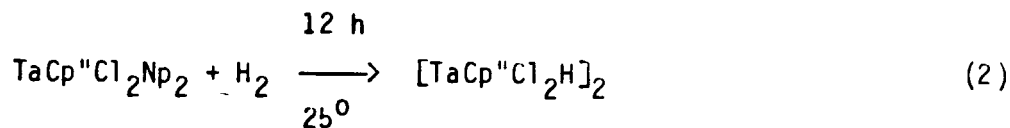
Preparation and Properties of  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]_2$  ( $\text{Cp}'' = \eta^5\text{-C}_5\text{Me}_5$ ;  
 $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$ )

$\text{TaCp}''\text{Cl}_2(\text{propylene})$  and  $\text{TaCp}''\text{Cl}_2(\text{styrene})$  react cleanly in pentane with molecular hydrogen at 20-40 psi to give insoluble green  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  in high yield and a mixture of the olefin and the alkane in a ratio of approximately 2:1. In the case of  $\text{TaCp}''\text{Cl}_2(\text{propylene})$ , the yield of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  is ~ 70% after one hour. The orange filtrate contains the remaining tantalum as the propylene metalacycle<sup>9b</sup> formed by addition of propylene to  $\text{TaCp}''\text{Cl}_2(\text{propylene})$  (Eq. 1). This metalacycle slowly decomposes to 2,3-dimethyl-1-butene and



$\text{TaCp}''\text{Cl}_2(\text{propylene})$ <sup>9b</sup> so that after ~ 24 h the yield of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  is essentially quantitative. In the case of  $\text{TaCp}''\text{Cl}_2(\text{styrene})$ , the yield of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  is ~ 70% after 20 hours; the remainder is starting material. (Note that "styrene tantalacycles" do not form.<sup>9b</sup>)  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  is moderately soluble in chlorobenzene and toluene, slightly soluble in tetrahydrofuran, and insoluble in ether and hydrocarbons. It reacts immediately with chloroform, more slowly with dichloromethane, to give sparingly soluble, yellow  $\text{TaCp}''\text{Cl}_4$ .

$[\text{TaCp}''\text{Cl}_2\text{H}]_2$  can also be prepared by reacting  $\text{TaCp}''\text{Cl}_2\text{Np}_2$  ( $\text{Np} = \text{CH}_2\text{CMe}_3$ ) in pentane with hydrogen (Eq. 2). The product is inferior to that obtained by reacting  $\text{TaCp}''\text{Cl}_2(\text{propylene})$  with  $\text{H}_2$ , since an impurity with solubility characteristics similar to those of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  cannot be removed by recrystallization.



$[\text{TaCp}'\text{Cl}_2\text{H}]_2$  can be prepared by methods analogous to those shown in equations 1 and 2. One redeeming feature of this more complicated molecule is that it is more soluble than  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$ . Therefore, we could show that it is a dimer in benzene. What will turn out to be an important fact, once we know the structure of this molecule, is that the molecule appears to have two planes of symmetry; only two types of methyl groups are found on the equivalent  $\eta^5\text{-C}_5\text{Me}_4\text{Et}$  rings.

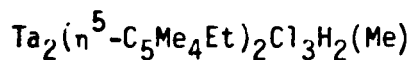
All reactions of the type shown in equations 1 and 2 work best in a relatively large volume of pentane. Some solvents are dismal failures. For example, the yield of  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}_2\text{H}]_2$  in tetrahydrofuran is only ~ 10%. In ether or toluene the yields are intermediate.

The hydride ligands can be observed by NMR or IR. In the  $^1\text{H}$  NMR spectrum a hydride resonance of area one relative to each  $\text{C}_5\text{Me}_4\text{R}$  group is found at ~10.4 ppm in each case. The spectrum does not change upon cooling or heating the sample. In the IR spectrum a medium strength, broad peak at  $1580 \text{ cm}^{-1}$  can be assigned to a metal-hydride mode. The position of the peak is consistent with equivalent, bridging hydrides, but the possibility that the hydrides are terminally bound cannot be excluded by this data alone.

One major goal was to obtain x-ray quality crystals of either the  $\text{Cp}''$  or  $\text{Cp}'$  complex. Unfortunately, we did not succeed in spite of a great deal of effort. Our search for a suitable derivative led us to prepare some monoalkyl derivatives, one of which did provide adequate x-ray quality crystals. Therefore we must describe the monoalkyl derivatives and the x-ray structure before

returning to some important results concerning how these dimeric molecules behave in solution.

Preparation of Monoalkyl Derivatives and the X-Ray Structure of



$[Ta(n^5-C_5Me_4R)Cl_2H]_2$  reacts with half an equivalent of  $Mg(CH_2CMe_3)_2$ ,  $Mg(CH_2SiMe_3)_2$ , or  $ZnMe_2$  to give blue to violet dimeric alkyl hydride complexes,  $Ta_2(n^5-C_5Me_4R)_2Cl_3H_2(R')$  ( $R' = Me, CH_2CMe_3, CH_2SiMe_3$ ), in moderate yields (30-60%). All are extremely soluble in hydrocarbon or aromatic solvents and crystallize only from concentrated pentane solutions at  $-30^\circ$ . Attempts to add a second alkyl group yielded only orange-brown oils which could not be characterized. An ethyl derivative could be prepared at  $-50^\circ C$  using  $ZnEt_2$ , but it could be characterized only in solution. After  $\sim 0.5$  h at  $0^\circ$  it had largely decomposed to give approximately 0.5 equivalents of  $[Ta(n^5-C_5Me_4R)Cl_2H]_2$  as the only characterizable complex. In all alkyl hydride complexes a peak for a metal-hydride stretching mode is still observable in the IR spectrum at  $1580-1600\text{ cm}^{-1}$ .

A crystal of  $Ta_2(n^5-C_5Me_4Et)_2Cl_3H_2(Me)$  was finally obtained which was suitable for a single crystal x-ray diffraction study. One complicating feature is that the asymmetric unit contains two independent molecules (Figure 1). The difference between the two is primarily how the  $n^5-C_5Me_4Et$  ring is oriented on  $Ta_b$ ; turning the  $n^5-C_5Me_4Et$  ring on  $Ta_b$  in molecule 1 clockwise by  $72^\circ$  gives molecule 2. Final atomic coordinates for all atoms in both molecules can be found in Table I and anisotropic thermal parameters for the non-hydrogen atoms in Table II.<sup>10</sup> Bond lengths can be found in Table III and bond angles in Table IV.



If we ignore the hydride ligands and say the metal-metal bond and the  $\eta^5\text{-C}_5\text{Me}_4\text{Et}$  group each take up one coordination site, then the geometry about each metal is roughly tetrahedral. The "tetrahedral bond angles" around Ta range from  $96.6^\circ$  to  $126.3^\circ$ , with those larger than the idealized tetrahedral value of  $109.5^\circ$  involving the bulky, sterically-demanding Cp' ligand or the other TaCp'Cl(Cl/C) group. (See below for a discussion of the Cl/C nomenclature.) The two ends of the molecule are eclipsed and joined by a Ta-Ta single bond with a length of  $2.854(1)\text{\AA}$  in molecule 1 and  $2.815(1)\text{\AA}$  in molecule 2. The  $\eta^5\text{-C}_5\text{Me}_4\text{Et}$  groups are the normal, slightly "dish-shaped" variety with normal Ta-C bond lengths (average  $2.44(2,2,6,20)\text{\AA}^{11}$ ).

The methyl group almost certainly occupies one of the "eclipsed chloride" sites. However, one problem (which we discuss at length in the experimental section) is that the methyl group is disordered with the chloride in a similar position at the other end of the molecule. Therefore these ligands are labeled Cl/C in Figure 1. The Cl/C ligands were included in the final cycles of least-squares refinement at an occupancy of 1.00 with atomic scattering factors having 50% Cl and 50% C character. In the end we could not tell by metal-ligand bond lengths alone which sites were occupied by Cl and which by "Cl/C"; the four independent Ta-Cl bond lengths in the two molecules differ negligibly from the four involving the disordered Cl/C sites ( $2.357(5,8,13,4)\text{\AA}$  vs.  $2.375(7,5,10,4)\text{\AA}$ , respectively). If we replace the ethyl group in each Cp' ring by a methyl group, then each independent  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{H}_2(\text{Me})$  molecule has approximate idealized  $C_2$  symmetry with the pseudo- $C_2$  axis being oriented perpendicular to and bisecting the Ta-Ta bond.

Unfortunately, determination of the hydride ligand positions from the x-ray data was prevented by the presence of relatively heavy Ta atoms, the

previously described Cl/methyl disorder, and a relatively low yield (53%) of "observed" ( $I/\sigma(I) > 3.0$ ) diffracted intensities. If we assume they are bridging and interchanged by a  $C_2$  operation, then they must be above and below the  $Ta_2(C/Cl)_2$  plane. By analogy with the structures of two derivatives of  $[TaCp'Cl_2H]_2$ ,  $[TaCp'Cl_2]_2(H)(CHO)^{12}$  and  $[TaCp'Cl_2H]_2(H)(Me_3PCH)(O)^{13}$ , we believe each hydride is most likely trans to one of the Cp' groups. This is shown schematically for the parent tetrachloro complex in Figure 2. The  $C_2$  axis passes between the two bridging hydrides, between the two eclipsed chloride ligands, and through the Ta-Ta bond.

It is interesting and potentially important to note that the  $^1H$  NMR spectrum of  $[TaCp'Cl_2H]_2$  is not consistent with the solid state structure. If the solid state structure is preserved in solution, then four, not two, different  $n^5-C_5Me_4Et$  methyl groups should be observed. A proposal which is consistent with this fact and all other behavior of this species in solution which we will talk about later is that the two ends of the molecule can rotate to produce a molecule with pseudo-trans Cp' ligands, but the two ends cannot rotate a full  $360^\circ$  because of steric interaction between the two Cp' rings.

#### NMR Studies of Monoalkyl Derivatives

The NMR spectra of the monoalkyl derivatives reflect the fact that the  $C_2$  axis is destroyed when one of the chloride ligands is replaced by an alkyl ligand. The  $n^5-C_5Me_4Et$  groups are now inequivalent, the methyl groups in each ring are unique, and  $\alpha$ -protons in the Et, Np, or Np' group are diastereotopic. However, the hydride ligands in  $Ta_2Cp'_2Cl_3H_2(R)$  ( $R = Et, Np, Np'$ ) are inequivalent only at low temperatures ( $J_{HH} \sim 6$  Hz). At higher temperatures they interconvert, but the diastereotopic protons in the Et, Np, or Np' ( $Np' =$

CH<sub>2</sub>SiMe<sub>3</sub>) group do not. Therefore the process which exchanges the two hydride ligands does not generate a plane of symmetry which passes through the methylene group of the Et, Np, or Np' ligands. Since the two Cp' ligands also do not equilibrate, the alkyl ligand does not move from one metal center to the other. The most consistent explanation is that the molecular framework remains largely unchanged while hydrides themselves exchange. Note that a partial rotation of the two ends of the monoalkyl derivative similar to the partial rotation in the parent molecule is still possible as long as the geometry about the metal at each end (not counting the hydrides) is preserved. One possibility is an intermediate which contains terminal hydride and bridging chloride ligands. This type of tautomer is attractive since we will show later that although the dimer does not break up in solution, hydrides slowly scramble intermolecularly.

An interesting question is whether the hydride ligands exchange with one another as a result of this twisting process. Some evidence that this is the case is that the activation energy for the hydride exchange process varies in the order R = Me < Et < Np < Np' (respectively, not observable, 13.8, 14.5, and 14.9 kcal mol<sup>-1</sup>). A smaller R group would allow the molecule to twist more easily. However, as we mentioned above, full rotation about the Ta-Ta bond is unlikely for steric reasons, consistent with the fact that the molecule remains asymmetric on the time scale of the fluxional process.

#### Exchange Reactions in Tetrachlorodihydride Dimers

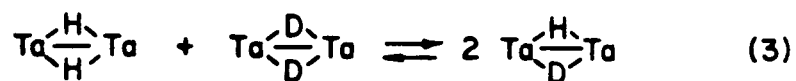
A mixture of TaCp'Cl<sub>2</sub>(propylene) and TaCp''Cl<sub>2</sub>(propylene) reacts with hydrogen to give a 1:2:1 mixture of [TaCp''Cl<sub>2</sub>H]<sub>2</sub>, Ta<sub>2</sub>Cp'Cp''Cl<sub>4</sub>H<sub>2</sub>, and [TaCp'Cl<sub>2</sub>H]<sub>2</sub>. The hydride signals for each can be distinguished at 250 MHz

(Figure 3a). Note that the hydrides should no longer be equivalent in  $\text{Ta}_2\text{Cp}'\text{Cp}''\text{Cl}_4\text{H}_2$ . Since we see only one signal, the hydrides are either exchanging rapidly on the NMR time scale, or their chemical shifts are essentially identical. We favor the former explanation, since we observed rapid exchange of inequivalent hydrides in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_3\text{H}_2(\text{R})$  (see above). In any case, the fact that we can see three separate hydride signals allowed us to do the following experiment. A 250 MHz spectrum of a mixture of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  ( $\sim 3.5$  parts) and  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  ( $\sim 1$  part) in  $\text{C}_6\text{D}_6$  showed two hydride signals at 10.42 and 10.38 ppm (the positions of the hydride signals in each alone in  $\text{C}_6\text{D}_6$ ) in a ratio of  $\sim 3.5:1$  (Figure 3b). No  $\text{Ta}_2\text{Cp}'\text{Cp}''\text{Cl}_4\text{H}_2$  was present. The spectrum did not change upon warming the sample to  $75^\circ$  for 10 minutes. The results of a similar experiment demonstrated that  $< 5\%$   $\text{Ta}_2\text{Cp}'\text{Cp}''\text{Cl}_4\text{H}_2$  is present after five hours at  $70^\circ$ . Therefore, the dimer does not break up into monomeric units at any significant rate at  $70\text{-}75^\circ$ .

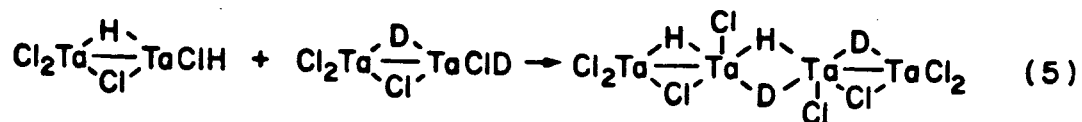
Deuteride complexes can be prepared by reacting either propylene or di-neopentyl complexes with  $\text{D}_2$ . The deuterides show a peak in their IR spectra at  $1140\text{-}1145\text{ cm}^{-1}$  instead of  $\sim 1580\text{ cm}^{-1}$ . In each case, however, some intensity is present at  $\sim 1580\text{ cm}^{-1}$ . The presence of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{D})$  can be confirmed and the absolute and relative amounts quantitated by  $^1\text{H}$  NMR since the signal for the hydride in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{D})$  is found 0.06 ppm upfield from that in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$ . The amount of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{D})$  is well above the amount of  $\text{H}_2$  and HD impurities in  $\text{D}_2$  and also increases markedly if only 1-2 equivalents of  $\text{D}_2$  are used to form the deuteride. For example, when one equivalent of  $\text{D}_2$  was added to  $\text{TaCp}'\text{Cl}_2$ - (propylene), the product contained  $\sim 0.6$  protons per dimer due to the presence of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{D})$  (4-5 parts) and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$  (1 part). Under the best

conditions (large excess of  $D_2$ ) the "deuteride" still contains 10-15%  $Ta_2Cp'_2Cl_4(H)(D)$  and 1 or 2%  $Ta_2Cp'_2Cl_4H_2$ . No additional  $Ta_2Cp'_2Cl_4(H)(D)$  or  $Ta_2Cp'_2Cl_4H_2$  forms in a given sample of the "deuteride". Later we will propose a reasonable mechanism for forming these hydride impurities.

The situation with regard to deuterium labeling is actually more complicated and more informative. If one mixes a sample of the purest  $Ta_2Cp'_2Cl_4D_2$  and pure  $Ta_2Cp'_2Cl_4H_2$  one observes a hydride signal due to  $Ta_2Cp'_2Cl_4H_2$  and a signal due to  $Ta_2Cp'_2Cl_4(H)(D)$  in a ratio of  $\sim 8:1$  ( $\sim 20\%$   $Ta_2Cp'_2Cl_4(H)(D)$ ). After one hour at  $25^\circ$  the amount of  $Ta_2Cp'_2Cl_4(H)(D)$  is  $\sim 30\%$ , and after 30 minutes at  $45^\circ$  the amount of  $Ta_2Cp'_2Cl_4(H)(D)$  is  $\sim 40\%$ . Little further change occurs. Since the dimer does not break into monomeric units (vide supra) H and D must scramble intermolecularly between dimeric units (equation 3). One reasonable way for this to happen is for the dimers to form which contain one



or more terminal hydride (deuteride) ligands (equation 4) which can be used to form a tetramer containing a central TaHDTa unit (equation 5).



The above findings raise the possibility that halides exchange between dimers.  $[\text{TaCp}'\text{Br}_2\text{H}]_2$  can be prepared straightforwardly from  $\text{TaCp}'\text{Br}_2$  (propylene). Its hydride resonance is found at 11.27 ppm. After addition of one equivalent of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  to  $[\text{TaCp}'\text{Br}_2\text{H}]_2$  five hydride resonances are found at 11.27 (due to  $[\text{TaCp}'\text{Br}_2\text{H}]_2$ ), 11.08, 10.93, 10.68, and 10.42 ppm (due to  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ ) in a ratio of a trace:5:18:16:3. We assign the three additional resonances to  $\text{Ta}_2\text{Cp}'_2\text{Br}_3\text{ClH}_2$  (H at 11.08 ppm),  $\text{Ta}_2\text{Cp}'_2\text{Br}_2\text{Cl}_2\text{H}_2$  (H at 10.93 ppm), and  $\text{Ta}_2\text{Cp}'_2\text{BrCl}_3\text{H}_2$  (H at 10.68 ppm). We might expect such an exchange reaction to be ionic were it not for two facts. First, it proceeds very rapidly at 25°C in benzene. Second, halide exchange between Ta and Li is slow. (Primarily  $\text{Ta}_2\text{Cp}'_2\text{BrCl}_3\text{H}_2$  was present after stirring a sample of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$  with excess LiBr in ether for two hours at 25°C). This apparently intermolecular, non-ionic halide exchange between  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  molecules is probably related to the H/D exchange described above. It is not surprising that halides exchange much more rapidly than hydrides, since two halides are always terminally bound, while the hydrides are in the bridging positions most of the time.

#### Preparation of Other Tantalum Hydride Complexes

When the reaction between  $\text{TaCp}'\text{Cl}_2\text{Np}_2$  and  $\text{H}_2$  is done on a large scale, a small yield of an orange-red crystalline product is obtained which is less soluble than  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ . We propose that it is  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5\text{H}$  formed by intermolecular halide/hydride or halide/alkyl exchange at some intermediate stage in the hydrogenation/decomposition reaction. It can be obtained in better yield (~20%) by reacting equimolar amounts of  $\text{TaCp}'\text{Cl}_3\text{Np}$  and  $\text{TaCp}'\text{Cl}_2\text{Np}_2$  with  $\text{H}_2$  in pentane. An attempt to prepare it by reacting  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  with HCl

(one equivalent) gave only 0.5 equivalents of  $\text{TaCp}'\text{Cl}_4$  and starting material. The metal-hydride mode must be shifted to lower energy in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5\text{H}$  than it is in  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  since we could not find it in a Nujol mull IR spectrum. In the  $^1\text{H}$  NMR spectrum the hydride resonance is found at 6.08 ppm. We propose that  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5\text{H}$  contains a bridging chloride in place of one of the bridging hydrides in  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ , although there is at least some possibility that  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5\text{H}$  has a different basic structure than  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$ .

$\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)\text{Cl}_2$  reacts readily with  $\text{H}_2$  (20 psi) in one hour in ether to give a green solid which is insoluble in common solvents. Its IR spectrum shows an absorption at  $1620\text{ cm}^{-1}$ . We propose that the green solid is  $[\text{TaCpCl}_2\text{H}]_x$ . Since it is so insoluble  $x$  may be  $>2^{14}$ . If so, then the coordination sphere must be too crowded when  $\text{Cp}'$  or  $\text{Cp}''$  ligands are present to form any units larger than dimers.

#### Mechanism of Formation of $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]_2$

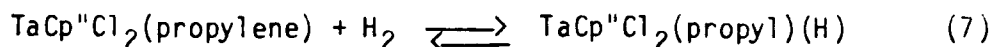
$\text{TaCp}''\text{Cl}_2\text{Np}_2$  reacts readily with hydrogen at  $-30^\circ$  in butane to give an orange solution. There is no further change at  $-30^\circ$ . A yellow solid remains after removing all the volatiles in vacuo. Three pieces of evidence suggest that this compound is  $\text{TaCp}''\text{Cl}_2(\text{Np})(\text{H})$  (equation 6). First, its  $^1\text{H}$  NMR spectrum shows a peak of area one at 22.87 ppm. Second, its IR spectrum shows a



peak at  $1750\text{ cm}^{-1}$ . Third, it reacts with chloroform to give  $\text{TaCp}''\text{Cl}_3\text{Np}$  in high yield. On warming the yellow solution of  $\text{TaCp}''\text{Cl}_2(\text{Np})(\text{H})$  to  $25^\circ$  under  $\text{H}_2$  it turns green and  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  can be isolated in a yield comparable to that

obtained if the entire reaction is done at 25°. If a solution containing TaCpCl<sub>2</sub>(Np)(H) (prepared analogously) is warmed to 25° in the absence of H<sub>2</sub>, it turns brown and the dark brown oil which remains after removing the volatiles contains no [TaCp'Cl<sub>2</sub>H]<sub>2</sub> by <sup>1</sup>H NMR. However, this brown oil reacts with H<sub>2</sub> to give a moderate yield (~ 50%) of [TaCp'Cl<sub>2</sub>H]<sub>2</sub>.

We have no direct evidence for formation of an analogous propyl hydride complex when Ta( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>R)Cl<sub>2</sub>(propylene) reacts with hydrogen. Indirect evidence that it is formed consists of the fact that the reaction of TaCp"Cl<sub>2</sub>(propylene) with hydrogen at <0° in chloroform gives TaCp"Cl<sub>3</sub>(propyl) in good yield. We believe TaCp"Cl<sub>2</sub>(propyl)(H) is formed and trapped by reaction with chloroform. In the absence of chloroform TaCp"Cl<sub>2</sub>(propyl)(H) probably loses H<sub>2</sub> to reform TaCp"Cl<sub>2</sub>(propylene) (equation 7). We propose that this equilibrium is the primary reason why 0.6 protons are present per dimer in the "deuteride" prepared by adding one equivalent of D<sub>2</sub> to TaCp'Cl<sub>2</sub>(propylene).



An intriguing result, and one which might be important in elucidating the details of how hydrogen reacts with d<sup>0</sup> alkyl complexes, is that TaCp"Cl<sub>2</sub>Me<sub>2</sub> reacts very slowly and reluctantly with molecular hydrogen. After 12 hours at 20°C and 1000 psi in toluene the yield of [TaCp"Cl<sub>2</sub>H]<sub>2</sub> was ~ 50%; ~ 30% of the TaCp"Cl<sub>2</sub>Me<sub>2</sub> did not react. The remaining 20% consisted of a product which could not be identified. Our experience has been that the ease with which molecular hydrogen reacts with an alkyl complex is directly related to the tendency for that alkyl complex to decompose by  $\alpha$ -abstraction to give an alkylidene complex. For example, in the TaCp"Cl<sub>2</sub>R<sub>2</sub> series the rate of reaction with H<sub>2</sub> is R = CH<sub>2</sub>CMe<sub>3</sub> > CH<sub>2</sub>SiMe<sub>3</sub> >> Me. Since the intricacies of



$\alpha$ -abstraction are not yet on firm quantitative ground, we could only wildly speculate as to why the ease with which hydrogen reacts with alkyl complexes parallels the ease of  $\alpha$ -abstraction.

## DISCUSSION

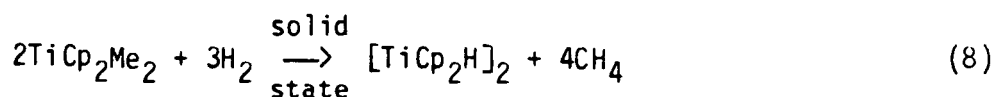
The preparation of metal hydride complexes by addition of  $H_2$  to a metal-alkyl complex has ample precedent<sup>15</sup>. While addition of  $H_2$  to the metal is a reasonable first step in the reaction of a  $d^8$  metal alkyl with  $H_2$ ,  $H_2$  cannot oxidatively add to Ta(V) in  $TaCp'Cl_2Np_2$ . One could postulate that Ta is first reduced to Ta(IV) or Ta(III), or that neopentane is first lost in an  $\alpha$ -abstraction step to give  $TaCp'Cl_2(CHCMe_3)$ . Neither postulate is necessary, however. Since  $LiC_6H_5$  reacts with  $H_2$  at  $25^\circ$  to give LiH and benzene<sup>16</sup>, a  $d^0$  metal alkyl complex in which the metal is sufficiently electropositive and the alkyl sufficiently anionic also should be able to react directly with  $H_2$ . On this basis it is at least consistent that a neopentyl ligand would be more nucleophilic toward  $H_2$  than a methyl group.

It is perhaps less surprising that Ta(olefin) complexes react with  $H_2$ , either because the metal is Ta(III), or (if one insists it is actually a Ta(V) tantalacyclopropane complex) because the small, strained  $TaC_2$  ring should be susceptible to opening up to an alkyl hydride on reaction with  $H_2$ .

It is difficult at this stage to say exactly how  $[TaCp'Cl_2H]_2$  forms from  $TaCp'Cl_2(R)(H)$ . We do not believe that intermediate  $Ta(\eta^5-C_5Me_4R)Cl_2(R)(H)$  complexes lose RH to give a  $Ta(\eta^5-C_5Me_4R)Cl_2$  fragment which then reacts with  $H_2$  to give the complex we originally sought,  $Ta(\eta^5-C_5Me_4R)Cl_2H_2$ . Unimolecular reductive elimination reactions appear to be unlikely when the fragment which results is incapable of independent existence<sup>17</sup>. When ligands which can

stabilize the lower oxidation state metal complex are present, reductive elimination can become favorable once again. Such is not the case in our system, however. The two alternatives are that  $Ta(n^5-C_5Me_4R)Cl_2(R)(H)$  reacts directly with  $H_2$  to give  $RH$  and  $Ta(n^5-C_5Me_4R)Cl_2H_2$ , or that  $Ta(n^5-C_5Me_4R)Cl_2(R)(H)$  decomposes bimolecularly in a complex manner to give one or more species which react rapidly with  $H_2$  to ultimately give the final product. Although we cannot exclude one or the other alternative at this stage, it is perhaps important to note two things. The first is that although  $Ta(n^5-C_5Me_4R)Cl_2Np_2$  reacts with  $H_2$  at  $-78^\circ$ ,  $Ta(n^5-C_5Me_4R)Cl_2(R)(H)$  is stable at  $0^\circ$  under  $H_2$ . The second is that  $Ta(n^5-C_5Me_4R)Cl_2(Np)(H)$  decomposes to a brown oil which reacts readily with  $H_2$  to give the final product. These observations suggest to us that a complex bimolecular decomposition reaction is the more likely alternative. Bimolecular decomposition reactions in general appear to be much more common in organotransition metal chemistry than originally believed<sup>17</sup>.

The closest analogy in the literature to the chemistry we describe here is the reaction of  $Ti(n^5-C_5H_5)_2Me_2$  with  $H_2$  (equation 8)<sup>18</sup>.  $[TiCp_2H]_2$  is a



violet, diamagnetic molecule with a metal hydride peak in the IR spectrum at  $1450\text{ cm}^{-1}$  ( $1050\text{ cm}^{-1}$  in  $[TiCp_2D]_2$ ). Although no x-ray structural data are available, a Ti-Ti bond must be present because of the compound's diamagnetism and the fact that it reacts with some donor ligands to give Ti(III) species (e.g.  $TiCp_2(H)(PPh_3)$ ). The IR data are most compatible with a double  $\mu$ -hydride bridge. It was proposed that if the molecule was centrosymmetric,

then the metal-hydride mode at  $1450\text{ cm}^{-1}$  was analogous to the antisymmetric metal-hydride stretching mode found at  $1600\text{--}1500\text{ cm}^{-1}$  in centrosymmetric diboranes or  $1350\text{ cm}^{-1}$  in  $\text{TiCp}_2(\text{BH}_4)$ . It was not thought to be the symmetric metal-hydride stretching mode analogous to that at  $1942\text{ cm}^{-1}$  in non-centrosymmetric  $\text{TiCp}_2(\text{BH}_4)$ .

Another compound related to  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]_2$  is  $\text{Ir}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_2\text{H}_2$ <sup>19</sup>. The metal-hydride peak is found at  $1162\text{ cm}^{-1}$  (metal-deuteride =  $830\text{ cm}^{-1}$ ) in the IR spectrum and a peak for the bridging hydrides at high field in the  $^1\text{H}$  NMR spectrum. Its crystal structure has not been determined but structures of closely related  $\text{Ir}_2\text{Cp}''_2\text{Cl}_3\text{H}^{20}$  and  $\text{Rh}_2\text{Cp}''_2\text{Cl}_3\text{H}^{21}$ , as well as the perhalides,  $\text{M}_2\text{Cp}''_2\text{X}_4$  (X = a halide),<sup>20,22</sup> have been determined. The  $\text{M}_2\text{Cp}''_2\text{Cl}_3\text{H}$  species have planar central  $\text{M}(\text{Cl})(\text{H})\text{M}$  cores with a  $\text{Cp}''$  group and a chloride ligand on each metal extending above and below this plane. The two  $\text{Cp}''$  groups are trans to one another about this  $\text{Ir}_2\text{ClH}$  core. The bridging hydride ligand pulls the metals together to form a 3-center, 2-electron bonding system ( $\text{Ir}\text{---}\text{Ir} = 2.903\text{ \AA}$ ). This is in marked contrast to the  $\text{M}_2\text{Cp}''_2\text{X}_4$  complexes where the  $\text{M}\text{---}\text{M}$  distance is too large for a significant binding interaction ( $\text{Ir}\text{---}\text{Ir} = 3.769\text{ \AA}$ ). From these studies one can conclude that hydride ligands will bridge between monomeric fragments having less than 18 valence electrons in preference to chloride ligands.

There is little doubt that the hydride ligands in  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]_2$  are bridging. It is likely, however, due to the low symmetry of the molecule, that the site on one metal where a given hydride is bonded is different than the site on the other metal to which it is bonded (Fig. 2). Therefore there is an inherent asymmetry to each hydride bridge which may make a bridge to terminal conversion easier.

## EXPERIMENTAL

All operations, except where otherwise specified, were performed under dinitrogen either by Schlenk techniques or in a dry box.  $\text{PMe}_3$  was prepared by the method of Wolfsberger and Schmidbaur<sup>23</sup> with modifications by P. Sharp<sup>24</sup>. Published procedures were used to prepare  $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ <sup>8</sup>,  $\text{TaCp}''\text{Cl}_2\text{Np}_2$ <sup>8</sup>, and  $\text{TaCp}''\text{Cl}_2(\text{CH}_2=\text{CHCH}_3)$ .<sup>9b</sup> The preparation of  $\text{TaCp}'\text{Cl}_2\text{Np}_2$  was analogous to that of  $\text{TaCp}''\text{Cl}_2\text{Np}_2$ .  $\text{TaCp}''\text{Cl}_2\text{Me}_2$  was prepared by treating  $\text{TaMe}_2\text{Cl}_3$  with one equivalent of  $\text{LiC}_5\text{Me}_5$  in ether<sup>25</sup>. Alkylcyclopentadienes were prepared by Bercaw's procedure<sup>26</sup>.  $\text{TiCp}$  was sublimed prior to use.

Pentane, hexane and petroleum ether were washed with 5% nitric acid in sulfuric acid, stored over calcium chloride and distilled under dinitrogen from n-butyl lithium. Reagent grade diethyl ether, tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl under dinitrogen. Reagent grade benzene, methylene chloride, chloroform and chlorobenzene were dried by refluxing overnight with calcium hydride and distilled. Butane was condensed into a flask at  $-78^\circ$ , freeze/thaw degassed and distilled from n-butyl lithium. All deuterated NMR solvents were passed through a column of activated alumina.

NMR data are listed in ppm relative to internal TMS for  $^1\text{H}$  and  $^{13}\text{C}$  and relative to external  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$ .

Preparation of  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\text{H}]_2$

$\text{TaCp}''\text{Cl}_2(\text{propylene})$  (1.1 g, 2.6 mmol) was dissolved in 20 ml of pentane. The solution was placed in a glass bomb and the bomb was flushed and pressurized with hydrogen (25 psi). After stirring the solution for one day, green  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  (0.92 g, 92% yield) was filtered off.

In a similar experiment employing 0.25 g  $\text{TaCp}''\text{Cl}_2(\text{propylene})$  in 5 ml pentane the color of the reaction changed from dark purple to orange after 20 minutes. The solution was cooled to  $0^\circ$  and the gas above the solution sampled for propane and propylene; a 30:70 ratio was found by GLC. All solvent was removed in vacuo and the residue was dissolved in chlorobenzene. An  $^1\text{H}$  NMR spectrum showed ~65%  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$ , ~15%  $\text{Cp}''\text{Cl}_2\overline{\text{TaCHCHMeCHMeCH}_2}$ , and ~20%  $\text{TaCp}''\text{Cl}_2(\text{propylene})$ .

A similar reaction employing  $\text{TaCp}''\text{Cl}_2(\text{styrene})$  gave a 65% yield of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  after 20 hours at  $25^\circ$  and a 70% yield of a 2:3 mixture of ethylbenzene and styrene.

A similar reaction employing 0.39 g  $\text{TaCp}''\text{Cl}_2\text{Np}_2$  in 10 ml pentane gave 0.23 g  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  after 1 hour at  $25^\circ\text{C}$  under 40 psi  $\text{H}_2$ . The product was contaminated with an unidentified impurity (~20%).

Anal. Calcd for  $\text{TaC}_{10}\text{H}_{16}\text{Cl}_2$ : C, 30.95; H, 4.15. Found: C, 30.86; H, 4.20. This sample had been prepared from  $\text{TaCp}''\text{Cl}_2(\text{propylene})$  and recrystallized from chlorobenzene with pentane at  $-30^\circ$ .

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): ppm 10.382 (s, 1, Ta-H), 2.039 (s, 15, Cp'').  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ): 123.0 (s,  $\text{C}_5\text{Me}_5$ ), 13.4 (q,  $\text{C}_5\text{Me}_5$ ). IR (Nujol):  $\text{cm}^{-1}$  1580 (m, br, Ta-H). MS: m/e 135 (rel intensity 100,  $\text{C}_5\text{Me}_5$ ), 386 (20,  $\text{TaCp}''\text{Cl}_2$ ), 387 (60,  $\text{TaCp}''\text{Cl}_2\text{H}$ ).

Preparation of  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\text{D}]_2$

$[\text{TaCp}''\text{Cl}_2\text{D}]_2$  was prepared by reacting  $\text{TaCp}''\text{Cl}_2(\text{propylene})$  with a large

excess of  $D_2$ . Use of a stoichiometric amount of  $D_2$  results in formation of a significant quantity of  $Ta_2Cp''_2Cl_4HD$  and  $Ta_2Cp''_2Cl_4H_2$  (see text).

#### Preparation of $[Ta(\eta^5-C_5Me_4Et)Cl_2H]_2$

$[TaCp'Cl_2H]_2$  was prepared using methods analogous to those used to prepare  $[TaCp''Cl_2H]_2$ . From  $TaCp'Cl_2Np_2$  the yield was  $\sim 75\%$ , from  $TaCp'Cl_2$ - (propylene)  $\sim 95\%$ .

Anal. Calcd for  $TaC_{11}H_{18}Cl_2$ : C, 32.86; H, 4.51. Found: C, 32.97; H, 4.64.

$^1H$  NMR ( $C_6D_6$ ): ppm 10.420 (s, 1, Ta-H), 2.57 (q, 2,  $J = 7.7$  Hz,  $\underline{CH_2}CH_3$ ), 2.14 (s, 6, ring- $CH_3$ ), 2.01 (s, 6, ring- $CH_3$ ), 0.81 (t, 3,  $J = 7.7$  Hz,  $CH_2\underline{CH_3}$ ).  $^{13}C$  NMR ( $C_6D_6$ ): ppm 123.2 and 121.9 (two of three ring carbon atoms), 22.2 (q,  $\underline{CH_2}CH_3$ ), 15.1 (t,  $\underline{CH_2}CH_3$ ), 13.2 (q, accidentally equivalent ring methyl groups). MS: m/e 149 (relative intensity 20,  $C_5Me_4Et$ ), 400 (6,  $TaCp'Cl_2$ ), 401 (10,  $TaCp'Cl_2H$ ). MW (benzene, cryosc): Calcd: 804. Found: 840.

#### Preparation of $[Ta(\eta^5-C_5Me_4Et)Br_2H]_2$

$[TaCp'Br_2H]_2$  was prepared from  $TaCp'Br_2$  (propylene) in a manner analogous to that used to prepare  $[TaCp'Cl_2H]_2$ . The product is light green; its solutions are orange. Yield: 83%.

$^1H$  NMR ( $C_6D_6$ ): ppm 11.266 (s, 1, Ta-H), 2.608 (q, 2,  $J = 7.4$  Hz,  $\underline{CH_2}CH_3$ ), 2.214 (s, 6, ring- $CH_3$ ), 2.102 (s, 6, ring- $CH_3$ ), 0.817 (t, 3,  $J = 7.4$  Hz,  $CH_2\underline{CH_3}$ ).

#### Preparation of $Ta_2Cp_2'Cl_4H_2/Ta_2Cp_2'Cl_4HD/Ta_2Cp_2'Cl_4D_2$ Mixture

A mixture of  $H_2$  (10 ml) and  $D_2$  (10 ml) was added by syringe to a sample

of  $\text{TaCp}'\text{Cl}_2(\text{propylene})(0.2 \text{ g}, 0.45 \text{ mmol})$  in 20 ml of pentane in a closed vessel. The reaction mixture was warmed to room temperature and the solvent was removed in vacuo. At 250 MHz by integration the mixture consisted of  $\sim 30\%$   $\text{Ta}_2\text{Cp}_2'\text{Cl}_4\text{H}_2$  (H at 10.43 ppm),  $\sim 40\%$   $\text{Ta}_2\text{Cp}_2'\text{Cl}_4\text{HD}$  (H at 10.38 ppm), and  $\sim 30\%$   $\text{Ta}_2\text{Cp}_2'\text{Cl}_4\text{D}_2$  (by difference).

Preparation of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{H}_2(\text{CH}_2\text{CMe}_3)$

$[\text{Cp}'\text{TaCl}_2\text{H}]_2$  (0.8g, 1 mmol) was dissolved in 50 ml toluene and an ether solution of  $\text{NpMgCl}$  (0.5 mmol) was added dropwise over a 10 minute period. The color changed from bright green to dark grey. After 0.5 hr a white solid was filtered off and the filtrate was concentrated to approximately 2 ml in vacuo. Violet-blue crystals formed in this solution at  $-30^\circ\text{C}$ . These were collected by filtration and washed with cold ( $-30^\circ$ ) pentane; yield 0.67 g (78%).

Anal. Calcd for  $\text{Ta}_2\text{C}_{27}\text{H}_{47}\text{Cl}_3$ : C, 38.61; H, 5.64. Found: C, 38.80; H, 5.70.  $^1\text{H}$  NMR (tol- $d_8$ , 250 MHz, 320 K): ppm 10.483 (s, 2, MH), 4.71 (d, 1,  $J = 14 \text{ Hz}$ ,  $\text{CH}_A\text{CH}_B\text{CMe}_3$ ), 2.57 (m, 2, ring- $\text{CH}_2\text{CH}_3$ ), 2.48 (m, 2, ring- $\text{CH}_2\text{CH}_3$ ), 2.213 (s, 6, ring- $\text{CH}_3$ ), 2.104 (s, 6, ring- $\text{CH}_3$ ), 2.122 (s, 3, ring- $\text{CH}_3$ ), 2.089 (s, 3, ring- $\text{CH}_3$ ), 2.091 (s, 3, ring- $\text{CH}_3$ ), 1.995 (s, 3, ring- $\text{CH}_3$ ), 1.93 (d, 1,  $J = 14 \text{ Hz}$ ,  $\text{CH}_A\text{H}_B\text{CMe}_3$ ), 1.260 (s, 9,  $\text{CMe}_3$ ), 0.91 (m, 6, ring- $\text{CH}_2\text{CH}_3$ ). At 274K the hydride doublet resonances are found at 10.298 and 10.583 ppm ( $J_{\text{HH}} = 5.9 \text{ Hz}$ ). IR (nujol):  $1578 \text{ cm}^{-1}$  ( $\nu_{\text{MH}}$ ).

Preparation of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3\text{H}_2(\text{CH}_2\text{CMe}_3)$

$[\text{TaCp}''\text{Cl}_2\text{H}]_2$  (1.41 g, 1.8 mmol) was dissolved in 20 ml of toluene and 1.1 mmol of  $\text{MgNp}_2$  in ether was added. After 30 m the solvents were removed in vacuo and the residue was extracted with pentane. The extract was filtered and the filtrate was concentrated and cooled to  $-30^\circ$  to give blue crystals; yield 0.8 g (54%).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 60 MHz): ppm 10.6 (brs, 2, MH), 1.87 (s, 15, Cp"), 1.75 (s, 15, Cp"), 1.12 (s, 9,  $\text{CMe}_3$ ). IR (Nujol):  $\text{cm}^{-1}$  1580 (M-H). Mol Wt (cryoscopic in  $\text{C}_6\text{H}_{12}$ ): Calcd: 812. Found:  $800 \pm 100$ .

Preparation of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{H}_2(\text{CH}_2\text{SiMe}_3)$

This complex was prepared from 0.8 g (1 mmol) of  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}_2\text{H}]_2$  and 0.14 g (0.5 mmol) of  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2 \cdot \text{dioxane}$  in 30 ml of toluene for 30 m and isolated as for the neopentyl derivative; yield 0.53 g (62%). The high solubility of this product in pentane is what limits its isolated yield.

$^1\text{H}$  NMR (tol- $d_8$ , 243 K): ppm 10.540 (d, 1,  $J = 6$  Hz, MH), 9.480 (d, 1,  $J = 6$  Hz, MH), 4.663 (d, 1,  $J = 13$  Hz,  $\text{CH}_A\text{H}_B\text{SiMe}_3$ ), 1.665 (d, 1,  $J = 13$  Hz,  $\text{CH}_A\text{H}_B\text{SiMe}_3$ ), 0.356 (s, 9,  $\text{SiMe}_3$ ), 2.158, 2.023, 2.008, 1.990, 1.970, 1.890, 1.846 (ring methyl groups), 2.64 - 2.59 (m, 4, ring- $\text{CH}_2\text{CH}_3$ ), 0.85 (m, 6, ring- $\text{CH}_2\text{CH}_3$ ). IR (Nujol):  $1590 \text{ cm}^{-1}$  ( $\nu_{\text{MH}}$ ).

Preparation of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{H}_2\text{Me}$

A solution of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  (0.4 g, 0.5 mmol) in 25 ml toluene was cooled to  $0^\circ$ . A pentane solution of  $\text{ZnMe}_2$  was added dropwise until the color of the solution remained violet. Solvent was removed in vacuo and the residue was extracted with 100 ml pentane. The pentane solution was filtered, concentrated and cooled to give deep violet microcrystals; yield 0.265 g (68%).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 250 MHz, 295 K): ppm 10.256 (s, 2, MH), 2.69 (m, 2, ring- $\text{CH}_2\text{CH}_3$ ), 2.417 (m, 2, ring- $\text{CH}_2\text{CH}_3$ ), 2.186, 2.050, 2.038, 2.026, 1.921, 1.899 (s, ring- $\text{CH}_3$ ), 1.985 (s, 3,  $\text{TaCH}_3$ ), 0.894 (t, 3, ring- $\text{CH}_2\text{CH}_3$ ), 0.835 (t, 3, ring- $\text{CH}_2\text{CH}_3$ ). IR (Nujol mull):  $\text{cm}^{-1}$  1590 ( $\nu_{\text{MH}}$ ).



Preparation of  $Ta_2(\eta^5-C_5Me_5)_2Cl_3H_2(Me)$

A solution of  $[TaCp''Cl_2H]_2$  (0.3 g, 0.39 mmol) in 20 ml toluene was cooled to  $-78^\circ$  and  $ZnMe_2$  (0.02 g, 0.2 mmol) was added by syringe. No reaction occurred at  $-78^\circ$ . The reaction solution was slowly warmed to room temperature over a 30 minute period. During this time, the color of the solution changed from green to violet and white solid precipitated. An NMR spectrum of an aliquot of the solution showed only  $Ta_2Cp''_2Cl_3H_2Me$ . Violet crystals were obtained from toluene/pentane at  $-30^\circ$ ; yield 0.1 g (30%).

$^1H$  NMR ( $C_6D_6$ , 60 MHz): ppm 10.27 (s, 2, MH), 2.20 (s, 15, Cp''), 2.03 (s, 15, Cp''), 1.97 (s, 3, Me).

Observation of  $Ta_2(\eta^5-C_5Me_4Et)_2Cl_3H_2(CH_2CH_3)$

To a solution of  $[TaCp'Cl_2H]_2$  (0.05 g, 0.06 mmol) in 1 ml of toluene- $d_8$  was added 3.2  $\mu$ l (0.03 mmol) of diethylzinc. The color of the solution changed immediately from green to violet. The  $^1H$  NMR spectrum at  $-50^\circ C$  was consistent with that expected for  $Ta_2Cp'_2Cl_3H_2Et$ . After 0.5 h at  $0^\circ$  the sample had decomposed.

$^1H$  NMR (tol- $d_8$ , 90 MHz,  $-50^\circ C$ ): 10.395 (brs, 1, MH), 10.297 (brs, 1, MH), 3.3 (brq, 2,  $MCH_2CH_3$ ), 2.35 (m, 4, ring- $CH_2CH_3$ ), 2.18 and 1.89 (s, ring-Me), 0.86 (m, 9,  $MCH_2CH_3$  and ring- $CH_2CH_3$ ).

Preparation of  $Ta_2(\eta^5-C_5Me_4Et)_2Cl_5H$

In a large scale preparation of  $[TaCp'Cl_2H]_2$  starting with 10.6 g of  $TaCp'Cl_2Np_2$  in 100 ml of pentane  $\sim$ 1 g of the green product would not dissolve in ether. This brown solid was recrystallized from toluene/pentane to give  $\sim$ 25 mg of  $Ta_2Cp'_2Cl_5H$ .

A mixture of  $\text{TaCp}'\text{Cl}_3\text{Np}$  (0.5 g) and  $\text{TaCp}'\text{Cl}_2\text{Np}_2$  (0.5 g) were dissolved in 75 ml of pentane and the solution was stirred under 45 psi of  $\text{H}_2$  for 1 h at  $25^\circ\text{C}$ . The pentane insolubles (0.38 g) were shown to contain  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  and  $\text{Ta}_2\text{Cp}_2'\text{Cl}_5\text{H}$  by  $^1\text{H}$  NMR. Recrystallization from toluene/pentane gave 0.13 g of less soluble, red-orange  $\text{Ta}_2\text{Cp}_2'\text{Cl}_5\text{H}$  (20% yield).

Anal. Calcd for  $\text{Ta}_2\text{C}_{22}\text{H}_{35}\text{Cl}_5$ : C, 31.50; H, 4.20. Found: C, 31.16; H, 4.44.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): ppm 6.08 (s, 1, hydride), 2.6 (q, 4,  $J = 8$  Hz, ring- $\text{CH}_2\text{CH}_3$ ), 2.2 (s, 12, ring- $\text{CH}_3$ ), 2.15 (s, 12, ring- $\text{CH}_3$ ), 0.93 (t, 6,  $J = 12$  Hz, ring- $\text{CH}_2\text{CH}_3$ ).

#### Preparation of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2(\text{CH}_2\text{CMe}_3)(\text{H})$

Butane (distilled from Li butyl) was condensed onto  $\text{TaCp}''\text{Cl}_2\text{Np}_2$  (0.26 g, 0.5 mmol) in a 50 ml flask and 20 ml of  $\text{H}_2$  added by syringe after cooling the solution to  $-78^\circ$ . The temperature was slowly raised to  $-30^\circ$  as the solution was stirred. After one-half hour at  $-30^\circ$  the color of the solution was orange. The solvent was removed in vacuo at  $-30^\circ$ , leaving a yellow solid which was characterized by NMR and IR methods.

$^1\text{H}$  NMR (toluene- $d_8$ ,  $-30^\circ$ ): ppm 22.87 (s, 1, Ta-H), 1.779 (s, 15,  $\text{C}_5\text{Me}_5$ ), 1.421 (s, 9,  $\text{CMe}_3$ ), 0.921 (s, 2,  $\text{CH}_2\text{CMe}_3$ ).  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $-50^\circ$ ): ppm  $\sim 120$  (ring carbon signals), 94.7 (t,  $\text{CH}_2\text{CMe}_3$ ), 35.6 (q,  $\text{CH}_2\text{CMe}_3$ ), 12.4 (q, ring- $\text{CH}_3$  groups). IR (neat oil on NaCl,  $35^\circ$ ):  $\text{cm}^{-1}$  1750 (w, br, Ta-H).

Reaction of Ta( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)(H) with chloroform

A 0.53 g (1.0 mmol) sample of TaCp"Cl<sub>2</sub>Np<sub>2</sub> was dissolved in 50 ml of pentane containing ~3 ml of chloroform. The reaction was cooled to -78° and 25 ml (1.1 mmol) H<sub>2</sub> was added by syringe. The reaction was warmed slowly to 25°. The deep red color lightened to orange at -10° but did not change further. The solvent was removed in vacuo and the residue was recrystallized from pentane to give 0.35 g (0.71 mmol) of pure TaCp"Cl<sub>3</sub>Np. It was identified by NMR comparison with an authentic sample.

Reaction of Ta( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>(propylene) with H<sub>2</sub> in the presence of chloroform

A reaction analogous to that above starting with TaCp"Cl<sub>2</sub>(propylene) (0.43 g, 1 mmol) under excess H<sub>2</sub> gave an orange solution from which yellow-orange needles of TaCp"Cl<sub>3</sub>(propyl) (0.29 g, 0.61 mmol) could be isolated by concentrating and cooling the solution.

Anal. Calcd for TaC<sub>13</sub>H<sub>22</sub>Cl<sub>3</sub>: C, 33.53; H, 4.76. Found: C, 33.54; H, 4.58.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): ppm 2.551 (sextet, 2, J = 6.7 Hz, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.970 (s, 15, C<sub>5</sub>Me<sub>5</sub>), 1.162 (t, 3, J = 6.7 Hz, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.985 (t, 2, J = 6.5 Hz, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): ppm ~127 (ring carbons), 90.5 (t, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.5 (t, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 15.2 (q, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.14 (q, ring methyl groups).

X-Ray Crystallographic Study of  $Ta_2(n^5-C_5Me_4Et)_2Cl_3H_2(Me)$

Single crystals of  $Ta_2Cp'_2Cl_3H_2(Me)$  were sealed under nitrogen in thin-walled glass capillaries. They are monoclinic, space group  $P2_1/c-C_{2h}^5$  (No. 14)<sup>27</sup>, with  $\underline{a} = 20.084(6)\text{\AA}$ ,  $\underline{b} = 16.972(4)\text{\AA}$ ,  $\underline{c} = 15.869(4)\text{\AA}$ ,  $\beta = 96.86(2)^\circ$ , and  $Z = 8$  (dimeric species) at  $20 \pm 1^\circ\text{C}$ .

Intensity measurements were made on a Nicolet P $\bar{1}$  autodiffractometer using  $1.0^\circ$  wide  $\omega$  scans and graphite-monochromated  $MoK\bar{\alpha}$  radiation for an irregularly-shaped crystal with minimum and maximum dimensions of 0.20 and 0.75 mm, respectively. This crystal was oriented with its long dimension nearly parallel to the phi axis of the diffractometer.

A total of 12340 independent reflections having  $2\theta_{MoK\bar{\alpha}} < 55.0^\circ$  (the equivalent of 1.0 limiting  $CuK\bar{\alpha}$  spheres) were measured in two concentric shells of increasing  $2\theta$ . A scanning rate of  $6.0^\circ/\text{min.}$  was employed for the scan between  $\omega$  settings at  $0.50^\circ$  respectively above and below the calculated  $K\bar{\alpha}$  doublet value ( $\lambda_{K\bar{\alpha}} = 0.71073 \text{\AA}$ ) for those reflections having  $3^\circ < 2\theta_{MoK\bar{\alpha}} < 43^\circ$ ; a scanning rate of  $4.0^\circ/\text{min.}$  was used for those reflections having  $43^\circ < 2\theta_{MoK\bar{\alpha}} < 55.0^\circ$ . Each of these  $1^\circ$  scans was divided into 19 equal (time) intervals and those 15 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-fourth of the total time used for the net scan (15/19 of the total scan time), were measured at  $\omega$  settings  $1^\circ$  above and below the calculated value for each reflection. The intensity data were corrected empirically for absorption effects ( $\mu_a^{28a}(MoK\bar{\alpha}^-) = 8.86 \text{ mm}^{-1}$ ) using psi scans for 4 reflections having  $2\theta$  values between  $7^\circ$  and  $22^\circ$  and were then reduced to relative squared amplitudes,  $|F_0|^2$ , by means of standard Lorentz and polarization corrections.

The four tantalum atoms were located by direct methods. Cycles of isotropic unit-weighted full-matrix least-squares refinement for the structural parameters of the metal atoms gave  $\underline{R}_1$  (unweighted, based on  $F$ )<sup>29</sup> = 0.182 for those 4339 reflections having  $2\theta_{\text{MoK}\alpha} < 43^\circ$  and  $I > 3\sigma(I)$ . The remaining non-hydrogen atoms were located from a series of difference Fourier syntheses using more complete structural models. While locating these remaining non-hydrogen atoms, it was not possible to distinguish between the chloride and methyl ligands based on their difference Fourier peak heights. This, as well as the results from least-squares refinement cycles with all eight groups treated as full-occupancy chlorine atoms, indicated disordering of the methyl ligand among two (or more) sites per dimer. After the structure had been refined to convergence ( $\underline{R}_1 = 0.049$  for 4339 reflections) as  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$  with anisotropic thermal parameters for all 56 nonhydrogen atoms, the occupancies of all eight "chlorine" sites were allowed to vary. After convergence, two of the "chlorine" sites on each dimer ( $\text{Cl}_a$  and  $\text{Cl}_b$  in Figure 1) had refined occupancies near 1.00, while the other two ( $\text{Cl}/\text{C}_a$  and  $\text{Cl}/\text{C}_b$  in Figure 1) had refined occupancies near 0.85. Mixed scattering factors (50% Cl and 50% C) were then calculated and used with fixed occupancies of 1.00 for the Cl/C sites in all subsequent structure factor calculations.

Unit-weighted full-matrix least-squares refinement which utilized anisotropic thermal parameters for all 56 nonhydrogen atoms converged to  $\underline{R}_1 = 0.048$  and  $\underline{R}_2$  (weighted, based on  $F$ )<sup>29</sup> = 0.052 for 4339 independent reflections having  $2\theta_{\text{MoK}\alpha} < 43^\circ$  and  $I > 3\sigma(I)$ ; similar refinement cycles with the more complete ( $2\theta_{\text{MoK}\alpha} < 55^\circ$ ) data set gave  $\underline{R}_1 = 0.056$  and  $\underline{R}_2 = 0.061$  for 6542 absorption-corrected reflections having  $I > 3\sigma(I)$ . These and all subsequent structure factor calculations employed recent tabulations of atomic form

factors<sup>28b</sup> and anomalous dispersion corrections<sup>28c</sup> to the scattering factors of the Ta and Cl atoms. The final cycles<sup>10</sup> of empirically-weighted<sup>30</sup> full-matrix least-squares refinement which utilized anisotropic thermal parameters for all nonhydrogen atoms converged to  $R_1 = 0.056$  and  $R_2 = 0.070$  for 6542 independent reflections having  $2\theta_{\text{MoK}\alpha} < 55^\circ$  and  $I > 3\sigma(I)$ . The four crystallographically independent hydride atoms did not appear in the final difference Fourier.

All calculations were performed on a Data General Eclipse S200 computer with 64K of 16-bit words, a floating-point processor for 32- and 64-bit arithmetic and versions of the Nicolet E-XTL interactive crystallographic software package as modified at Crystalytics Company.

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SUPPLEMENTARY MATERIAL AVAILABLE. Crystal Structure Analysis Report, listings of anisotropic thermal parameters for nonhydrogen atoms (Table II) and observed and calculated structure factors from the final cycle of least-squares refinement for  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3(\text{H})(\text{Me})$  (39 pages).

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29. The R values are defined as

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and

$$R_2 = \left\{ \frac{\sum w (|F_o| - |F_c|)^2}{\sum w |F_o|^2} \right\}^{1/2}$$

where w is the weight given each reflection. The function minimized is

$$\sum w (|F_o| - K|F_c|)^2$$

where K is the scale factor.

30. Empirical weights were calculated from the equation

$$\sigma = \sum_0^3 a_n |F_o|^n = 6.66 - 1.57 \times 10^{-2} |F_o| + 9.87 \times 10^{-5} |F_o|^2 - 6.82 \times 10^{-8} |F_o|^3$$

the  $a_n$  being coefficients derived from the least-squares fitting of the curve

$$||F_0| - |F_c|| = \sum_0^3 a_n |F_0|^n$$

where the  $F_c$  values were calculated from the fully-refined model using unit weighting and an  $I > 3\sigma(I)$  rejection criterion.

Atomic Coordinates for Nonhydrogen Atoms in Crystalline  $Ta_2(n^5-C_5Me_4Et)_2Cl_3H_2(Me)^a$ 

Atom Type <sup>b</sup>	Fractional Coordinates		
	x	y	z
	Molecule 1		
Ta <sub>a</sub>	-0.04374(4)	0.28325(4)	0.49345(4)
Ta <sub>b</sub>	0.09893(4)	0.27279(4)	0.52400(4)
Cl <sub>a</sub>	-0.0839(3)	0.1621(3)	0.4328(4)
Cl/C <sub>a</sub>	-0.0637(4)	0.3622(4)	0.3693(3)
Cl <sub>b</sub>	0.1357(3)	0.3584(3)	0.6359(4)
Cl/C <sub>b</sub>	0.1342(4)	0.3510(4)	0.4143(5)
C <sub>a1</sub>	-0.0700(9)	0.3751(9)	0.5994(11)
C <sub>a2</sub>	-0.0624(10)	0.3011(11)	0.6398(10)
C <sub>a3</sub>	-0.1157(10)	0.2538(10)	0.6005(12)
C <sub>a4</sub>	-0.1547(9)	0.2989(14)	0.5370(13)
C <sub>a5</sub>	-0.1257(11)	0.3757(11)	0.5386(12)
C <sub>b1</sub>	0.1291(13)	0.1472(10)	0.4684(12)
C <sub>b2</sub>	0.1066(9)	0.1331(11)	0.5491(12)
C <sub>b3</sub>	0.1526(11)	0.1676(11)	0.6102(13)
C <sub>b4</sub>	0.2049(9)	0.2035(11)	0.5660(14)
C <sub>b5</sub>	0.1881(10)	0.1882(12)	0.4790(14)
C <sub>a6</sub>	-0.0289(12)	0.4484(12)	0.6258(14)
C <sub>a7</sub>	-0.0171(11)	0.2802(15)	0.7182(12)
C <sub>a8</sub>	-0.1329(13)	0.1701(14)	0.6281(17)
C <sub>a9</sub>	-0.2177(11)	0.2720(18)	0.4862(18)
C <sub>a10</sub>	-0.1573(13)	0.4445(14)	0.4894(15)
C <sub>a11</sub>	-0.0590(13)	0.4861(13)	0.7073(16)
C <sub>b6</sub>	0.0940(14)	0.1135(13)	0.3828(14)
C <sub>b7</sub>	0.0497(13)	0.0792(13)	0.5737(16)
C <sub>b8</sub>	0.1554(13)	0.1652(15)	0.7071(13)
C <sub>b9</sub>	0.2663(13)	0.2442(16)	0.6071(21)
C <sub>b10</sub>	0.2345(17)	0.2115(20)	0.4126(20)
C <sub>b11</sub>	0.1304(20)	0.0341(17)	0.3649(20)

Atomic Coordinates for Nonhydrogen Atoms in Crystalline  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{H}_2(\text{Me})^a$

Atom Type	Fractional Coordinates		
	x	y	z
Molecule 2			
Ta <sub>a</sub>	0.62362(4)	0.08862(4)	0.23668(5)
Ta <sub>b</sub>	0.48432(4)	0.06757(4)	0.23354(5)
Cl <sub>a</sub>	0.6439(3)	0.1457(4)	0.1066(3)
Cl/C <sub>a</sub>	0.6615(4)	-0.0415(5)	0.2126(6)
Cl <sub>b</sub>	0.4607(3)	0.0604(4)	0.3751(3)
Cl/C <sub>b</sub>	0.4703(4)	-0.0671(4)	0.1941(5)
C <sub>a1</sub>	0.6587(11)	0.1011(12)	0.3873(11)
C <sub>a2</sub>	0.6350(8)	0.1748(10)	0.3580(11)
C <sub>a3</sub>	0.6801(10)	0.2049(11)	0.3019(12)
C <sub>a4</sub>	0.7317(8)	0.1468(12)	0.2944(12)
C <sub>a5</sub>	0.7211(9)	0.0825(13)	0.3503(12)
C <sub>b1</sub>	0.4533(10)	0.1889(10)	0.1607(12)
C <sub>b2</sub>	0.4082(9)	0.1788(12)	0.2216(11)
C <sub>b3</sub>	0.3673(8)	0.1102(13)	0.2008(13)
C <sub>b4</sub>	0.3868(9)	0.0818(13)	0.1219(13)
C <sub>b5</sub>	0.4405(8)	0.1271(11)	0.0965(10)
C <sub>a6</sub>	0.6338(12)	0.0536(16)	0.4585(13)
C <sub>a7</sub>	0.5827(11)	0.2249(16)	0.3966(14)
C <sub>a8</sub>	0.6751(12)	0.2848(14)	0.2583(17)
C <sub>a9</sub>	0.7897(10)	0.1517(18)	0.2419(16)
C <sub>a10</sub>	0.7668(15)	0.0167(16)	0.3724(19)
C <sub>a11</sub>	0.6700(15)	0.0791(19)	0.5452(16)
C <sub>b6</sub>	0.4951(12)	0.2602(12)	0.1498(14)
C <sub>b7</sub>	0.3989(12)	0.2326(13)	0.2937(15)
C <sub>b8</sub>	0.3120(10)	0.0789(15)	0.2428(17)
C <sub>b9</sub>	0.3528(12)	0.0147(13)	0.0702(14)
C <sub>b10</sub>	0.4709(11)	0.1205(14)	0.0148(11)
C <sub>b11</sub>	0.4569(15)	0.3262(15)	0.0989(20)

<sup>a</sup>

The numbers in parentheses are the estimated standard deviations in the last significant digit.

<sup>b</sup>

Atoms are labelled in agreement with figure.

Bond Lengths Involving Nonhydrogen Atoms in Crystalline  $Ta_2(\eta^5-C_5Me_4Et)_2Cl_3H_2(Me)^a$

Type <sup>b</sup>	Length, Å		Type <sup>b</sup>	Length, Å	
	<u>Molecule 1</u>	<u>Molecule 2</u>		<u>Molecule 1</u>	<u>Molecule 2</u>
$Ta_a-Cl_a$	2.370(5)	2.359(5)	$Ta_a-Cl/C_a$	2.377(6)	2.381(8)
$Ta_b-Cl_b$	2.344(6)	2.354(5)	$Ta_b-Cl/C_b$	2.365(7)	2.378(7)
$Ta_a-C_{a1}$	2.40(2)	2.42(2)	$Ta_b-C_{b1}$	2.41(2)	2.41(2)
$Ta_a-C_{a2}$	2.42(2)	2.41(2)	$Ta_b-C_{b2}$	2.41(2)	2.42(2)
$Ta_a-C_{a3}$	2.41(2)	2.44(2)	$Ta_b-C_{b3}$	2.42(2)	2.45(2)
$Ta_a-C_{a4}$	2.43(2)	2.46(2)	$Ta_b-C_{b4}$	2.45(2)	2.49(2)
$Ta_a-C_{a5}$	2.44(2)	2.50(2)	$Ta_b-C_{b5}$	2.47(2)	2.46(2)
$Ta_a-C_{ga}^c$	2.10(-)	2.12(-)	$Ta_b-C_{gb}^c$	2.12(-)	2.12(-)
$Ta_a \cdots Ta_b$	2.854(1)	2.815(1)			
$C_{a1}-C_{a2}$	1.41(2)	1.40(3)	$C_{b1}-C_{b2}$	1.43(3)	1.41(3)
$C_{a2}-C_{a3}$	1.42(3)	1.44(3)	$C_{b2}-C_{b3}$	1.39(3)	1.44(3)
$C_{a3}-C_{a4}$	1.42(3)	1.45(3)	$C_{b3}-C_{b4}$	1.46(3)	1.44(3)
$C_{a4}-C_{a5}$	1.43(3)	1.44(3)	$C_{b4}-C_{b5}$	1.41(3)	1.42(3)
$C_{a5}-C_{a1}$	1.39(3)	1.48(3)	$C_{b5}-C_{b1}$	1.37(3)	1.46(3)
$C_{a1}-C_{a6}$	1.52(3)	1.52(3)	$C_{b1}-C_{b6}$	1.56(3)	1.49(3)
$C_{a2}-C_{a7}$	1.49(3)	1.54(3)	$C_{b2}-C_{b7}$	1.55(3)	1.49(3)
$C_{a3}-C_{a8}$	1.54(3)	1.52(3)	$C_{b3}-C_{b8}$	1.53(3)	1.46(3)
$C_{a4}-C_{a9}$	1.49(3)	1.51(3)	$C_{b4}-C_{b9}$	1.49(3)	1.52(3)
$C_{a5}-C_{a10}$	1.50(3)	1.46(4)	$C_{b5}-C_{b10}$	1.54(4)	1.50(4)
$C_{a6}-C_{a11}$	1.62(3)	1.54(4)	$C_{b6}-C_{b11}$	1.57(4)	1.53(4)

<sup>a</sup> The numbers in parentheses are the estimated standard deviations in the last significant digit.

<sup>b</sup> Atoms are labelled in agreement with figure.

<sup>c</sup> The symbols  $C_{ga}$  and  $C_{gb}$  refer to the centers of gravity for the five-membered rings of the a and b  $\eta^5-C_5Me_4Et$  ligands.

Bond Angles Involving Nonhydrogen Atoms in Crystalline  $Ta_2(n^5-C_5Me_4Et)_2Cl_3H_2(Me)^a$ 

Type <sup>b</sup>	Angle, deg.		Type <sup>b</sup>	Angle, deg.	
	<u>Molecule 1</u>	<u>Molecule 2</u>		<u>Molecule 1</u>	<u>Molecule 2</u>
$Ta_a Ta_b Cl_a$	107.5(1)	108.2(2)	$Ta_a Ta_b Cl_b$	108.0(2)	107.6(1)
$Ta_b Ta_a Cl/C_a$	104.0(2)	102.5(2)	$Ta_a Ta_b Cl/C_b$	102.9(2)	102.3(2)
$Ta_b Ta_a C_{ga}^c$	124.7(-)	123.9(-)	$Ta_a Ta_b C_{gb}^c$	126.3(-)	124.0(-)
$Cl_a Ta_a Cl/C_a$	97.9(2)	98.5(3)	$Cl_b Ta_b Cl/C_b$	96.6(2)	99.8(2)
$Cl_a Ta_a C_{ga}^c$	109.8(-)	110.2(-)	$Cl_b Ta_b C_{gb}^c$	110.0(-)	109.9(-)
$Cl/C_a Ta_a C_{ga}^c$	109.6(-)	110.5(-)	$Cl/C_b Ta_b C_{gb}^c$	108.8(-)	110.4(-)
$C_{a5}C_{a1}C_{a2}$	111(2)	109(2)	$C_{b5}C_{b1}C_{b2}$	110(2)	108(2)
$C_{a1}C_{a2}C_{a3}$	106(2)	108(2)	$C_{b1}C_{b2}C_{b3}$	107(2)	110(2)
$C_{a2}C_{a3}C_{a4}$	109(2)	109(2)	$C_{b2}C_{b3}C_{b4}$	107(2)	105(2)
$C_{a3}C_{a4}C_{a5}$	107(2)	108(2)	$C_{b3}C_{b4}C_{b5}$	107(2)	111(2)
$C_{a4}C_{a5}C_{a1}$	107(2)	106(2)	$C_{b4}C_{b5}C_{b1}$	109(2)	106(2)
$C_{a2}C_{a1}C_{a6}$	125(2)	126(2)	$C_{b2}C_{b1}C_{b6}$	124(2)	126(2)
$C_{a5}C_{a1}C_{a6}$	123(2)	123(2)	$C_{b5}C_{b1}C_{b6}$	126(2)	124(2)
$C_{a1}C_{a2}C_{a7}$	128(2)	126(2)	$C_{b1}C_{b2}C_{b7}$	130(2)	127(2)
$C_{a3}C_{a2}C_{a7}$	126(2)	124(2)	$C_{b3}C_{b2}C_{b7}$	122(2)	123(2)
$C_{a2}C_{a3}C_{a8}$	125(2)	126(2)	$C_{b2}C_{b3}C_{b8}$	129(2)	129(2)
$C_{a4}C_{a3}C_{a8}$	125(2)	126(2)	$C_{b4}C_{b3}C_{b8}$	123(2)	125(2)
$C_{a3}C_{a4}C_{a9}$	125(2)	128(2)	$C_{b3}C_{b4}C_{b9}$	126(2)	125(2)
$C_{a5}C_{a4}C_{a9}$	128(2)	124(2)	$C_{a5}C_{a4}C_{a9}$	127(2)	124(2)
$C_{a4}C_{a5}C_{a10}$	124(2)	126(2)	$C_{b4}C_{b5}C_{b10}$	122(2)	127(2)
$C_{a1}C_{a5}C_{a10}$	129(2)	127(2)	$C_{b1}C_{b5}C_{b10}$	129(2)	127(2)
$C_{a1}C_{a6}C_{a11}$	107(2)	111(2)	$C_{b1}C_{b6}C_{b11}$	108(2)	114(2)

a

The numbers in parentheses are the estimated standard deviations in the last significant digit.

b

Atoms are labelled in agreement with figure.

c

The symbols  $C_{ga}$  and  $C_{gb}$  refer to the centers of gravity for the five-membered rings of the a and b  $n^5-C_5Me_4Et$  ligands.

Figure 1. ORTEP Drawings of the two independent molecules of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_3\text{H}_2(\text{Me})$ .

Figure 2. A Schematic Drawing of the Proposed Structure of  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}_2\text{H}]_2$ .

Figure 3. The 250 MHz NMR Spectrum of (a) 1:2:1 mixture of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$ ,  $\text{Ta}_2\text{Cp}'\text{Cp}''\text{Cl}_4\text{H}_2$ , and  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ ; (b) an approximately 3.5:1 mixture of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  and  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ . (Solvent =  $\text{C}_6\text{D}_6$ ,  $T = 22^\circ$ ).

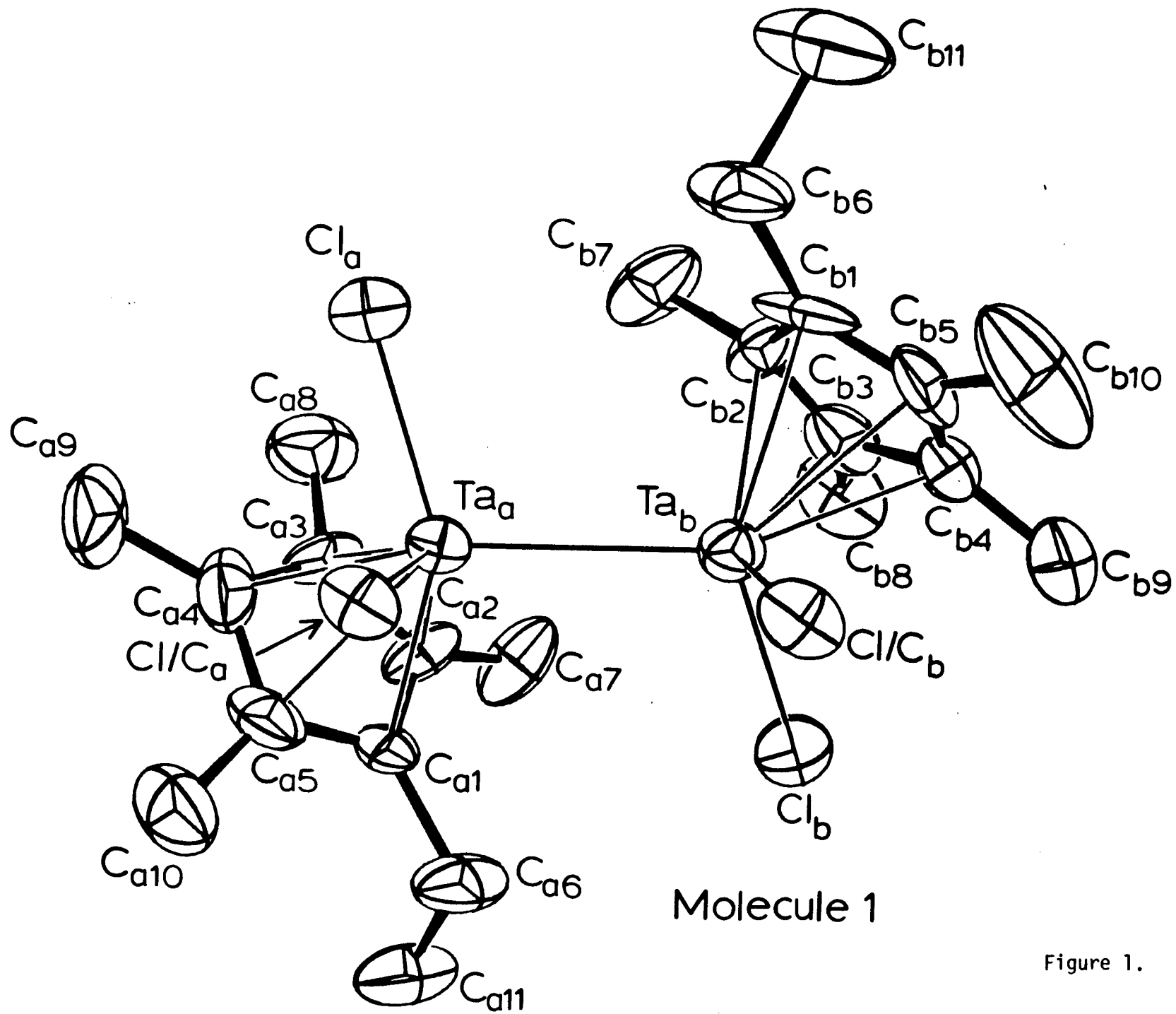


Figure 1.



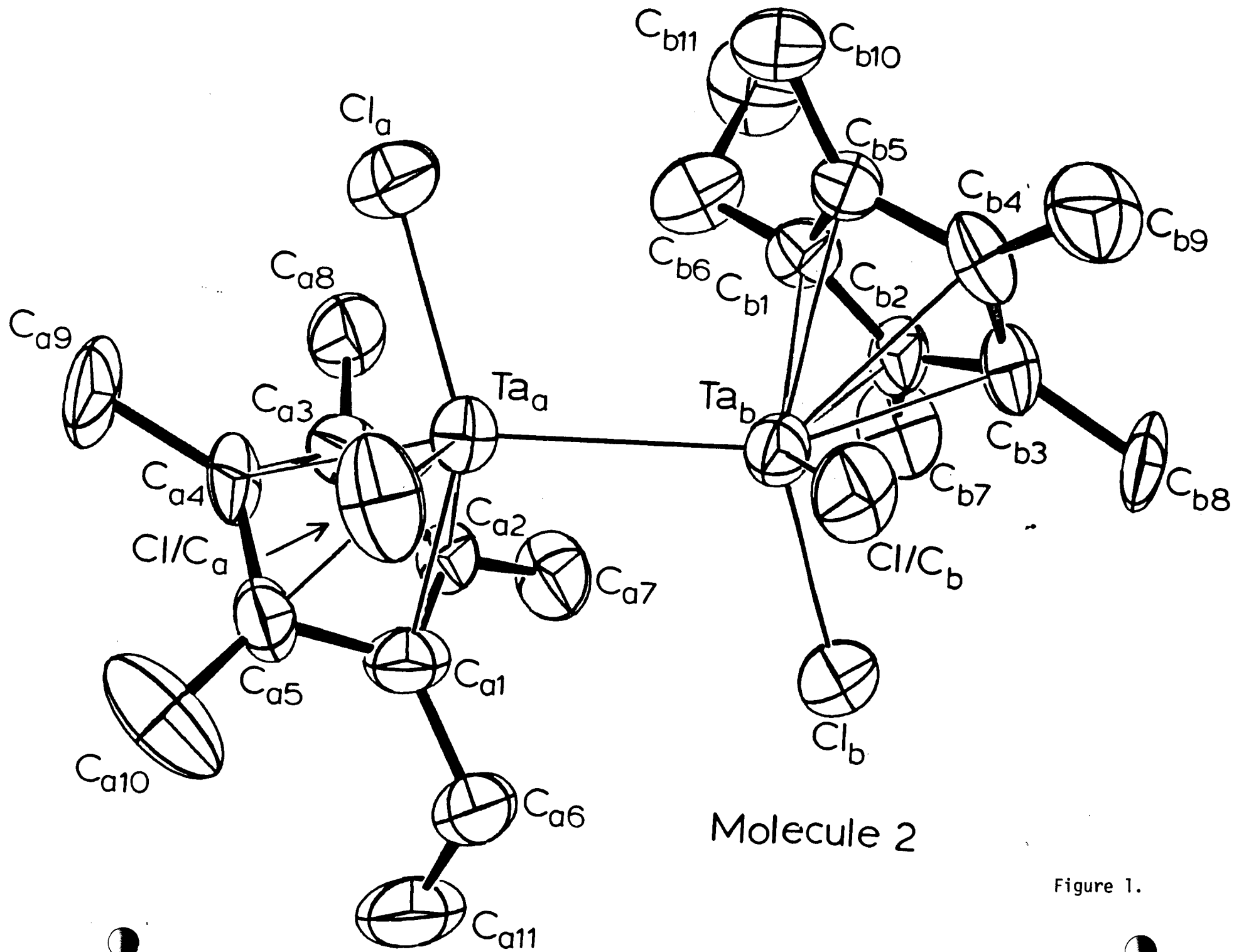


Figure 1.

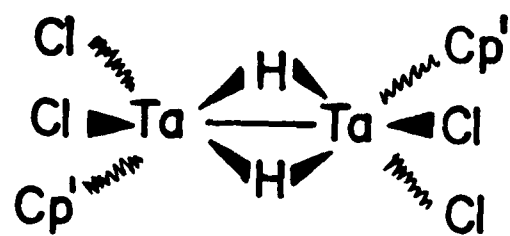
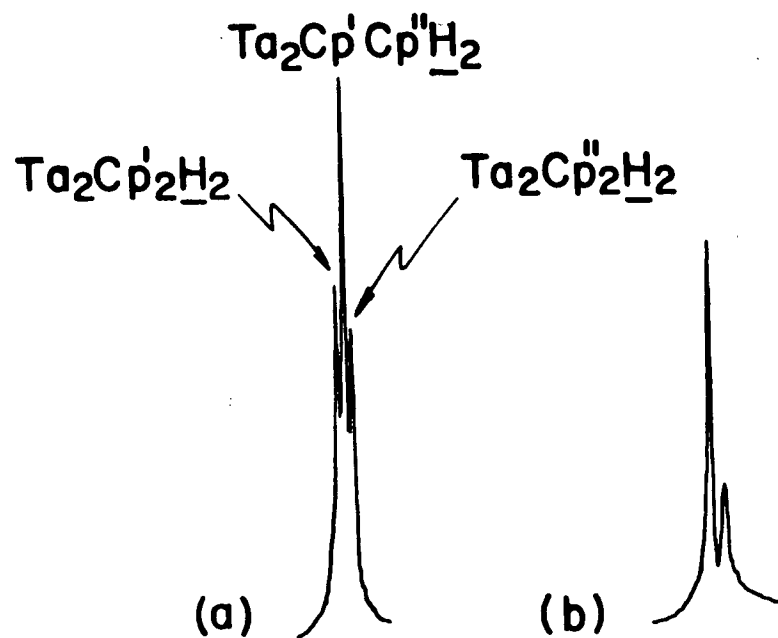
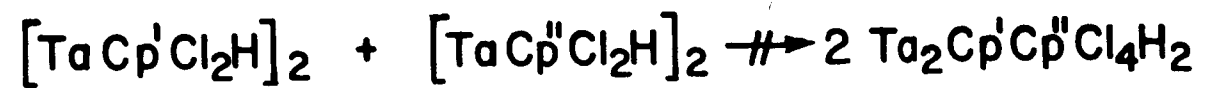


Figure 2.

Richard R. Schrock

Papers in Press

1. "Binuclear Tantalum Hydride Complexes", P.A. Belmonte, R.R. Schrock and C.S. Day.
2. "The Reduction of Carbon Monoxide by a Binuclear Tantalum Complex", P.A. Belmonte and R.R. Schrock.
3. "Trigonal Bipyramidal Bisneopentylidene, Neopentylidene/Ethylene, and Bisethylene Complexes of Tantalum and How They React With Ethylene", J.D. Fellmann, R.R. Schrock and G.A. Rupprecht.
4. " $\alpha$ -Hydride Elimination: The First Observable Equilibria Between Alkylidene Complexes and Alkylidyne Hydride Complexes", M.R. Churchill, H.J. Wasserman, H.W. Turner and R.R. Schrock.
5. "The Synthesis and Characterization of Tungsten Oxo Alkylidene Complexes", J.H. Wengrovius and R.R. Schrock.
6. " $\alpha$ -Hydride vs.  $\beta$ -Hydride Elimination. An Example of an Equilibrium Between Two Tautomers", J.D. Fellman, R.R. Schrock and D.D. Traficante.
7. "Imido and  $\mu$ -Dinitrogen Complexes Prepared from Niobium and Tantalum Neopentylidene Complexes", S.M. Rocklage and R.R. Schrock.
8. " $\alpha$ -Hydride Elimination in Tungsten(IV) Alkylidene Complexes", S.J. Holmes and R.R. Schrock.



APPENDIX II

REDUCTION OF CARBON MONOXIDE AND ISONITRILES  
BY A BINUCLEAR TANTALUM HYDRIDE COMPLEX

by

Patricia A. Belmonte and Richard R. Schrock

Contribution from the

Department of Chemistry  
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## ABSTRACT

$[\text{TaCp}'\text{Cl}_2\text{H}]_2$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$ ) reacts with CO to give yellow, crystalline  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ , in which the formyl fragment and the hydride are bonded side-on between the two metals. When  $\text{PMe}_3$  is added the HC-O bond is broken to give  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{O})(\text{CHPMe}_3)$ . The reaction of a mixture of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  and  $[\text{TaCp}'\text{Cl}_2\text{D}]_2$  with CO followed by  $\text{PMe}_3$  to give only a mixture of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{O})(\text{CHPMe}_3)$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{D}(\text{O})(\text{CDPMe}_3)$  suggests that the dimer does not fragment when it reacts with CO.  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  reacts analogously with isocyanides to give formimidoyl complexes,  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHNR})$  ( $\text{R} = \text{Me}, \text{CMe}_3$ ). When  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  is treated with  $\text{AlCl}_3$  under  $\text{H}_2$ ,  $\text{CH}_4$  is formed in ca. 80% yield. When  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  is hydrolyzed with aqueous HCl, methanol is formed quantitatively.

## INTRODUCTION

There is now a lively interest in the selective reduction of carbon monoxide to a product containing two or more carbon atoms.<sup>1</sup> It is thought that such selectivity is more likely with a homogeneous catalyst, and that an oxygenate, rather than a hydrocarbon, is the most likely reduction product.<sup>2</sup> The best example so far of some degree of selectivity to a two carbon product is the Rh catalyzed reduction of CO to ethylene glycol.<sup>2g</sup>

Although there have been many elegant studies of the chemistry of formyl complexes and other likely intermediates in systems in which CO is reduced,<sup>3</sup> several important questions have not been answered. One of the most important is whether one metal center is sufficient for the formation of an intermediate formyl complex which is long-lived and reactive enough to be reduced further, or whether one or more other metals must be present in order to stabilize the formyl ligand by interacting with its oxygen atom. (We need not at this point specify whether the metals are constrained in a metal cluster or simply reacting in a bimolecular fashion.) Evidence in model studies points to the latter as at least a potentially important feature of CO reduction.<sup>4,5</sup>

The most dramatic example of the role a second metal might play is addition of a zirconium hydride to a carbonyl ligand bound to another metal to give "zirconoxycarbene" complexes; e.g.  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr(H)[O(H)C=W}(\eta^5\text{-C}_5\text{H}_5)_2]$ .<sup>5</sup> The "carbene-type" CHO ligand is potentially an important type of "stabilized formyl" complex. So far this is the only example of reduction of a carbonyl ligand by a transition metal hydride complex to give a CHO fragment. Reactions between  $\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)_2\text{H}_2$  and CO may involve similar but as yet unobserved intermediates.<sup>6</sup>

Recently we prepared a new binuclear tantalum hydride complex for the ultimate purpose of attempting to reduce CO.<sup>7</sup> (Known niobium and tantalum

hydride complexes simply form hydrido carbonyl complexes in the presence of CO.<sup>8</sup>) We soon discovered that it does indeed reduce carbon monoxide to give a dimeric formyl hydride complex in high yield. It will also reduce isonitriles to give related formimidoyl hydride complexes. These reductions, and related chemistry such as the formation of methane and methanol from the formyl hydride complex, are the subjects we will discuss in this paper. Some of these results have been reported in a preliminary communication.<sup>9</sup>

## RESULTS

### Reaction of $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]_2$ with CO

$[\text{TaCp}'_2\text{Cl}_2\text{H}]_2$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$ ) reacts within ten minutes at 0°C with carbon monoxide (one equivalent or excess at  $\sim 1$  atm) to give yellow, crystalline  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ .  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  is soluble in THF, chlorocarbons, and aromatic hydrocarbons, sparingly soluble in diethyl ether, and insoluble in pentane.  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{D})(\text{CDO})$ ,  $\text{Ta}_2\text{Cp}'_2\text{Br}_4(\text{H})(\text{CHO})$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$  were prepared similarly.  $\text{Ta}_2\text{Cp}''_2\text{Cl}_4(\text{H})(\text{CHO})$  ( $\text{Cp}'' = \eta^5\text{-C}_5\text{Me}_5$ ) can be prepared straightforwardly but since it is only sparingly soluble in aromatic hydrocarbons it is less convenient to manipulate than  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ .

The IR spectrum of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  has a peak at  $1275\text{ cm}^{-1}$  which shifts to  $920\text{ cm}^{-1}$  in the spectrum of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{D})(\text{CDO})$ . We assign this peak to a metal-hydride mode.

The  $^1\text{H}$  NMR spectrum of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  at 233K (Figure 1) suggests that the molecule has no symmetry. The two singlets at ca. 5.6 and 7.5 ppm can be assigned to the hydride and formyl protons, respectively, based on the spectrum of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$ . At 298K the two peaks in the  $^1\text{H}$  NMR spectrum of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$  are split into doublets with  $J_{\text{CH}} = 20$  and 168 Hz,



respectively. In the  $^{13}\text{C}$  NMR spectrum of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$  at 298K the formyl carbon atom resonance is found as a broad doublet ( $J_{\text{CH}} = 168$  Hz) at 168 ppm. The 20 Hz coupling to the hydride could not be resolved under these conditions.

A complicating feature of the  $^1\text{H}$  NMR spectrum is its temperature dependence (Fig. 1). As the temperature is raised from 233K to 337K, the formyl and hydride signals broaden, shift toward one another, and then sharpen into doublets with  $J_{\text{HH}} \approx 4$  Hz. The resonances due to the Cp' ligands shift somewhat but the molecule remains asymmetric. In the  $^{13}\text{C}$  NMR spectrum the resonance for the formyl carbon atom shifts from  $\sim 168$  to  $\sim 176$  ppm and the coupling constant to the formyl proton drops from  $\sim 175$  to 165 Hz over this temperature range. One could ascribe this behavior simply to ordinary temperature dependent chemical shifts if the formyl proton resonance did not collapse to the extent it does. The only explanation we feel comfortable with is that one structural form predominates at low temperatures but at high temperatures there is a significant amount of a second species present with which the first species interconverts rapidly. (Note that the hydride and formyl protons do not exchange during this process.) The structural difference between these two species may be slight. Although we cannot speculate what these two structures might be at this time, we should point out that the inequivalent hydride ligands in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_3\text{H}_2(\text{R})$  complexes exchange over the same temperature range without destroying the asymmetry of the molecule.<sup>7</sup> The temperature dependent process in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_3\text{H}_2(\text{R})$  could involve a related structural change. Also note that in the structurally related molecules,  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{Me}_3\text{PCH})$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHNR})$  (see later), coupling between what were the two initial hydride ligands can be resolved, and it is of the same magnitude as that found in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  at 70°.

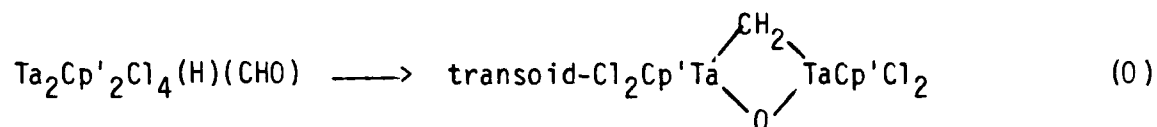
Churchill and Wasserman have determined the structure of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$  by single crystal x-ray diffraction.<sup>10</sup> A schematic drawing of the molecule is shown in Figure 2. The hydride and formyl fragment bridge between two skewed  $\text{TaCp}'\text{Cl}_2$  fragments. Neither the hydride nor the formyl proton was located, although a hole for the bridging hydride is present at a position trans to the  $\text{Cp}'$  group bound to  $\text{Ta}(2)$  such that the  $\text{Ta}(\text{C})(\text{O})(\text{H})\text{Ta}$  core of this molecule approximates a trigonal bipyramid. The formyl proton must be terminally bound to the formyl carbon atom, since if the formyl proton were bridging a Ta-C edge of the  $\text{Ta}(\text{C})(\text{O})(\text{H})\text{Ta}$  core,  $J_{\text{CH}}$  would almost certainly be about half (or even less than half) what it is (168 Hz).<sup>3h,11</sup> The Ta---Ta distance (3.186(1) Å) is too long for there to be a full Ta-Ta single bond between the two metals (cf.  $[\text{TaCp}'\text{Cl}_2\text{H}]_2^7$ ), although it is too short to propose that there is no bond at all. The C-O bond is significantly longer (by ca. 0.02 Å) than one would expect to find in a typical alcohol or ether.

A related hydride complex whose structure has not been determined,  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5(\text{H})$ ,<sup>7</sup> reacts relatively slowly with carbon monoxide (30 psi, 12 h, 25°) to give an orange solid which is much less soluble than  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  and which could not be obtained in crystalline form. It must be a related species,  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5(\text{CHO})$ , since its  $^{13}\text{C}$  NMR spectrum shows a formyl carbon atom resonance at 169 ppm, and its  $^1\text{H}$  NMR spectrum a formyl proton resonance at 8.2 ppm. The poor yield of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5(\text{H})$  has thus far prevented any detailed study of the preparation and reactions of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5(\text{CHO})$ .

An alkyl derivative of the formyl hydride complex,  $\text{Ta}_2\text{Cp}'_2\text{Cl}_3(\text{H})(\text{CHO})(\text{CH}_2\text{SiMe}_3)$ , can be prepared in poor yield (17%) from  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (dioxane). Its NMR spectra are similar to those of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  ( $\text{HCO}$  at 167.4 ppm,  $\text{HCO}$  at 5.23 ppm,  $\text{TaH}$  at 7.26

ppm). The methylene protons of the  $\text{CH}_2\text{SiMe}_3$  group are diastereotopic, as they are in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_3\text{H}_2(\text{CH}_2\text{SiMe}_3)$ .<sup>7</sup>  $\text{Ta}_2\text{Cp}'_2\text{Cl}_3(\text{H})(\text{CHO})(\text{CH}_2\text{SiMe}_3)$  could not be prepared from  $\text{Ta}_2\text{Cp}'_2\text{Cl}_3\text{H}_2(\text{CH}_2\text{SiMe}_3)$  and CO.

$\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  decomposes readily at ca.  $80^\circ\text{C}$  in solution to a complex mixture of products, as judged by the  $^{13}\text{C}$  NMR spectrum of a decomposed sample of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$ . A rapid pyrolysis of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  ( $100^\circ$ , 5 minutes) produces one of these decomposition products in ca. 25-50% yield. Although it has not yet been obtained free of minor impurities, NMR studies support the proposal that a methylene group is present. The  $^{13}\text{C}$  NMR spectrum of a sample prepared from  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$  shows a triplet  $^{13}\text{C}$  resonance at 171 ppm with  $J_{\text{CH}} = 131$  Hz. The two methylene protons are equivalent and give rise to a resonance in the  $^1\text{H}$  NMR spectrum at 5.10 ppm ( $J_{\text{HC}} = 131$  Hz). Our working hypothesis is that  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  decomposes as shown in equation 0.



The Reaction of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  with  $\text{PMe}_3$  and Proof that Hydrides do not Scramble Intermolecularly When  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  Reacts with CO

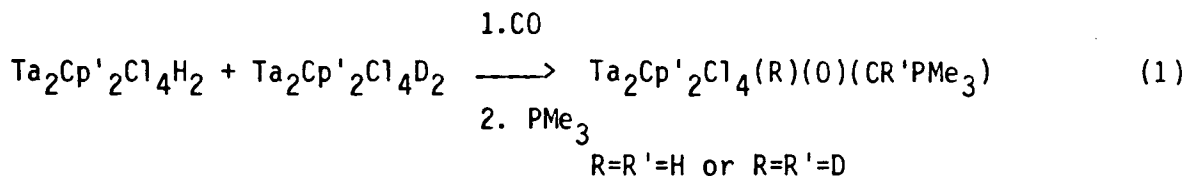
$\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  reacts with  $\text{PMe}_3$  in 30 minutes at  $25^\circ\text{C}$  to give  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{CHPMe}_3)$  quantitatively. This product is soluble in aromatic hydrocarbons and diethyl ether, and it is stable in chlorocarbons.  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{D})(\text{O})(\text{CDPMe}_3)$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(^{13}\text{CHPMe}_3)$  can be prepared straightforwardly.

The structure of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{CHPMe}_3)$ , as determined by Churchill and Youngs,<sup>12</sup> is shown schematically in Figure 3. Overall it is closely related to that of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ . The most important features are that  $\text{PMe}_3$  has attacked the formyl carbon atom and that the C-O bond has been broken. The two metals therefore are pulled closer together ( $\text{Ta} \cdots \text{Ta} = 2.992(1) \text{ \AA}$ ), close enough to propose that a Ta-Ta bond is present. The hydride ligand again could not be located although there is an obvious hole between the two metals where it should be.

The  $^1\text{H}$  NMR spectrum of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{CHPMe}_3)$  is shown in Figure 4a. The hydride resonance at 9.84 ppm is a double doublet due to coupling of the ylide proton (5 Hz) and to phosphorus (2 Hz). The ylide proton resonance at 1.44 ppm shows a larger  $J_{\text{HP}}$  (13 Hz). The hydride and ylide proton signals in the analogous spectrum of a product prepared from an approximate 1:2:1 mixture of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$ ,  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{D})$ , and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{D}_2$ , are shown in Figure 4b. The doublet due to the ylide proton in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{D})(\text{O})(\text{CHPMe}_3)$  is clearly observable slightly further upfield of the double doublet for the ylide proton in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{CHPMe}_3)$  as a result of the normal deuterium isotope effect. The hydride signal for the mixture of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{CDPMe}_3)$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{CHPMe}_3)$  is virtually the same pattern as in Figure 4a except the right branch is more intense; the hydride signal is not suitable for accurately detecting the amount of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{CDPMe}_3)$  in the mixture.

The fact that we can detect  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{D})(\text{O})(\text{CHPMe}_3)$  in the presence of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{O})(\text{CHPMe}_3)$  allowed us to do the following experiment. A mixture of equal parts of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}_2$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{D}_2$  was treated first with CO, and then with  $\text{PMe}_3$ . (Note that it was necessary to mix  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  and  $[\text{TaCp}'\text{Cl}_2\text{D}]_2$  at low temperature in order to avoid slow formation of

$\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{D})$ .<sup>7)</sup> The recrystallized final product had an  $^1\text{H}$  NMR spectrum identical to that shown in Figure 4a; i.e. no (estimated < 10%)  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{D})(\text{O})(\text{CHPMe}_3)$  was present (equation 1). This result suggests that



if the dimeric molecule breaks into monomeric fragments when it reacts with CO, both hydrides (or deuterides) must remain with one fragment, and in addition, H and D must not scramble between monomeric fragments. We consider this possibility unlikely with respect to the possibility that the molecule does not fragment at all before a hydride transfers to CO.

#### The Reaction of $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ with Isonitriles

Addition of one equivalent of  $\text{Me}_3\text{CNC}$  or  $\text{MeNC}$  to  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  produces blue and red dimeric products, respectively, in high yield. They are both soluble in aromatic hydrocarbons, ethers, and chlorocarbons. No carbon-nitrogen stretch was observed in the IR spectrum of either product, and since we did not prepare the deuterides, we could not locate the metal-hydride peak.

Pertinent  $^{13}\text{C}$  and  $^1\text{H}$  NMR data for these two products are listed in Table I. Unfortunately, there is no way, short of  $^{13}\text{C}$  labelling, to assign the hydride and "formimidoyl" proton resonances unambiguously. Since the hydride resonance in  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  is found downfield of the resonance for the formyl proton, we have tentatively assigned the peak of area one at lower field in each case to the hydride ligand. Other assignments are less likely but certainly plausible based on what is known about formimidoyl ligands in

the literature.<sup>13</sup> The formimidoyl carbon resonances in the  $^{13}\text{C}$  NMR spectrum are at least in the right range and they are doublets with believable values for  $J_{\text{CH}}$ .

One could argue with some conviction that the basic structure of the two formimidoyl complexes should be the same, and similar to the structure of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ , even though there is no close correlation of the NMR data for the three compounds. We think this is, in fact, true, and that configurational isomers of these three unsymmetric molecules are responsible for the variation in the NMR data, and for the rather different colors (yellow, red, and blue). (Note that the positions of the hydride and formyl proton and carbon resonances changed significantly with temperature (Figure 1), and we ascribed this change to the presence of rapidly interconverting isomers.) We cannot suggest any other reasons for these differences until there is more reason to do so.

Unlike  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ , both  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHNMe})$  and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHNCMe}_3)$  are relatively robust molecules. They are stable to air in the solid state for at least one hour.  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHNMe})$  is unchanged after heating in vacuo at  $100^\circ\text{C}$  for 24 hours. Neither reacts with  $\text{PMe}_3$  at  $25^\circ\text{C}$ .  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHNMe})$  is unchanged after two days under 1500 psi of  $\text{H}_2$ .

#### The Formation of Adducts Between $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ and Pyridine, $\text{PMe}_3$ , or CO

$[\text{TaCp}'\text{Cl}_2\text{H}]_2$  reacts with pyridine to form dark green needles of a 1:1 diamagnetic adduct. The IR spectrum of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{py})$  shows a metal-hydride peak at  $1625\text{ cm}^{-1}$ ; in  $[\text{TaCp}'\text{Cl}_2\text{D}]_2(\text{py})$  the peak is observed at  $1165\text{ cm}^{-1}$ . In the NMR spectrum we see only one hydride resonance at 0.287 ppm, but in the spectrum of  $[\text{TaCp}''\text{Cl}_2\text{H}]_2(\text{py})$  in bromobenzene we see two hydride signals at

0.273 and 0.456 ppm. (The second hydride peak must be obscured by other resonances in the spectrum of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{py})$ .) Since the two resonances are so close to one another we assume the two inequivalent hydrides are of the same type. They almost certainly must still be bridging, but it is peculiar that the signals are shifted to such a higher field than where they are found in the parent complex. But the most unusual feature of the NMR spectrum of the pyridine adducts is that all five pyridine protons are different. This implies that the pyridine has slipped into a coordination site where it is too crowded for rotation of the pyridine about the pyridine-Ta bond axis. The pyridine adduct reacts relatively slowly with CO (1 atm, 10 min,  $25^\circ$ ) to give  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$ .

The reaction between  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  and  $\text{PMe}_3$  is substantially different. Addition of one equivalent of  $\text{PMe}_3$  to  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  at  $-78^\circ$  in ether produces a purple solution. At  $20^\circ$  a shiny grey-purple solid precipitated. It would not redissolve in ether, but it would dissolve in benzene or chlorobenzene to give purple solutions. The purple adduct is unstable; it decomposes to a completely insoluble black solid at  $25^\circ$  in benzene in one hour. At  $0^\circ\text{C}$  the decomposition is slow enough to determine the molecular weight of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{PMe}_3)$  in benzene by cryoscopy; it is dimeric, as expected.  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{PMe}_3)$  will react with CO much more slowly than  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  does to give a moderate (40%) yield of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHPMe}_3)(\text{O})$ . The most peculiar feature of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{PMe}_3)$  is that it is paramagnetic ( $\mu = 2.5 \text{ BM}$  (Evan's method) at  $0^\circ\text{C}$ ).

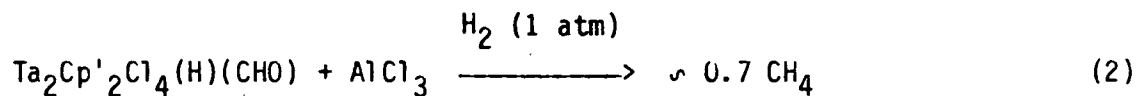
If a green solution of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  is treated with excess CO at  $-78^\circ$  it slowly turns a deep blue-purple. One equivalent of CO is sufficient although the rate of formation of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{CO})$  is relatively slow under these

conditions. Above  $-60^{\circ}\text{C}$  the blue-purple solution turns green and then yellow.  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ , the only observable product, can be isolated in essentially quantitative yield.

Attempted  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{CO})$  were precluded by the fact that it too is paramagnetic. At  $-60^{\circ}\text{C}$  in toluene the magnetic moment is 2.5 BM. These results suggest that  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{PMe}_3)$  and  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{CO})$  are analogs. Unfortunately, the instability of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{CO})$  prevented measuring its molecular weight. The green color which forms as the blue-purple color of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{CO})$  changes to the yellow color of  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$  is most likely simply due to the blue to yellow color change involved, rather than to a loss of CO to give green  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  before formation of  $[\text{TaCp}'\text{Cl}_2]_2(\text{H})(\text{CHO})$ .

#### The Reaction of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ with Lewis Acids to Give Methane

Aluminum trichloride reacts with  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  readily to give a single product which rapidly decomposes to a complex mixture of unidentifiable products. Methane is produced in  $\sim 30\%$  yield, but no ethylene or ethane. If  $\text{AlCl}_3$  is added to  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  under one atmosphere of excess  $\text{H}_2$  the yield of methane rises to  $\sim 70\%$  (equation 2). If  $\text{D}_2$  is used the methane



consists of about a 2:3 mixture of  $\text{CH}_4$  and  $\text{CH}_3\text{D}$  by  $^{13}\text{C}$  NMR; the signal to noise ratio was not good enough to rule out up to 15%  $\text{CH}_2\text{D}_2$ . We propose that



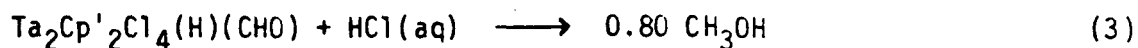
$\text{AlCl}_3$  attacks the formyl oxygen atom and causes the C-O bond to break. The CH fragment is then reduced by the hydride in the same molecule, or hydride ligands in other molecules. We cannot rule out the Cp groups as a source of H. However, it is clear that  $\text{H}_2$  or  $\text{D}_2$ , even at 1 atm, can also help reduce the CH fragment at some point in the complex decomposition process.

Trimethylaluminum also reacts with  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ . In the presence of four equivalents of  $\text{AlMe}_3$  the  $^1\text{H}$  NMR spectrum of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  shows a hydride resonance at 8.33 ppm and a formyl proton resonance at 6.5 ppm ( $J_{\text{HH}} = 3$  Hz). Two formyl carbon resonances are observed at 227 and 214 ppm, the first a broad doublet ( $J = 156$  Hz), the second a double doublet ( $J = 153$  and 9 Hz). This product can be isolated as a pentane soluble yellow oil which decomposes slowly  $25^\circ$  to give methane (not quantified). If less than 3-4 equivalents of  $\text{AlMe}_3$  are added a more complex mixture of products is generated. Almost certainly the metals are being alkylated step-wise by  $\text{AlMe}_3$ . Since the methyl groups initially in  $\text{AlMe}_3$  are likely sources of at least some of the methane, we did not study the formation and decomposition of the  $\text{AlMe}_3$  product in detail.

$\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  also reacts with  $\text{BH}_3 \cdot \text{THF}$  to yield a substantial quantity of methane (not quantified). Borane (or  $\text{BH}_4^-$ ) has been used in several instances to reduce a carbon monoxide ligand, ultimately to methane.<sup>14</sup> Initial attack at the formyl oxygen atom is again a likely first step.

#### The Reaction of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ with HCl

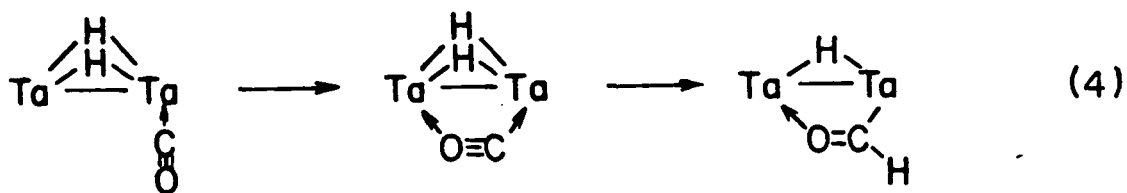
Methanol (>80%) is produced when excess aqueous HCl is added to  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  in propanol (equation 3). If HCl gas is used in aprotic



solvents no methanol is formed. Mixtures of yellow to orange products are obtained which show  $^{13}\text{C}$  resonances characteristic of methoxide groups bound to tantalum ( $\sim 60$  ppm,  $J_{\text{CH}} \sim 145$  Hz). These are most easily observed starting with  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$ . For example, the  $^{13}\text{C}$  NMR spectrum of the product of the reaction of two equivalents of HCl with  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$  in bromobenzene showed two methoxide peaks, one at 66.84 ppm (major), the other at 62.85 ppm (minor). We believe, therefore, that the original C-O bond remains intact but the Ta-OCH<sub>3</sub> bond can only be cleaved by HCl in the presence of water or alcohol.

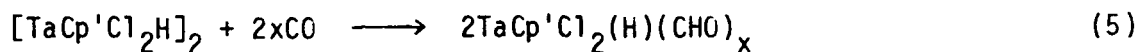
#### DISCUSSION

The two most important features of the reaction of CO with  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  to give  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  are, first, that the dimeric hydride complex probably remains intact throughout, and second, that the resulting formyl fragment is securely sequestered between the two metals. Had we no knowledge of the nature of the initial CO adduct we would suggest that CO first adds to one of the metals and is activated toward migration of a hydride to it when its oxygen atom begins to bond to the other metal (equation 4).



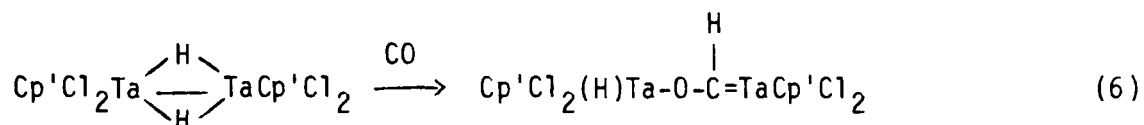
This proposal is appealing in one sense since for some time it has been proposed that "semi-bridging"<sup>15</sup> or "Lewis Acid activated" CO ligands<sup>4</sup> should be more susceptible to reduction by a transition metal hydride. However, it is unlikely that the hydrides remain in the bridging positions. The reason is simply that the CO adduct is paramagnetic, and probably a dimer, and to our knowledge no paramagnetic dimeric molecule which contains a total even number of electrons and one or two bridging hydride ligands is known. In contrast, there are some classic examples of paramagnetic even-electron dimers containing bridging chlorides such as  $[\text{Cu}_2\text{Cl}_6]^{2-}$  (ref. 16). Relevant to this argument is the fact that in a molecule which is related to  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ ,  $\text{Ir}_2\text{Cp}''_2\text{Cl}_3\text{H}$ , the Ir-Ir distance is 2.903 Å,<sup>17</sup> while in  $\text{Ir}_2\text{Cp}''_2\text{Cl}_4$ ,<sup>18</sup> the Ir-Ir distance (3.769 Å) is too large for any significant bonding interaction. We propose that the hydride ligands in the CO (and  $\text{PMe}_3$ ) adduct are terminal, that chlorides bridge the two metals, and that CO is bound to one metal only in a terminal fashion. Extensive EPR and FT IR studies of the "simple"  $\text{PMe}_3$  and CO adducts of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  are required in order to test this proposal and solve what may prove to be a crucial part of the puzzle concerning how and why the hydride complex reduces CO.

The simplest function of the Ta-Ta bond one could propose is simply to hold the metals together long enough to complete the sequence which gives  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ . A competing reaction should be cleavage of the dimer to give Ta(IV) complexes (equation 5), since a compound which is related to



$[\text{TaCp}'\text{Cl}_2\text{H}]_2$ ,  $[\text{TiCp}_2\text{H}]_2$ , reacts with donor molecules such as  $\text{PPh}_3$  to give monomeric Ti(III) complexes,  $\text{TiCp}_2(\text{H})(\text{L})$ .<sup>19</sup> However, Ti(III) should be more accessible than Ta(IV). It is interesting to note that preliminary results suggest that  $[\text{NbCp}'\text{Cl}_2\text{H}]_2$  reacts with CO to give  $\text{NbCp}'\text{Cl}_2(\text{CO})_2$ , but no formyl complex analogous to  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$ . Again the explanation could be that the Nb-Nb bond is more susceptible to cleavage to give Nb(IV) species than the Ta-Ta bond to give a Ta(IV) species. While the interpretation of the role of the Ta-Ta bond as solely a link holding the two metals together is plausible, its role may be far more subtle. For example, the formation of paramagnetic centers in the CO adduct (see above) may be important in order to insure rapid hydride transfer to CO at a rate which competes with Ta-Ta bond cleavage.

One plausible variation of the result we have found here would be formation of a "tantaloxy-carbene" complex (equation 6) analogous to Bercaw's



"zirconoxy-carbene" complexes.<sup>5</sup> This seems plausible since complexes such as  $\text{TaCp}''(\text{CHCMe}_3)\text{Cl}_2$ <sup>20</sup> and  $\text{TaCp}''(\text{CHPh})\text{Cl}_2$ ,<sup>21</sup> as well as  $\text{Cp}_2(\text{R})\text{Nb}=\text{CHOZr}(\text{H})\text{Cp}''_2$ ,<sup>5</sup> are known. Almost certainly the reason why the "open" structure shown in equation 6 is not found is that each metal in such a species would be electron deficient (14 electrons). By "closing up" the structure each metal achieves a maximum electron count. A closed structure for  $\text{Cp}''_2(\text{H})\text{ZrO}(\text{H})\text{C}=\text{WCp}_2$ , for example, would be less likely since the count about tungsten is 18 electrons and about zirconium is that preferred for biscyclopentadienyl complexes, 16 electrons. It must be in part this sequestering of the formyl ligand between the two metals which stabilizes the formyl complex toward the back reaction, but,

unfortunately, probably also to a facile subsequent reaction with CO to yield some species containing a C-C bond, or with molecular hydrogen to give a methoxide ligand.

Sequestering the formyl ligand does not prevent what overall could be called an electrophilic or nucleophilic attack on it by acids and bases. There is some consistency in how  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$  reacts with Lewis acids and bases. Trimethylphosphine attacks the formyl carbon atom and aluminum chloride attacks the formyl oxygen atom, the C-O bond being broken in each case. Aluminum chloride is believed to act as an oxygen acceptor in a system in which CO is reduced by hydrogen to hydrocarbons using an iridium catalyst.<sup>22</sup> The precedent for nucleophilic attack on a formyl atom is further reduction of formyl ligands by boron hydrides.<sup>14</sup> The result shown in equation O would be consistent with attack by "hydride" on the formyl carbon atom.

## EXPERIMENTAL

All operations, except where otherwise specified, were performed under dinitrogen either by Schlenk techniques or in a dry box.  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$ ,  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$ , and  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5\text{H}$  were prepared as described in the literature.<sup>7</sup>

Pentane, hexane and petroleum ether were washed with 5% nitric acid in sulfuric acid, stored over calcium chloride and distilled under dinitrogen from n-butyl lithium. Reagent grade diethyl ether, tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl under dinitrogen. Reagent grade benzene, methylene chloride, chloroform and chlorobenzene were dried by refluxing overnight with calcium hydride and distilled. All deuterated NMR solvents were passed through a column of activated alumina.

NMR data are listed in ppm relative to internal TMS for  $^1\text{H}$  and  $^{13}\text{C}$  and relative to external  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$ .

#### Preparation of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHO})$

$[\text{TaCp}'\text{Cl}_2\text{H}]_2$  (0.8 g, 1.0 mmol) was dissolved in 150 ml of diethyl ether in a 250 ml round bottom flask. This was sealed with a septum cap and cooled to  $-78^\circ$ . Carbon monoxide (25 ml, 1.1 mmol) was added by syringe through the septum and the reaction mixture was slowly warmed to  $0^\circ$  and stirred. The color of the solution changed from green to orange. After two days at  $0^\circ$ , yellow needles (0.65 g, 78%) were filtered off. The filtrate was concentrated and cooled to  $-30^\circ$  to give an additional 0.1 g (12%) as a yellow powder which was pure by  $^1\text{H}$  NMR.

Anal. Calcd. for  $\text{Ta}_2\text{C}_{23}\text{H}_{36}\text{Cl}_4\text{O}$ : C, 33.19; H, 4.36. Found: C, 33.62, H, 4.40. Mol. Wt. (cryoscopic in benzene): Calcd, 832. Found:  $800 \pm 50$ . IR (Nujol):  $1265\text{ cm}^{-1}$  (TaH).  $^{13}\text{C}$  NMR ( $d_8$ -toluene, 233K, gated proton de-

coupled): ppm 11.3, 12.3, 12.4, 14.5, 15.1 (alkyl carbons), 168 (d,  $J_{\text{CH}} = 169$  Hz, CHO).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 296K): 7.52 (br s, 1, MH), 5.73 (br s, 1, CHO), 2.71 (m 4,  $\text{C}_5\text{CH}_2\text{CH}_3$ ), 2.23 (br s, 6,  $\text{C}_5\text{CH}_3$ ), 2.16 (br s, 6,  $\text{C}_5\text{CH}_3$ ), 1.98 (br s, 3,  $\text{C}_5\text{CH}_3$ ), 1.96 (br s, 3,  $\text{C}_5\text{CH}_3$ ), 1.84 (br s, 6,  $\text{C}_5\text{CH}_3$ ), 0.8 (m, 6,  $\text{C}_5\text{CH}_2\text{CH}_3$ ). In  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(^{13}\text{CHO})$  (prepared similarly using Toepler pump techniques) the hydride resonance at 7.52 ppm is a doublet ( $J_{\text{HC}} = 20$  Hz) and the formyl proton resonance at 6.08 ppm is a doublet ( $J_{\text{HC}} = 168$  Hz).

#### Preparation of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{D}(\text{CDO})$

$\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{D}(\text{CDO})$  was prepared in the same manner from  $[\text{TaCp}'\text{Cl}_2\text{D}]_2$  and carbon monoxide in diethyl ether.

IR (Nujol):  $920\text{ cm}^{-1}$  (TaD).

#### Observation of $\text{Ta}_2\text{Cp}'_2\text{Br}_4\text{H}(\text{CHO})$

Carbon monoxide (10 ml) was added to an NMR sample of  $[\text{TaCp}'\text{Br}_2\text{H}]_2$  (approximately 0.5 g) in 0.5 ml  $\text{C}_6\text{D}_6$ . The color immediately changed from brown-orange to red.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 295K): ppm 9.22 (br s, 1, TaH), 5.80 (br s, 1, CHO), 2.70 (m, 4,  $\text{C}_5\text{CH}_2\text{CH}_3$ ), 2.37 (br s, 12,  $\text{C}_5\text{CH}_3$ ), 2.25 (br s, 12,  $\text{C}_5\text{CH}_3$ ), 0.89 (m, 6,  $\text{C}_5\text{CH}_2\text{CH}_3$ ).

#### Preparation of $\text{Ta}_2\text{Cp}'_2\text{Cl}_5(\text{CHO})$

A solution of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5\text{H}$  (0.4 g, 0.48 mmol) in 100 ml of diethyl ether was treated with 30 psi CO for 12 hours at  $22^\circ$ . The solvent was removed in vacuo and the residue was dissolved in a minimum amount of toluene. The volume was doubled with pentane and the solution was cooled to  $-30^\circ$  to give a yellow solid (0.14 g). Solvent was again removed from the filtrate. The

residue was dissolved in diethyl ether and the solution was filtered and cooled to give an additional 0.1 g of yellow solid; total yield 0.24 g (58%).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $30^\circ\text{C}$ ): ppm 134.4, 131.6, 131.1, 128.1, 128.0, 126.6 (ring carbons), 20.7, 19.9, 13.9, 12.9, 12.4, 11.8 (alkyl carbons).  $^1\text{H}$  NMR ( $d_8$ -toluene, 297K): ppm 8.22 (br s, CHO), 2.77 (m,  $\text{C}_5\text{CH}_2\text{CH}_3$ ), 2.55 (m,  $\text{C}_5\text{CH}_2\text{CH}_3$ ), 2.36-2.19 (m,  $\text{C}_5\text{CH}_3$ ), 0.84 (m,  $\text{C}_5\text{CH}_2\text{CH}_3$ ).

In order to observe the formyl carbon atom in the  $^{13}\text{C}$  NMR spectrum  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5(^{13}\text{CHO})$  was prepared from  $\text{Ta}_2\text{Cp}'_2\text{Cl}_5\text{H}$  (0.18 g in 20 ml toluene) and two equivalents of  $^{13}\text{CO}$  by heating the mixture to  $100^\circ$  to 0.5 hr. The toluene was removed in vacuo and the residue was extracted with  $\text{C}_6\text{D}_6$ . The formyl carbon atom resonance was observed at 169.0 ppm.

#### Preparation of $\text{Ta}_2\text{Cp}'_2\text{Cl}_3\text{H}(\text{CHO})(\text{CH}_2\text{SiMe}_3)$

A toluene solution of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$  (0.42 g, 0.5 mmol) was cooled to  $-30^\circ$ .  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{dioxane})$  (0.07 g, 0.25 mmol) was added and the solution was stirred for two hours at  $25^\circ$ . The solution was filtered and the solvent was removed in vacuo. The residue was dissolved in ether. Pentane was added and the solution was cooled to  $-30^\circ$  to give orange crystals (0.15g, 17%).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_8$ -toluene,  $35^\circ$ ): ppm 167.4 (CHO), 120-124 (ring carbons), 55.3 ( $\text{CH}_2\text{SiMe}_3$ ), 22.1-18.7 ( $\text{C}_5\text{CH}_2\text{CH}_3$  carbons), 14.7, 14.1, 12.1-11.1 ( $\text{C}_5\text{CH}_3$  carbons), 3.15 ( $\text{SiMe}_3$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $30^\circ$ ): ppm 7.37 (br s, 1, TaH), 5.27 (br s, 1, CHO), 1.6-3.0 (m,  $\text{C}_5\text{CH}_3$ ), 1.4-0.8 (m,  $\text{C}_5\text{CH}_2\text{CH}_3$ ), 0.27 (s, 9,  $\text{SiMe}_3$ ).  $^1\text{H}$  NMR ( $d_8$ -toluene,  $-30^\circ\text{C}$ ): ppm 7.26 (br s, 1, TaH), 5.23 (br s, 1, CHO), 3.43 (d, 1,  $J_{\text{HH}} = 12$  Hz,  $\text{CH}_a\text{H}_b\text{SiMe}_3$ ), 2.69 (m,  $\text{C}_5\text{CH}_2\text{CH}_3$ ), 2.23, 2.225, 2.14, 2.13, 1.74, 1.65, 1.60, 1.55 (s, 3 each,  $\text{C}_5\text{CH}_3$ ), 1.93 (d, 1,  $J_{\text{HH}} = 12$  Hz,  $\text{CH}_a\text{H}_b\text{SiMe}_3$ ), 0.81 (m,  $\text{C}_5\text{CH}_2\text{CH}_3$ ), 0.24 (s, 9,  $\text{SiMe}_3$ ).



### Preparation of $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$

$PMe_3$  (0.2 ml, 2.6 mmol) was added to a solution of  $Ta_2Cp'_2Cl_4H(CHO)$  (0.83 g, 1 mmol) in 50 ml of benzene. The color changed from orange to yellow in 0.5 h. Solvent was removed under vacuum, leaving crude, yellow  $Ta_2Cp'_2Cl_4H(O)(CHPMe_3)$ . Recrystallization from toluene/pentane gave 0.76 g (84%) yellow crystals in two crops.

Anal. Calcd. for  $Ta_2C_{26}H_{45}Cl_4OP$ : C, 34.38; H, 4.99. Found: C, 34.47; H, 5.10.  $^1H$  NMR ( $CDCl_3$ ): ppm 9.84 (dd, 1,  $J_{HH} = 5$  Hz,  $J_{HP} = 2$  Hz, TaH), 2.47 (m, 1,  $C_5CH_2CH_3$ ), 2.44 (m, 1,  $C_5CH_2CH_3$ ), 2.21 (d, 2,  $C_5CH_2CH_3$ ), 2.19-2.13 (6 singlets, 24 total,  $C_5CH_3$ ), 1.69 (d, 9,  $J_{HP} = 12$  Hz,  $PMe_3$ ), 1.44 (dd, 1,  $J_{PH} = 13$  Hz,  $J_{HH} = 5$  Hz,  $CHPMe_3$ ), 1.05 (t, 3,  $C_5CH_2CH_3$ ), 0.99 (t, 3,  $C_5CH_2CH_3$ ).  $^{31}P\{^1H\}$  NMR ( $CHCl_3$ ): 22.5 ppm (s).

$Ta_2Cp'_2Cl_4H(O)(^{13}CHPMe_3)$  was prepared similarly from  $Ta_2Cp'_2Cl_4H(^{13}CHO)$  and  $PMe_3$  in benzene.  $^{13}C$  NMR ( $CDCl_3$ , gated, proton decoupled): ppm 94.13 (ddd,  $J_{CP} = 44$  Hz,  $J_{CH} = 122$  Hz,  $J_{CH} = 10$  Hz,  $CHPMe_3$ ).

### Preparation of $[Ta(n^5-C_5Me_4R)Cl_2H]_2(py)$

Pyridine (1.48 mmol) was added to an incompletely dissolved sample of  $[TaCp''Cl_2H]_2$  (0.59 g) in 50 ml of toluene. The starting material dissolved to give a deep green solution which was filtered and concentrated to ~ 35 ml. Pentane (~ 15 ml) was added and the reaction was cooled to  $-30^\circ$ . The product crystallized as dark green, almost black, crystals (0.6 g, 92%). It is less soluble than the starting material (in the absence of excess pyridine) in benzene or toluene. Pyridine of crystallization can be observed in the NMR spectra of most samples.

Anal. Calcd. for  $\text{Ta}_2\text{C}_{27}\text{H}_{41}\text{NCl}_4$ : C, 36.71; H, 4.68; N, 1.59. Found: C, 37.22; H, 4.69; N, 2.00. Calcd. for  $\text{Ta}_2\text{C}_{28}\text{H}_{42}\text{N}_{1.2}\text{Cl}_4(1.2\text{py})$ : C, 37.38; H, 4.70; N, 1.87.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): ppm 9.61, 8.87, 6.78, 6.76, 6.59 (m, 1 each, py), 2.3, 2.16 (s, inequivalent Cp" groups), 0.102 (s, 1, Ta-H). The other hydride resonance could not be found. In bromobenzene both hydride resonances could be found at 0.28 and 0.46 ppm. IR ( $\text{cm}^{-1}$ , Nujol): 1625 (Ta-H).

$[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{py})$  and deuterated derivatives were prepared similarly.  $\nu_{\text{TaD}} = 1165 \text{ cm}^{-1}$  in  $[\text{TaCp}'\text{Cl}_2\text{D}]_2(\text{py})$ .

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 9.719, 8.938, 6.733, 6.600, 6.382 (br, 1 each, pyridine), 2.63 (m, Cp- $\text{CH}_2\text{CH}_2$ ), 2.443, 2.403, 2.367, 2.341, 2.301, 2.225, 2.110 (s, Cp- $\text{CH}_3$ ), 0.863 (m, Cp- $\text{CH}_2\text{CH}_3$ ), 0.287 (br s, 1, MH). IR (Nujol): 1625 (s, br, MH).

#### Reaction of $\text{PMe}_3$ with $[\text{TaCp}'\text{Cl}_2\text{H}]_2$

A solution of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  (0.4 g, 0.5 mmol) in 30 ml of ether was cooled to  $-78^\circ\text{C}$ . A solution of  $\text{PMe}_3$  (5 mmol) in ether was added by cannula. The color of the solution changed from green to purple. The color of the solution changed from green to purple. A shiny grey solid precipitated as the temperature was raised to approximately  $20^\circ\text{C}$ . This was collected by filtration; yield 0.32 g (73%).

Anal. Calcd. for  $\text{Ta}_2\text{Cl}_4\text{C}_{25}\text{H}_{45}\text{P}$ : C, 34.11; H, 4.92. Found: C, 33.29; H, 4.99. Mol. Wt. Calcd.: 880. Found: 803.

#### Reaction of $\text{PMe}_3$ with $[\text{TaCp}''\text{Cl}_2\text{H}]_2$

The  $[\text{TaCp}''\text{Cl}_2\text{H}]_2$  (0.1 g, 0.13 mmol) was dissolved in toluene and cooled

to  $-78^{\circ}$ . A solution of  $\text{PMe}_3$  in toluene was added dropwise to the stirred solution until the color of the solution changed from green to purple. Pentane was added and the mixture was filtered to give a light purple powder; yield 0.085 g (77%).

#### Reaction of $[\text{TaCp}'\text{Cl}_2\text{H}]_2(\text{PMe}_3)$ with Carbon Monoxide

To a solution of  $[\text{TaCp}'\text{Cl}_2\text{H}]_2$  (1.0 g, 1.2 mmol) in 150 ml of ether, was added 0.4 ml  $\text{PMe}_3$ . A purple solution resulted and some grey solid precipitated. The reaction mixture was pressurized with CO (30 psi). The grey solid dissolved. After 3 hours, the color had changed from purple to yellow-brown. The solvent was removed in vacuo and the residue was crystallized from toluene/pentane (80:20). Cubic crystals were obtained in 2 crops; yield 0.45 g (41%).  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were identical to those of an authentic sample of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4(\text{H})(\text{CHPMe}_3)(\text{O})$ .

#### Reaction of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$ with $\text{AlCl}_3$

$\text{AlCl}_3$  (0.2 g, 1.5 mmol) was added to a toluene solution of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$  (0.83 g, 1 mmol) along with 20  $\mu\text{l}$  (0.11 mmol) of nonane as an internal standard. Some  $\text{AlCl}_3$  did not dissolve. The mixture was stored at  $0^{\circ}$  for 16 hours, then a sample was removed for GLC analysis. Methane (0.3 mmol) was found.

#### Reaction of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$ with $\text{AlCl}_3$ in the Presence of $\text{H}_2$

$\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$  (0.4 g, 0.48 mmol) and  $\text{AlCl}_3$  (0.08 g, 0.6 mmol) were added to a round bottom vacuum flask. The flask was evacuated and cooled to  $-78^{\circ}$ . Chlorobenzene (20 ml) saturated with  $\text{H}_2$  was added to the first flask

along with approximately 2 mmol of H<sub>2</sub> gas. The flask was warmed to 90° and magnetically stirred for 3 hours. The reaction mixture was freeze-thaw degassed four times and the gases along with 6 ml (0.27 mmol) of isobutylene were transferred to a second flask using a Toepler pump. By GLC the yield of methane was 70%. No C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> were found.

A slightly lower yield of methane was obtained (60% based on integration versus internal C<sub>2</sub>H<sub>4</sub>) when the amount of dihydrogen was reduced by half. The reaction was performed as above.

Reaction of Ta<sub>2</sub>Cp'<sub>2</sub>Cl<sub>4</sub>H(<sup>13</sup>CHO) with AlCl<sub>3</sub> in D<sub>2</sub>

An all glass reaction vessel was constructed which consisted of a 25 ml round bottom flask, a 5 ml solvent side-arm, a 100 ml gas bulb with stopcock, and a thick-walled NMR tube on a side-arm. Ta<sub>2</sub>Cp'<sub>2</sub>Cl<sub>4</sub>H(<sup>13</sup>CHO) (0.08 g, 0.1 mmol) and excess AlCl<sub>3</sub> were added to the reaction vessel. To the solvent container was added 0.5 ml d<sub>8</sub>-toluene. The gas bulb was filled with D<sub>2</sub> at 1 atmosphere pressure. The solvent in the side-arm was frozen and the reaction vessel was evacuated. The D<sub>2</sub> was admitted to the vessel and solvent was distilled over into the flask. The mixture was stirred and heated to 80°. The color of the solution changed from orange, to yellow, to green. The NMR tube was cooled in liquid nitrogen and the tube was flame sealed. A <sup>13</sup>C NMR spectrum at 62.8 MHz showed a singlet due to <sup>13</sup>CH<sub>4</sub> at 2.80 ppm and a 1:1:1 triplet ascribed to <sup>13</sup>CH<sub>3</sub>D at 2.60 ppm. If we assume that the peak areas are indicative of the relative amounts, then it is a 35:65 mixture of <sup>13</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>3</sub>D, respectively. No evidence for a quintet slightly further upfield assignable to <sup>13</sup>CH<sub>2</sub>D<sub>2</sub> could be found but poor signal to noise prevented our being certain none was produced.

### Reaction of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$ with Aqueous HCl

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$\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$  (0.09 g, 0.108 mmol) was added to a vial along with 0.2 ml of pentanediol. The solution was cooled to  $0^\circ$ . Aqueous HCl (12N, 60  $\mu\text{l}$ , 0.72 mmol) and ethanol (6.2  $\mu\text{l}$ , 0.106 mmol) were added. The solution was slowly warmed to  $25^\circ$ . Methanol was measured by GLC on Carbowax 20M using ethanol as the internal standard (0.088 mmol, 82%).

In a separate experiment  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$  (0.083 g, 0.1 mmol) in n-propanol was treated with 0.5 ml 12N HCl(aq) (6 mmol). After 0.5 hour a 1  $\mu\text{l}$  sample was withdrawn for GLC analysis. Methanol (4.1  $\mu\text{l}$ , 0.1 mmol) was added to the reaction mixture and another 1  $\mu\text{l}$  sample was withdrawn for GLC analysis. Comparison of peak areas indicated a 79% yield of methanol.

### Reaction of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$ with Anhydrous HCl

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A solution of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$  (0.42 g, 0.5 mmol) in 100 ml toluene was cooled to  $-78^\circ$ . HCl (25 ml, 1.1 mmol) was added to the flask by syringe. The reaction was slowly warmed to  $22^\circ$  with stirring. The color changed from orange-red to red and, after several hours at room temperature, to orange. The volume was reduced to approximately 80 ml under vacuum. The solution was transferred to another flask by cannula. Pentane (100 ml) was added. The solution was cooled to  $0^\circ$  for 12 hours. The reaction mixture was filtered and the solvent was removed from the filtrate in vacuo. An orange solid formed as the solution was concentrated; yield 0.3 g.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): ppm 4.381 (s,  $\text{OCH}_3$ ), 2.68 (m,  $\text{C}_5\text{CH}_2\text{CH}_3$ ), 2.338, 2.234, 2.213, 2.136, 2.098 (s,  $\text{C}_5\text{CH}_3$ ), 0.763 (t,  $\text{C}_5\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): ppm 133.7, 131.3, 130.1, 128.6, 128.3 (ring carbons), 21.2, 20.4 ( $\text{C}_5\text{CH}_2\text{CH}_3$  carbons), 15.2 ( $\text{C}_5\text{CH}_2\text{CH}_3$  carbons), 13.0, 12.7, 12.5, 12.0 ( $\text{C}_5\text{CH}_3$  carbons).

The  $^{13}\text{C}$  NMR spectrum of a sample of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(^{13}\text{CHO})$  in bromobenzene to which two equivalents of HCl had been added showed (besides a peak due to some unreacted starting material) a methoxide carbon peak at 66.84 ppm ( $J_{\text{CH}} = 146$  Hz, major product) and another at 62.85 ppm ( $J_{\text{CH}} = 146$  Hz, minor product).

If only one equivalent of HCl is used, half the starting material remains.

#### Reaction of $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$ with $\text{AlMe}_3$

$\text{AlMe}_3$  (0.14 g, 2 mmol) was added to a toluene solution of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(\text{CHO})$  (0.42 g, 0.5 mmol) at  $-30^\circ$ . The color changed from red to clear yellow. Solvent was removed in vacuo and the yellow oil was dissolved in  $\text{C}_6\text{D}_6$ . An  $^1\text{H}$  NMR spectrum showed a hydride resonance at 8.3 ppm and a formyl proton resonance at 6.6 ppm (d,  $J = 4$  Hz).

In a separate experiment excess  $\text{AlMe}_3$  was added to a solution of  $\text{Ta}_2\text{Cp}'_2\text{Cl}_4\text{H}(^{13}\text{CHO})$  in  $\text{C}_6\text{D}_6$ . The  $^{13}\text{C}$  NMR spectrum showed formyl carbon resonances at 227.47 ppm (d,  $J = 156$  Hz) and 214.36 ppm (dd,  $J = 152.6, 9.1$  Hz).

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TABLE I. NMR Data for  $\text{TaCp}'_2\text{Cl}_4(\text{H})(\text{CHNR}')$  Complexes

	$\text{Cp}'_2\text{Ta}_2\text{Cl}_4(\text{H})(\text{CHNCMe}_3)$	$\text{Cp}'_2\text{Ta}_2\text{Cl}_4(\text{H})(\text{CHNMe})$
$^1\text{H}$ NMR <sup>a</sup>		
MH <sup>b</sup>	8.91, d, J = 4.4 Hz	6.16, d, J = 2.2 Hz
CHN <sup>b</sup>	6.94, d, J = 4.4 Hz	3.35, d, J = 2.2 Hz
R'	1.38, s	3.97, s
$^{13}\text{C}$ NMR <sup>c</sup>		
CHN	211.1, d, J = 152 Hz	178.4, d, J = 185 Hz
R'	69.78, s	48.14, q, J = 139 Hz
	32.84, q, J = 127 Hz	

<sup>a</sup> 250 MHz,  $\text{C}_6\text{D}_6$ , 295K

<sup>b</sup> Assignments tentative (see text)

<sup>c</sup> 22.5 MHz,  $\text{CDCl}_3$ , 305K

## FIGURE CAPTIONS

Figure 1. The variable temperature  $^1\text{H}$  NMR spectrum of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{-Cl}_4(\text{H})(\text{CHO})$  in toluene- $d_8$  (\*) at 250 MHz (except  $T = 337\text{K}$ ).

Figure 2. A schematic drawing of the structure of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_4(\text{H})(\text{CHO})$ .

Figure 3. A schematic drawing of the structure of  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{-Cl}_4(\text{H})(\text{O})(\text{CHPMe}_3)$ .

Figure 4. The hydride and ylde proton signals in the 250 MHz NMR spectrum of

(a)  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_4(\text{H})(\text{O})(\text{CHPMe}_3)$ .

(b)  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{Cl}_4(\text{R})(\text{O})(\text{CR}'\text{PMe}_3)$  ( $\text{R}, \text{R}' = \text{H}$  or  $\text{D}$ ).

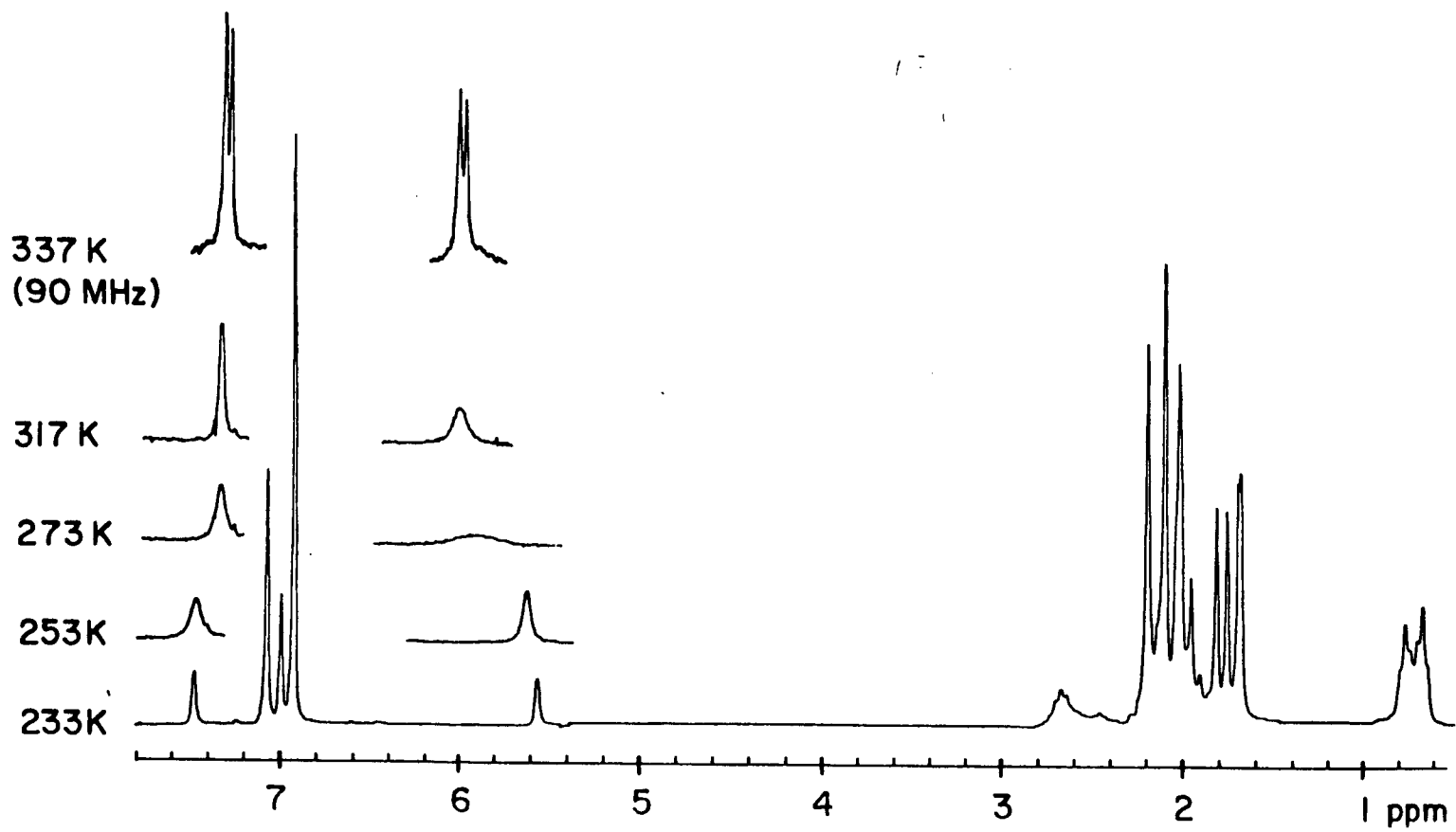
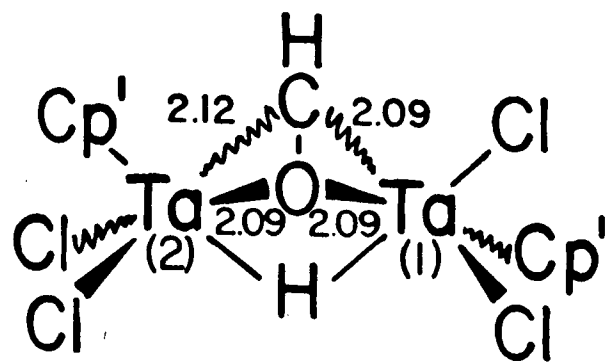


Figure 1



C-O = 1.496(14) Å  
 Ta····Ta = 3.186(1) Å

Figure 2

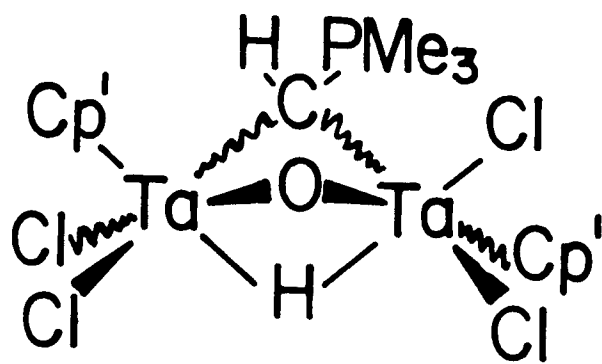


Figure 3

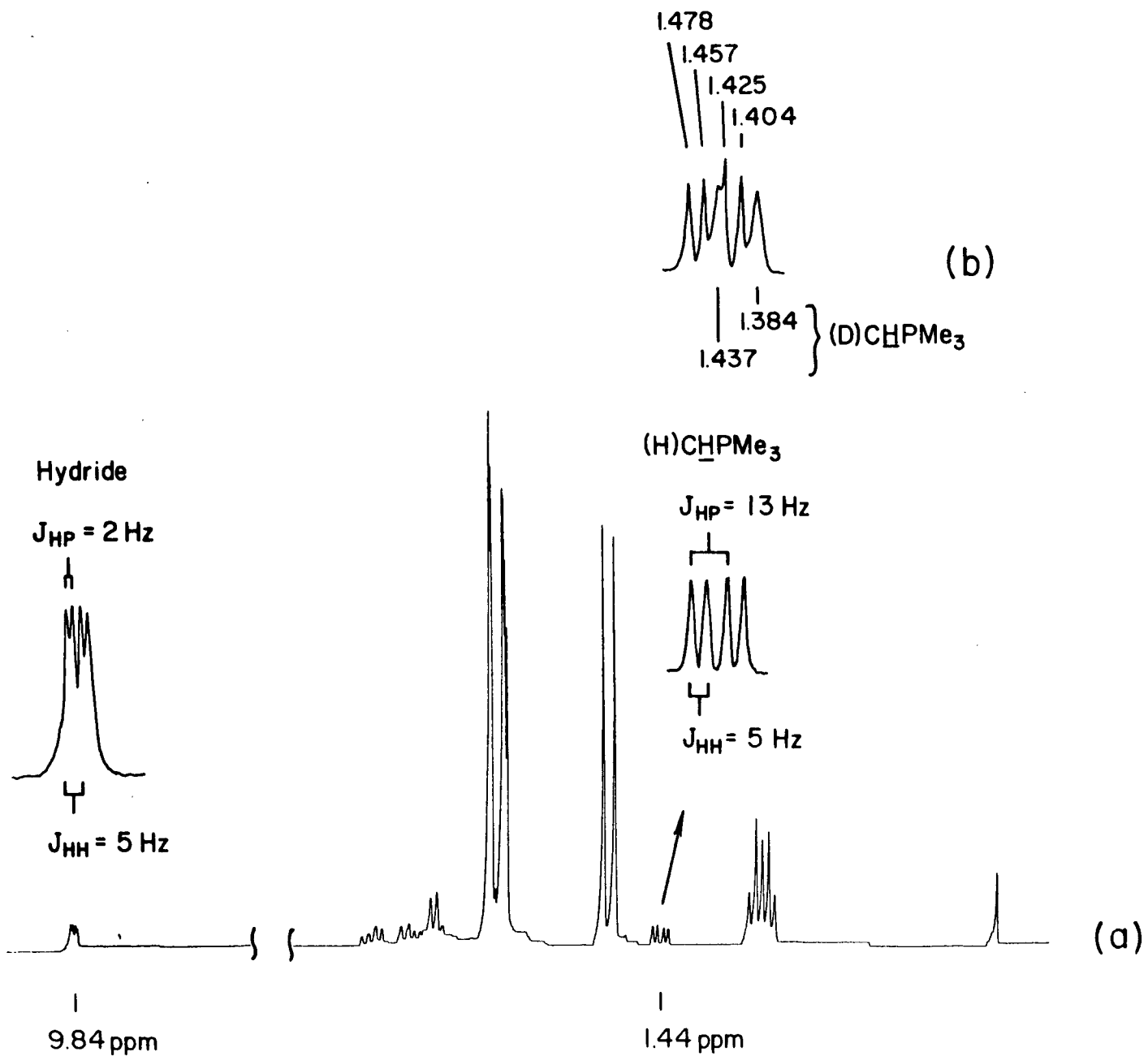


Figure 4