# Binuclear Tantalum Hydride Complexes

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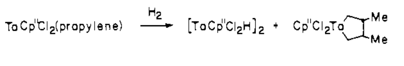
**Abstract:** Cyclopentadienyltantalum olefin or dineopentyl complexes react with molecular hydrogen to give binuclear hydride complexes, $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ (R = Me or Et). The dimeric hydride complexes react with alkylating agents to give monoalkyl derivatives (alkyl = Me, Et, $CH_2CMe_3$, or $CH_2SiMe_3$). $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 20.084$ (6) Å, $b = 16.972$ (4) Å, $c = 15.869$ (4) Å, and $\beta = 96.86$ (2)°. 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 $2\theta_{MoK\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$. There are two independent molecules per asymmetric unit. Each consists of two approximately tetrahedrally coordinated $Ta(\eta^5\text{-}C_5Me_4Et)Cl(Cl/C)$ fragments joined by a Ta–Ta bond (2.854 (1) Å 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 $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(R)$ which exchanges the two inequivalent hydrides, (ii) a bimolecular halide exchange process in $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$ which is slow on the NMR time scale but fast on the chemical time scale, and (iii) a bimolecular hydride-exchange process in $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$ which is slow on the chemical time scale. The formation of $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$ is believed to involve a complex bimolecular decomposition of intermediate $Ta(\eta^5\text{-}C_5Me_4Et)Cl_2(H)(R)$ complexes, one of which ($R = CH_2CMe_3$) has been isolated and characterized by IR and NMR methods.

There are now several homogeneous transition-metal systems which will catalyze the reduction of carbon monoxide by molecular hydrogen.[2] In all cases the catalyst contains a group 8 metal, the reduction products are oxygenates,[3] and with one possible exception,[4] the reductions are not selective for any oxygenate containing one or more C–C bonds.[2,3] Therefore, there is considerable room for improving the known catalyst systems. Studies of stoichiometric "model" reactions between hydride complexes of earlier transition metals and carbon monoxide might help determine how this can be done.[5] What model studies also do, however, is increase the probability of discovering a catalyst which does not contain a group 8 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, $MCp_2H_3$[6] ($Cp = \eta^5\text{-}C_5H_5$) and $MH_5(dmpe)_2$,[7] lose 1 and 2 equiv of $H_2$ in the presence of CO to give $MCp_2(H)(CO)$ and $M(H)(dmpe)_2(CO)_2$, respectively. The monohydride complexes do not reduce CO. Therefore our first task was to prepare new types of hydride complexes. Recently we discovered that $Ta(\eta^5\text{-}C_5H_5)Me_4$ 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.[8] Therefore we felt that $Ta(\eta^5\text{-}C_5H_5)H_4$ or $Ta(\eta^5\text{-}C_5H_5)Cl_2H_2$ might reduce CO. We opted to attempt to make the latter types of molecules since they should be obtained by reacting known monocyclopentadienyltantalum dialkyl,[9a] alkylidene,[9a] or olefin[9b] 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 $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ ($Cp'' = \eta^5\text{-}C_5Me_5$; $Cp' = \eta^5\text{-}C_5Me_4Et$).** $TaCp''Cl_2$(propylene) and $TaCp''Cl_2$(styrene) react cleanly in pentane with molecular hydrogen at 20–40 psi to give insoluble green $[TaCp''Cl_2H]_2$ in high yield and a mixture of the olefin and the alkane in a ratio of approximately 2:1. In the case of $TaCp''Cl_2$(propylene), the yield of $[TaCp''Cl_2H]_2$ is ~70% after 1 h. The orange filtrate contains the remaining tantalum as the propylene metallacycle[9b] formed by addition of propylene to $TaCp''Cl_2$(propylene) (eq 1). This metallacycle slowly decomposes to 2,3-dimethyl-1-butene and $TaCp''Cl_2$(propylene)[9b] so that after ~24 h the yield of $[TaCp''Cl_2H]_2$ is essentially quantitative. In the case of $TaCp''Cl_2$(styrene), the yield of $[TaCp''Cl_2H]_2$ is ~70% after 20 h; the remainder is starting material. (Note that "styrene tantalacycles" do not form.[9b]) $[TaCp''Cl_2H]_2$ 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 $TaCp''Cl_4$.



(1)

$[TaCp''Cl_2H]_2$ can also be prepared by reacting $TaCp''Cl_2Np_2$ ($Np = CH_2CMe_3$) in pentane with hydrogen (eq 2). The product is inferior to that obtained by reacting $TaCp''Cl_2$(propylene) with $H_2$, since an impurity with solubility characteristics similar to those of $[TaCp''Cl_2H]_2$ cannot be removed by recrystallization.

$$TaCp''Cl_2Np_2 + H_2 \xrightarrow[25°C]{12\ h} [TaCp''Cl_2H]_2 \qquad (2)$$

$[TaCp'Cl_2H]_2$ can be prepared by methods analogous to those shown in eq 1 and 2. One redeeming feature of this more complicated molecule is that it is more soluble than $[TaCp''Cl_2H]_2$.

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(1) Crystalytics Co., Lincoln, NE.

(2) (a) "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, DC, 1981; *ACS Symp. Ser. No. 152*. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. (d) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136–141. (e) Ponec, V. *Catal. Rev.—Sci. Eng.* **1978**, *18*, 151–171.

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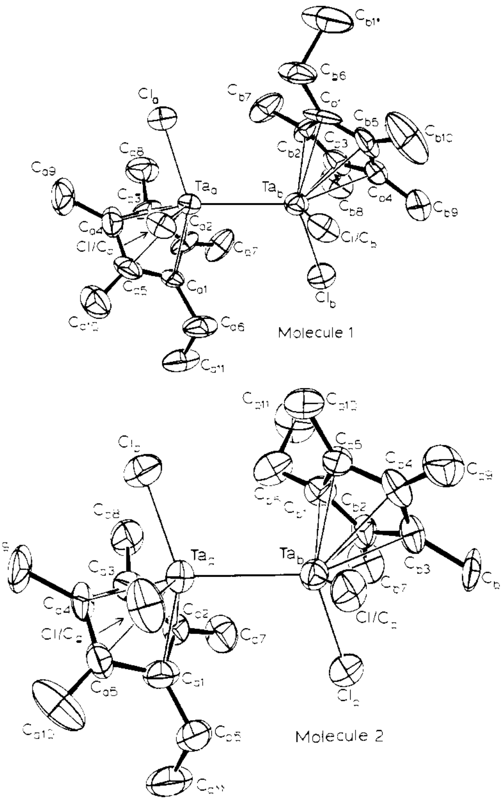

Figure 1. ORTEP drawings of the two independent molecules of $Ta_2$-($\eta^5$-$C_5Me_4Et)_2Cl_3H_2(Me)$.

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 $\eta^5$-$C_5Me_4Et$ rings.

All reactions of the type shown in eq 1 and 2 work best in a relatively large volume of pentane. In tetrahydrofuran the yield of $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$ is only approximately 10%. In ether or toluene the yields are on the order of 30–50%.

The hydride ligands can be observed by NMR or IR. In the $^1H$ NMR spectrum a hydride resonance of area 1 relative to each $C_5Me_4R$ 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 $cm^{-1}$ 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 Cp″ or 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 $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$.** $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ reacts with 0.5 equiv of $Mg(CH_2CMe_3)_2$, $Mg(CH_2SiMe_3)_2$, or $ZnMe_2$ to give blue to violet dimeric alkyl hydride complexes, $Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_3H_2(R')$ (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 °C. 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 °C by using $ZnEt_2$, but it could be characterized only in solution. After ~0.5 h at 0 °C, it had largely decomposed to give approximately 0.5 equiv of $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ as the only characterizable complex.

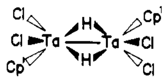

Figure 2. A schematic drawing of the proposed structure of $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$.

In all alkyl hydride complexes a peak for a metal–hydride stretching mode is still observable in the IR spectrum at 1580–1600 $cm^{-1}$.

A crystal of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$ 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 $\eta^5$-$C_5Me_4Et$ ring is oriented on $Ta_b$; turning the $\eta^5$-$C_5Me_4Et$ ring on $Ta_b$ in molecule 1 clockwise by 72° gives molecule 2. Final atomic coordinates for all atoms in both molecules can be found in Table I and anisotropic thermal parameters for the nonhydrogen atoms in Table II.[10] 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 $\eta^5$-$C_5Me_4Et$ 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° to 126.3°, with those larger than the idealized tetrahedral value of 109.5° 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) Å in molecule 1 and 2.815 (1) Å in molecule 2. The $\eta^5$-$C_6Me_4Et$ groups are the normal, slightly "dish-shaped" variety with normal Ta–C bond lengths (average 2.44 (2, 2, 6, 20) Å[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) Å vs. 2.375 (7, 5, 10, 4) Å, respectively). If we replace the ethyl group in each Cp′ ring by a methyl group, then each independent $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$ 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

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(10) See paragraph at end of paper regarding supplementary material.

(11) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged values, respectively. The fourth number represents the number of individual measurements which are included in the average value.

(12) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 226.

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Table I. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$[a]

| atom type[b] | fractional coordinates |  |  |
|---|---|---|---|
|  | *x* | *y* | *z* |
|  | Molecule 1 |  |  |
| $Ta_a$ | −0.04374 (4) | 0.28325 (4) | 0.49345 (4) |
| $Ta_b$ | 0.09893 (4) | 0.27279 (4) | 0.52400 (4) |
| $Cl_a$ | −0.0839 (3) | 0.1621 (3) | 0.4328 (4) |
| $Cl/C_a$ | −0.0637 (4) | 0.3622 (4) | 0.3693 (3) |
| $Cl_b$ | 0.1357 (3) | 0.3584 (3) | 0.6359 (4) |
| $Cl/C_b$ | 0.1342 (4) | 0.3510 (4) | 0.4143 (5) |
| $C_{a1}$ | −0.0700 (9) | 0.3751 (9) | 0.5994 (11) |
| $C_{a2}$ | −0.0624 (10) | 0.3011 (11) | 0.6398 (10) |
| $C_{a3}$ | −0.1157 (10) | 0.2538 (10) | 0.6005 (12) |
| $C_{a4}$ | −0.1547 (9) | 0.2989 (14) | 0.5370 (13) |
| $C_{a5}$ | −0.1257 (11) | 0.3757 (11) | 0.5386 (12) |
| $C_{b1}$ | 0.1291 (13) | 0.1472 (10) | 0.4684 (12) |
| $C_{b2}$ | 0.1066 (9) | 0.1331 (11) | 0.5491 (12) |
| $C_{b3}$ | 0.1526 (11) | 0.1676 (11) | 0.6102 (13) |
| $C_{b4}$ | 0.2049 (9) | 0.2035 (11) | 0.5660 (14) |
| $C_{b5}$ | 0.1881 (10) | 0.1882 (12) | 0.4790 (14) |
| $C_{a6}$ | −0.0289 (12) | 0.4484 (12) | 0.6258 (14) |
| $C_{a7}$ | −0.0171 (11) | 0.2802 (15) | 0.7182 (12) |
| $C_{a8}$ | −0.1329 (13) | 0.1701 (14) | 0.6281 (17) |
| $C_{a9}$ | −0.2177 (11) | 0.2720 (18) | 0.4862 (18) |
| $C_{a10}$ | −0.1573 (13) | 0.4445 (14) | 0.4894 (15) |
| $C_{a11}$ | −0.0590 (13) | 0.4861 (13) | 0.7073 (16) |
| $C_{b6}$ | 0.0940 (14) | 0.1135 (13) | 0.3828 (14) |
| $C_{b7}$ | 0.0497 (13) | 0.0792 (13) | 0.5737 (16) |
| $C_{b8}$ | 0.1554 (13) | 0.1652 (15) | 0.7071 (13) |
| $C_{b9}$ | 0.2663 (13) | 0.2442 (16) | 0.6071 (21) |
| $C_{b10}$ | 0.2345 (17) | 0.2115 (20) | 0.4126 (20) |
| $C_{b11}$ | 0.1304 (20) | 0.0341 (17) | 0.3649 (20) |
|  | Molecule 2 |  |  |
| $Ta_a$ | 0.62362 (4) | 0.08862 (4) | 0.23668 (5) |
| $Ta_b$ | 0.48432 (4) | 0.06757 (4) | 0.23354 (5) |
| $Cl_a$ | 0.6439 (3) | 0.1457 (4) | 0.1066 (3) |
| $Cl/C_a$ | 0.6615 (4) | −0.0415 (5) | 0.2126 (6) |
| $Cl_b$ | 0.4607 (3) | 0.0604 (4) | 0.3751 (3) |
| $Cl/C_b$ | 0.4703 (4) | −0.0671 (4) | 0.1941 (5) |
| $C_{a1}$ | 0.6587 (11) | 0.1011 (12) | 0.3873 (11) |
| $C_{a2}$ | 0.6350 (8) | 0.1748 (10) | 0.3580 (11) |
| $C_{a3}$ | 0.6801 (10) | 0.2049 (11) | 0.3019 (12) |
| $C_{a4}$ | 0.7317 (8) | 0.1468 (12) | 0.2944 (12) |
| $C_{a5}$ | 0.7211 (9) | 0.0825 (13) | 0.3503 (12) |
| $C_{b1}$ | 0.4533 (10) | 0.1889 (10) | 0.1607 (12) |
| $C_{b2}$ | 0.4082 (9) | 0.1788 (12) | 0.2216 (11) |
| $C_{b3}$ | 0.3673 (8) | 0.1102 (13) | 0.2008 (13) |
| $C_{b4}$ | 0.3868 (9) | 0.0818 (13) | 0.1219 (13) |
| $C_{b5}$ | 0.4405 (8) | 0.1271 (11) | 0.0965 (10) |
| $C_{b6}$ | 0.6338 (12) | 0.0536 (16) | 0.4585 (13) |
| $C_{a7}$ | 0.5827 (11) | 0.2249 (16) | 0.3966 (14) |
| $C_{a8}$ | 0.6751 (12) | 0.2848 (14) | 0.2583 (17) |
| $C_{a9}$ | 0.7897 (10) | 0.1517 (18) | 0.2419 (16) |
| $C_{a10}$ | 0.7668 (15) | 0.0167 (16) | 0.3724 (19) |
| $C_{a11}$ | 0.6700 (15) | 0.0791 (19) | 0.5452 (16) |
| $C_{b6}$ | 0.4951 (12) | 0.2602 (12) | 0.1498 (14) |
| $C_{b7}$ | 0.3989 (12) | 0.2326 (13) | 0.2937 (15) |
| $C_{b8}$ | 0.3120 (10) | 0.0789 (15) | 0.2428 (17) |
| $C_{b9}$ | 0.3528 (12) | 0.0147 (13) | 0.0702 (14) |
| $C_{b10}$ | 0.4709 (11) | 0.1205 (14) | 0.0148 (11) |
| $C_{b11}$ | 0.4569 (15) | 0.3262 (15) | 0.0989 (20) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labelled in agreement with figure.

state structure; *four*, not *two*, different $\eta^5$-$C_5Me_4Et$ 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. However, examination of a model of $[TaCp'Cl_2H]_2$ which was assembled by using the structural data for $Ta_2Cp'_2Cl_3H_2(Me)$ shows that the two ends of the molecule cannot rotate a full 360° with respect to one another unless engagement of the two Cp′ rings as they attempt to pass one another can be avoided by increasing the $TaTaC_g$ angles (already the largest "tetrahedral" angles; see Table IV) significantly.

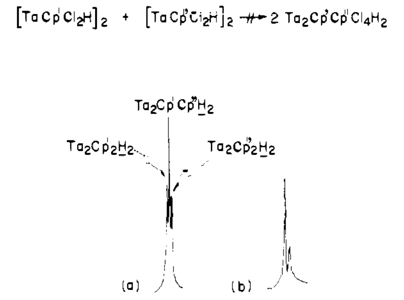


Figure 3. The 250-MHz NMR spectrum of (a) 1:2:1 mixture of $[TaCp''Cl_2H]_2$, $Ta_2Cp'Cp''Cl_4H_2$, and $[TaCp'Cl_2H]_2$ and (b) an approximately 3.5:1 mixture of $[TaCp'Cl_2H]_2$ and $[TaCp''Cl_2H]_2$ (solvent = $C_6D_6$, $T$ = 22 °C).

**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 $\eta^5$-$C_5Me_4Et$ groups are now inequivalent, the methyl groups in each ring are unique, and $\alpha$ protons in the Et, Np, or Np′ group (Np′ = $CH_2SiMe_3$) are diasterotopic. However, the hydride ligands are *equivalent*. In the Et, Np, and Np′ derivatives a low temperature can be reached where the hydride ligands become *inequivalent* (see Experimental Section). One explanation is that the molecular framework and the geometry about the metal at each end of the molecule remain unchanged while the hydride ligands themselves physically exchange, possibly concomitant with a twisting of the two ends of the molecule relative to one another. Some evidence which supports this proposal 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 $mol^{-1}$). A smaller R group would allow the molecule to twist more easily. Alternatively, the hydride ligands exchange by a more complicated process involving nonbridged or chloro-bridged intermediates. In this case, however, the overall asymmetry of the rest of the molecule requires that no symmetry plane be generated during the process which exchanges the hydride ligands.

**Exchange Reactions in Tetrachloro Dihydride Dimers.** A mixture of $TaCp'Cl_2$(propylene) and $TaCp''Cl_2$(propylene) reacts with hydrogen to give a 1:2:1 mixture of $[TaCp''Cl_2H]_2$, $Ta_2Cp'Cp''Cl_4H_2$, and $[TaCp'Cl_2H]_2$. The hydride signals for each can be distinguished at 250 MHz (Figure 3a). Note that the hydrides should no longer be equivalent in $Ta_2Cp'Cp''Cl_4H_2$. 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 $Ta_2Cp'_2Cl_3H_2(R)$ (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 $[TaCp'Cl_2H]_2$ (~3.5 parts) and $[TaCp''Cl_2H]_2$ (~1 part) in $C_6D_6$ showed two hydride signals at 10.42 and 10.38 ppm (the positions of the hydride signals in each alone in $C_6D_6$) in a ratio of ~3.5:1 (Figure 3b). No $Ta_2Cp'Cp''Cl_4H_2$ was present. The spectrum did not change upon warming the sample to 75 °C for 10 min. The results of a similar experiment demonstrated that <5% $Ta_2Cp'Cp''Cl_4H_2$ is present after 5 h at 70 °C. Therefore, the dimer does not break up into monomeric units at any significant rate at 70–75 °C.

Deuteride complexes can be prepared by reacting either propylene or dineopentyl complexes with $D_2$. The deuterides show a peak in their IR spectra at 1140–1145 $cm^{-1}$ instead of ~1580 $cm^{-1}$. In each case, however, some intensity is present at ~1580 $cm^{-1}$. The presence of $Ta_2Cp'_2Cl_4H_2$ and $Ta_2Cp'_2Cl_4(H)(D)$ can be confirmed and the absolute and relative amounts quantitated by $^1H$ NMR since the signal for the hydride in $Ta_2Cp'_2Cl_4(H)(D)$ is found 0.06-ppm upfield from that in $Ta_2Cp'_2Cl_4H_2$. The amount of $Ta_2Cp'_2Cl_4H_2$ and $Ta_2Cp'_2Cl_4(H)(D)$ is well above the amount

Table III. Bond Lengths Involving Nonhydrogen Atoms in Crystalline $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$[a]

| | length, Å | | | length, Å | |
|---|---|---|---|---|---|
| type[b] | molecule 1 | molecule 2 | type[b] | molecule 1 | molecule 2 |
| $Ta_a-Cl_a$ | 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) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled 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 $\eta^5\text{-}C_5Me_4Et$ ligands.

Table IV. Bond Angles Involving Nonhydrogen Atoms in Crystalline $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$[a]

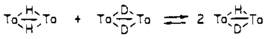
| | angle, deg | | | angle, deg | |
|---|---|---|---|---|---|
| type[b] | molecule 1 | molecule 2 | type[b] | molecule 1 | molecule 2 |
| $Ta_bTa_aCl_a$ | 107.5 (1) | 108.2 (2) | $Ta_aTa_bCl_b$ | 108.0 (2) | 107.6 (1) |
| $Ta_bTa_aCl/C_a$ | 104.0 (2) | 102.5 (2) | $Ta_aTa_bCl/C_b$ | 102.9 (2) | 102.3 (2) |
| $Ta_bTa_aC_{ga}$[c] | 124.7 (...) | 123.9 (...) | $Ta_aTa_bC_{gb}$[c] | 126.3 (...) | 124.0 (...) |
| $Cl_aTa_aCl/C_a$ | 97.9 (2) | 98.5 (3) | $Cl_bTa_bCl/C_b$ | 96.6 (2) | 99.8 (2) |
| $Cl_aTa_aC_{ga}$[c] | 109.8 (...) | 110.2 (...) | $Cl_bTa_bC_{gb}$[c] | 111.0 (...) | 109.9 (...) |
| $Cl/C_aTa_aC_{ga}$[c] | 109.6 (...) | 110.5 (...) | $Cl/C_bTa_bC_{gb}$[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 labeled 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 $\eta^5\text{-}C_5Me_4Et$ ligands.

of $H_2$ and HD impurities in $D_2$ and also increases markedly if only 1–2 equiv of $D_2$ are used to form the deuteride. For example, when 1 equiv of $D_2$ was added to $TaCp'Cl_2$(propylene), the product contained ~0.6 protons per dimer due to the presence of $Ta_2Cp'_2Cl_4(H)(D)$ (4–5 parts) and $Ta_2Cp'_2Cl_4H_2$ (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.

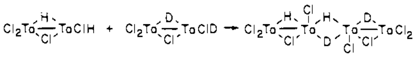
The situation with regard to deuterium labeling is actually more complicated and more informative. If one mixes a sample of the purest $Ta_2Cp'_2Cl_4D_2$ and pure $Ta_2Cp'_2Cl_4H_2$, one observes a hydride signal due to $Ta_2Cp'_2Cl_4H_2$ and a signal due to $Ta_2Cp'_2Cl_4(H)(D)$ in a ratio of ~8:1 (~20% $Ta_2Cp'_2Cl_4(H)(D)$). After 1 h at 25 °C the amount of $Ta_2Cp'_2Cl_4(H)(D)$ is ~30%, and after 30 min at 45 °C the amount of $Ta_2Cp'_2Cl_4(H)(D)$ is ~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 (eq 3). One reasonable way for this to happen is for the dimers to form which contain one or more terminal hydride (deuteride) ligands (eq 4) which can be used to form a tetramer containing a central TaHDTa unit (eq 5).

The above findings raise the possibility that halides exchange between dimers. $[TaCp'Br_2H]_2$ can be prepared straightforwardly from $TaCp'Br_2$(propylene). Its hydride resonance is found at 11.27 ppm. After addition of 1 equiv of $[TaCp'Cl_2H]_2$ to $[TaCp'Br_2H]_2$



$$\mathrm{Ta}\overset{\mathrm{H}}{\underset{\mathrm{H}}{-}}\mathrm{Ta} + \mathrm{Ta}\overset{\mathrm{D}}{\underset{\mathrm{D}}{-}}\mathrm{Ta} \rightleftharpoons 2\ \mathrm{Ta}\overset{\mathrm{H}}{\underset{\mathrm{D}}{-}}\mathrm{Ta} \quad (3)$$

$$\mathrm{Cl_2Ta}\overset{\mathrm{H}}{\underset{\mathrm{H}}{-}}\mathrm{TaCl_2} \longrightarrow \mathrm{HClTa}\overset{\mathrm{Cl}}{\underset{\mathrm{H}}{-}}\mathrm{TaCl_2} \quad (4)$$



$$\mathrm{Cl_2Ta}\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{-}}\mathrm{TaClH} + \mathrm{Cl_2Ta}\overset{\mathrm{D}}{\underset{\mathrm{Cl}}{-}}\mathrm{TaClD} \rightarrow \mathrm{Cl_2Ta}\overset{\mathrm{H}}{\underset{\mathrm{Cl}}{-}}\overset{\mathrm{Cl}}{\mathrm{Ta}}\overset{\mathrm{H}}{\underset{\mathrm{D}}{-}}\underset{\mathrm{Cl}}{\mathrm{Ta}}\overset{\mathrm{D}}{\underset{\mathrm{Cl}}{-}}\mathrm{TaCl_2} \quad (5)$$

five hydride resonances are found at 11.27 (due to $[\mathrm{TaCp'Br_2H}]_2$), 11.08, 10.93, 10.68, and 10.42 ppm (due to $[\mathrm{TaCp'Cl_2H}]_2$) in a ratio of a trace:5:18:16:3. We assign the three additional resonances to $\mathrm{Ta_2Cp'_2Br_3ClH_2}$ (H at 11.08 ppm), $\mathrm{Ta_2Cp'_2Br_2Cl_2H_2}$ (H at 10.93 ppm), and $\mathrm{Ta_2Cp'_2BrCl_3H_2}$ (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 $\mathrm{Ta_2Cp'_2BrCl_3H_2}$ was present after a sample of $\mathrm{Ta_2Cp'_2Cl_4H_2}$ was stirred with excess LiBr in ether for 2 h at 25 °C.) This apparently intermolecular, nonionic halide exchange between $[\mathrm{TaCp'Cl_2H}]_2$ 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 $\mathrm{TaCp'Cl_2Np_2}$ and $H_2$ is done on a large scale, a small yield of an orange-red crystalline product is obtained which is less soluble than $[\mathrm{TaCp'Cl_2H}]_2$. We propose that it is $\mathrm{Ta_2Cp'_2Cl_5H}$ 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 $\mathrm{TaCp'Cl_3Np}$ and $\mathrm{TaCp'Cl_2Np_2}$ with $H_2$ in pentane. An attempt to prepare it by reacting $[\mathrm{TaCp'Cl_2H}]_2$ with HCl (1 equiv) gave only 0.5 equiv of $\mathrm{TaCp'Cl_4}$ and starting material. The metal–hydride mode must be shifted to lower energy in $\mathrm{Ta_2Cp'_2Cl_5H}$ than it is in $[\mathrm{TaCp'Cl_2H}]_2$ since we could not find it in a Nujol mull IR spectrum. In the $^1$H NMR spectrum the hydride resonance is found at 6.08 ppm. We propose that $\mathrm{Ta_2Cp'_2Cl_5H}$ contains a bridging chloride in place of one of the bridging hydrides in $[\mathrm{TaCp'Cl_2H}]_2$, although there is at least some possibility that $\mathrm{Ta_2Cp'_2Cl_5H}$ has a different basic structure than $\mathrm{Ta_2Cp'_2Cl_4H_2}$.

$\mathrm{Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2}$ reacts readily with $H_2$ (20 psi) in 1 h in ether to give a green solid which is insoluble in common solvents. Its IR spectrum shows an absorption at 1620 cm$^{-1}$. We propose that the green solid is $[\mathrm{TaCpCl_2H}]_x$. Since it is so insoluble *x may* be >2.[14a] If so, then the coordination sphere must be too crowded when Cp′ or Cp″ ligands are present to form any units larger than dimers.

**Mechanism of Formation of $[\mathrm{Ta(\eta^5\text{-}C_5Me_4R)Cl_2H}]_2$.** $\mathrm{TaCp''Cl_2Np_2}$ reacts readily with hydrogen at −30 °C in butane to give an orange solution. There is no further change at −30 °C. A yellow solid remains after removing all the volatiles in vacuo. Three pieces of evidence suggest that this compound is $\mathrm{TaCp''Cl_2(Np)(H)}$ (eq 6). First, its $^1$H NMR spectrum shows

$$\mathrm{Ta(\eta^5\text{-}C_5Me_5)Cl_2(CH_2CMe_3)_2} + \mathrm{H_2} \rightarrow \mathrm{Ta(\eta^5\text{-}C_5Me_5)Cl_2(CH_2CMe_3)(H)} \quad (6)$$

a peak of area one at 22.87 ppm, the lowest field chemical shift (we believe) of any known, monomeric hydride complex.[14b] Second, its IR spectrum shows a peak at 1750 cm$^{-1}$. Third, it reacts with chloroform to give $\mathrm{TaCp''Cl_3Np}$ in high yield. On warming the yellow solution of $\mathrm{TaCp''Cl_2(Np)(H)}$ to 25 °C under $H_2$ it turns green and $[\mathrm{TaCp''Cl_2H}]_2$ can be isolated in a yield comparable to that obtained if the entire reaction is done at 25 °C. If a solution containing $\mathrm{TaCp'Cl_2(Np)(H)}$ (prepared analogously) is warmed to 25 °C in the absence of $H_2$, it turns brown and the dark brown oil which remains after the volatiles are removed contains no $[\mathrm{TaCp'Cl_2H}]_2$ by $^1$H NMR. However, this brown oil reacts with $H_2$ to give a moderate yield (~50%) of $[\mathrm{TaCp'Cl_2H}]_2$.

We have no direct evidence for formation of an analogous propyl hydride complex when $\mathrm{Ta(\eta^5\text{-}C_5Me_4R)Cl_2(propylene)}$ reacts with hydrogen. Indirect evidence that it is formed consists of the fact that the reaction of $\mathrm{TaCp''Cl_2(propylene)}$ with hydrogen at <0 °C in chloroform gives $\mathrm{TaCp''Cl_3(propyl)}$ in good yield. We believe $\mathrm{TaCp''Cl_2(propyl)(H)}$ is formed and trapped by reaction with chloroform. In the absence of chloroform $\mathrm{TaCp''Cl_2(propyl)(H)}$ probably loses $H_2$ to reform $\mathrm{TaCp''Cl_2(propylene)}$ (eq 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 $D_2$ to $\mathrm{TaCp'Cl_2(propylene)}$.

$$\mathrm{TaCp''Cl_2(propylene)} + \mathrm{H_2} \rightleftharpoons \mathrm{TaCp''Cl_2(propyl)(H)} \quad (7)$$

An intriguing result, and one which might be important in elucidating the details of how hydrogen reacts with d$^0$ alkyl complexes, is that $\mathrm{TaCp''Cl_2Me_2}$ reacts very slowly and reluctantly with molecular hydrogen. After 12 h at 20 °C and 1000 psi in toluene the yield of $[\mathrm{TaCp''Cl_2H}]_2$ was ~50%; ~30% of the $\mathrm{TaCp''Cl_2Me_2}$ 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 $\mathrm{TaCp''Cl_2R_2}$ series the rate of reaction with $H_2$ is R = $\mathrm{CH_2CMe_3} > \mathrm{CH_2SiMe_3} \gg$ 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.[15] 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 $\mathrm{TaCp'Cl_2Np_2}$. One could postulate that Ta is first reduced to Ta(IV) or Ta(III) or that neopentane is first lost in a $\alpha$ abstraction step to give $\mathrm{TaCp'Cl_2(CHCMe_3)}$. Neither postulate is necessary, however. Since $\mathrm{LiC_6H_5}$ reacts with $H_2$ at 25 °C to give LiH and benzene,[16] 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 $\mathrm{TaC_2}$ 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 $[\mathrm{TaCp'Cl_2H}]_2$ forms from $\mathrm{TaCp'Cl_2(R)(H)}$. We do not believe that intermediate $\mathrm{Ta(\eta^5\text{-}C_5Me_4R)Cl_2(R)(H)}$ complexes lose RH to give a $\mathrm{Ta(\eta^5\text{-}C_5Me_4R)Cl_2}$ fragment which then reacts with $H_2$ to give the complex we originally sought, $\mathrm{Ta(\eta^5\text{-}C_5Me_4R)Cl_2H_2}$. Unimolecular reductive elimination reactions appear to be unlikely when the fragment which results is incapable of independent existence.[17] 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 $\mathrm{Ta(\eta^5\text{-}C_5Me_4R)Cl_2(R)(H)}$ reacts directly with $H_2$ to give RH and $\mathrm{Ta(\eta^5\text{-}C_5Me_4R)Cl_2H_2}$, or that $\mathrm{Ta(\eta^5\text{-}C_5Me_4R)Cl_2(R)(H)}$ decomposes bimolecularly in a complex

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(14) (a) In this context it is interesting to note that while $[\mathrm{Rh(\eta^5\text{-}C_5Me_5)Cl_2}]_2$ is soluble, "$[\mathrm{Rh(\eta^5\text{-}C_5H_5)Cl_2}]_2$" is insoluble in common solvents. It is presumed to be polymeric (see ref 19b). (b) The chemical shift of the hydride in $[\mathrm{Co_6(CO)_{15}(H)}]^-$ is 23.2 ppm.[14c] (c) Bau, R., et al. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 80–81.

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(17) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139–145.

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 $Ta(\eta^5\text{-}C_5Me_4R)Cl_2Np_2$ reacts with $H_2$ at −78 °C, $Ta(\eta^5\text{-}C_5Me_4R)Cl_2(R)(H)$ is stable at 0 °C under $H_2$. The second is that $Ta(\eta^5\text{-}C_5Me_4R)Cl_2(Np)(H)$ 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.[17]

The closest analogy in the literature to the chemistry we describe here is the reaction of $Ti(\eta^5\text{-}C_5H_5)_2Me_2$ with $H_2$ (eq 8).[18]

$$2TiCp_2Me_2 + 3H_2 \xrightarrow[\text{state}]{\text{solid}} [TiCp_2H]_2 + 4CH_4 \qquad (8)$$

$[TiCp_2H]_2$ is a violet, diamagnetic molecule with a metal–hydride peak in the IR spectrum at 1450 $cm^{-1}$ (1050 $cm^{-1}$ in $[TiCp_2D]_2$). Although no X-ray structural data are available, a Ti–Ti bond must be present since the compound is diamagnetic and since it reacts with triphenylphosphine to give $TiCp_2(H)(PPh_3)$. The IR data are most compatible with a double $\mu$-hydride bridge. It was proposed that if the molecule were centrosymmetric, then the metal–hydride mode at 1450 $cm^{-1}$ would be analogous to the antisymmetric metal–hydride stretching mode found at 1500–1600 $cm^{-1}$ in centrosymmetric diboranes. Alternatively, it could be analogous to the antisymmetric mode found at 1350 $cm^{-1}$ in noncentrosymmetric $TiCp_2(BH_4)$. It is not likely to be a symmetric metal–hydride stretching mode analogous to that at 1942 $cm^{-1}$ in noncentrosymmetric $TiCp_2(BH_4)$.

Another compound related to $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ is $Ir_2(\eta^5\text{-}C_5Me_5)_2Cl_2H_2$.[19] The metal–hydride peak is found at 1162 $cm^{-1}$ (830 $cm^{-1}$ in $Ir_2Cp''_2Cl_2D_2$) in the IR spectrum and a peak for the bridging hydrides at high field in the $^1H$ NMR spectrum. Its crystal structure has not been determined but structures of closely related $Ir_2Cp''_2Cl_3H$[20] and $Rh_2Cp''_2Cl_3H$,[21] as well as the perhalides, $M_2Cp''_2X_4$ (X = a halide),[20,22] have been determined. The $M_2Cp''_2Cl_3H$ species have planar central M(Cl)(H)M cores with a Cp″ group and a chloride ligand on each metal extending above and below this plane. The two Cp″ groups are trans to one another about this $Ir_2ClH$ core. The bridging hydride ligand pulls the metals together to form a three-center, two-electron bonding system (Ir···Ir = 2.903 Å). This is in marked contrast to the $M_2Cp''_2X_4$ complexes where the M···M distance is too large for a significant binding interaction (Ir···Ir = 3.769 Å). 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 $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ 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 (Figure 2). Therefore there is an inherent symmetry to each hydride bridge which may make conversion of a bridging hydride to a terminal hydride easier than if the hydride were symmetrically placed between the two metals.

## Experimental Section

All operations, except where otherwise specified, were performed under dinitrogen either by Schlenk techniques or in a drybox. $PMe_3$ was prepared by the method of Wolfsberger and Schmidbaur[23] with modifications by P. Sharp.[24] Published procedures were used to prepare $TaCp(CHCMe_3)Cl_2$,[8] $TaCp''Cl_2Np_2$,[8] and $TaCp''Cl_2(CH_2{=}CHCH_3)$.[9b] The preparation of $TaCp'Cl_2Np_2$ was analogous to that of $TaCp''Cl_2Np_2$. $TaCp''Cl_2Me_2$ was prepared by treating the $TaMe_2Cl_3$ with 1 equiv of $LiC_5Me_5$ in ether.[25] Alkylcyclopentadienes were prepared by Bercaw's procedure.[26] TlCp 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*-butyllithium. 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 °C, freeze/thaw degassed, and distilled from *n*-butyllithium. All deuterated NMR solvents were passed through a column of activated alumina.

NMR data are listed in parts per million (positive downfield) relative to internal $Me_4Si$ for $^1H$ and $^{13}C$ and relative to external $H_3PO_4$ for $^{31}P$.

**Preparation of $[Ta(\eta^5\text{-}C_5Me_5)Cl_2H]_2$.** $TaCp''Cl_2$(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 the solution was stirred for 1 day, green $[TaCp''Cl_2H]_2$ (0.92 g, 92% yield) was filtered off.

In a similar experiment employing 0.25 g $TaCp''Cl_2$(propylene) in 5 mL of pentane the color of the reaction changed from dark purple to orange after 20 min. The solution was cooled to 0 °C 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 $^1H$ NMR spectrum showed ~65% $[TaCp''Cl_2H]_2$, ~15% $Cp''Cl_2\overline{TaCHCHMeCHMeC}H_2$, and ~20% $TaCp''Cl_2$(propylene).

A similar reaction employing $TaCp''Cl_2$(styrene) gave a 65% yield of $[TaCp''Cl_2H]_2$ after 20 h at 25 °C and a 70% yield of a 2:3 mixture of ethylbenzene and styrene.

A similar reaction employing 0.39 g of $TaCp''Cl_2Np_2$ in 10 mL of pentane gave 0.23 g of $[TaCp''Cl_2H]_2$ after 1 h at 25 °C under 40 psi of $H_2$. The product was contaminated with an unidentified impurity (~20%): $^1H$ NMR ($C_6D_6$) 10.382 (s, 1, Ta-H), 2.039 ppm (s, 15, Cp″); $^{13}C$ NMR ($C_6D_6$) 123.0 (s, $\mathit{C}_5Me_5$), 13.4 ppm (q, $C_5\mathit{Me}_5$); IR (Nujol) 1580 $cm^{-1}$ (m, br, Ta-H); MS, *m/e* 135 (relative intensity 100, $C_5Me_5$), 386 (20, $TaCp''Cl_2$), 387 (60, $TaCp''Cl_2H$). Anal. Calcd for $TaC_{10}H_{16}Cl_2$: C, 30.95; H, 4.15. Found: C, 30.86; H, 4.20. This sample had been prepared from $TaCp''Cl_2$(propylene) and recrystallized from chlorobenzene with pentane at −30 °C.

**Preparation of $[Ta(\eta^5\text{-}C_5Me_5)Cl_2D]_2$.** $[TaCp''Cl_2D]_2$ was prepared by reacting the $TaCp''Cl_2$(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 $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$.** $[TaCp'Cl_2H]_2$ was prepared by using methods analogous to those used to prepare $[TaCp''Cl_2H]_2$. From $TaCp'Cl_2Np_2$ the yield was ~75% and from $TaCp'Cl_2$(propylene) the yield was 95%: $^1H$ NMR ($C_6D_6$) 10.420 (s, 1, Ta-H), 2.57 (q, 2, $J$ = 7.7 Hz, $C\mathit{H}_2CH_3$), 2.14 (s, 6, ring-$CH_3$), 2.01 (s, 6, ring-$CH_3$), 0.81 ppm (t, 3, $J$ = 7.7 Hz, $CH_2C\mathit{H}_3$); $^{13}C$ NMR ($C_6D_6$) 123.2 and 121.9 (two of three ring carbon atoms), 2.22 (q, $CH_2\mathit{C}H_3$), 15.1 (t, $\mathit{C}H_2CH_3$), 13.2 ppm (q, accidentally equivalent ring methyl groups); MS, *m/e* 149 (relative intensity 20, $C_5Me_4Et$), 400 (6, $TaCp'Cl_2$), 401 (10, $TaCp'Cl_2H$); mol wt (benzene, cryoscopic) calcd, 804, found, 840. Anal. Calcd for $TaC_{11}H_{18}Cl_2$: C, 32.86; H, 4.51. Found: C, 32.97; H, 4.64.

**Preparation of $[Ta(\eta^5\text{-}C_5Me_4Et)Br_2H]_2$.** $[TaCp'Br_2H]_2$ 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 ($C_6D_6$) 11.266 (s, 1, Ta-H), 2.608 (q, 2, $J$ = 7.4 Hz, $C\mathit{H}_2CH_3$), 2.214 (s, 6, ring-$CH_3$), 2.102 (s, 6, ring-$CH_3$), 0.817 ppm (t, 3, $J$ = 7.4 Hz, $CH_2C\mathit{H}_3$).

**Preparation of $Ta_2Cp'_2Cl_4H_2/Ta_2Cp'_2Cl_4HD/Ta_2Cp'_2Cl_4D_2$ Mixture.** A mixture of $H_2$ (10 mL) and $D_2$ (10 mL) was added by syringe to a sample of $TaCp'Cl_2$(propylene) (0.2 g, 0.45 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 ~30% $Ta_2Cp'_2Cl_4H_2$ (H at 10.43 ppm), ~40% $Ta_2Cp'_2Cl_4HD$ (H at 10.38 ppm), and ~30% $Ta_2Cp'_2Cl_4D_2$ (by difference).

**Preparation of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(CH_2CMe_3)$.** $[Cp'TaCl_2H]_2$ (0.8 g, 1 mmol) was dissolved in 50 mL of toluene, and an ether solution

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of NpMgCl (0.5 mmol) was added dropwise over a 10-min period. The color changed from bright green to dark gray. After 0.5 h 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 °C. These were collected by filtration and washed with cold (−30 °C) penntane: yield 0.67 g (78%); $^1$H NMR (toluene-$d_8$, 250 MHz, 320 K) 10.483 (s, 2, MH), 4.71 (d, 1 $J$ = 14 Hz, $C\mathit{H}_AH_BCMe_3$), 2.57 (m, 2, ring-$C\mathit{H}_2CH_3$), 2.48 (m, 2, ring-$C\mathit{H}_2CH_3$), 2.213 (s, 6, ring-$CH_3$), 2.104 (s, 6, ring-$CH_3$), 2.122 (s, 3, ring-$CH_3$), 2.089 (s, 3, ring-$CH_3$), 2.091 (s, 3, ring-$CH_3$), 1.995 (s, 3, ring-$CH_3$), 1.93 (d, 1, $J$ = 14 Hz, $CH_A\mathit{H}_BCMe_3$), 1.260 (s, 9, $CMe_3$), 0.91 ppm (m, 6, ring-$CH_2C\mathit{H}_3$); at 274 K the hydride doublet resonances are found at 10.298 and 10.583 ppm ($J_{HH}$ = 5.9 Hz); IR (Nujol) 1578 cm$^{-1}$ ($\nu_{MH}$). Anal. Calcd for $Ta_2C_{27}H_{47}Cl_3$: C, 38.61; H, 5.64. Found: C, 38.80; H, 5.70.

**Preparation of $Ta(\eta^5\text{-}C_5Me_5)_2Cl_3H_2(CH_2CMe_3)$.** $[TaCp''Cl_2H]_2$ (1.41 g, 1.8 mmol) was dissolved in 20 mL of toluene and 1.1 mmol of $MgNp_2$ in ether was added. After 30 min 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 °C to give blue crystals; yield 0.8 g (54%); $^1$H NMR ($C_6D_6$, 60 MHz) 10.6 (br s, 2, MH), 1.87 (s, 15, Cp″), 1.75 (s, 15, Cp″), 1.12 ppm (s, 9, $CMe_3$); IR (Nujol) cm$^{-1}$ 1580 (M−H); mol wt (cryoscopic in $C_6H_{12}$) calcd 812, found 800 ± 100.

**Preparation of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(CH_2SiMe_3)$.** This complex was prepared from 0.8 g (1 mmol) of $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$ and 0.14 g (0.5 mmol) of $Mg(CH_2SiMe_3)_2$·dioxane in 30 mL of toluene 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: $^1$H NMR (toluene-$d_8$, 243 K) 10.540 (d, 1, $J$ = 6 Hz, MH), 9.480 (d, 1, $J$ = 6 Hz, MH), 4.663 (d, 1, $J$ = 13 Hz, $C\mathit{H}_AH_BSiMe_3$), 1.665 (d, 1, $J$ = 13 Hz, $CH_A\mathit{H}_BSiMe_3$), 0.356 (s, 9, $SiMe_3$), 2.158, 2.023, 2.008, 1.990, 1.970, 1.890, 1.846 (ring methyl groups), 2.64–2.59 (m, 4, ring-$C\mathit{H}_2CH_3$), 0.85 ppm (m, 6, ring-$CH_2C\mathit{H}_3$); IR (Nujol) 1590 cm$^{-1}$ ($\nu_{MH}$).

**Preparation of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2Me$.** A solution of $[TaCp'Cl_2H]_2$ (0.4 g, 0.5 mmol) in 25 mL of toluene was cooled to 0 °C. A pentane solution of $ZnMe_2$ was added dropwise until the color of the solution remained violet. Solvent was removed in vacuo, and the residue was extracted with 100 mL of pentane. The pentane solution was filtered, concentrated and cooled to give deep violet microcrystals: yield 0.265 g (68%); $^1$H NMR ($C_6D_6$, 250 MHz, 295 K) 10.256 (s, 2, MH), 2.69 (m, 2, ring-$C\mathit{H}_2CH_3$), 2.417 (m, 2, ring-$C\mathit{H}_2CH_3$), 2.186, 2.050, 2.038, 2.026, 1.921, 1.899 (s, ring-$CH_3$), 1.985 (s, 3, $TaCH_3$), 0.894 (t, 3, ring-$CH_2C\mathit{H}_3$), 0.835 ppm (t, 3, ring-$CH_2C\mathit{H}_3$); IR (Nujol mull) 1590 cm$^{-1}$ ($\nu_{MH}$).

**Preparation of $Ta_2(\eta^5\text{-}C_5Me_5)_2Cl_3H_2(Me)$.** A solution of $[TaCp''Cl_2H]_2$ (0.3 g, 0.39 mmol) in 20 mL of toluene was cooled to −78 °C, and $ZnMe_2$ (0.02 g, 0.2 mmol) was added by syringe. No reaction occurred at −78 °C. The reaction solution was slowly warmed to room temperature over a 30-min 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 °C: yield 0.1 g (30%); $^1$H NMR ($C_6D_6$, 60 MHz) 10.27 (s, 2, MH), 2.20 (s, 15, Cp″), 2.03 (s, 15, Cp″), 1.97 ppm (s, 3, Me).

**Observation of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(CH_2CH_3)$.** 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 μL (0.03 mmol) of diethylzinc. The color of the solution changed immediately from green to violet. The $^1$H NMR spectrum at −50 °C was consistent with that expected for $Ta_2Cp'_2Cl_3H_2Et$. After 0.5 h at 0 °C the sample had decomposed: $^1$H NMR (toluene-$d_8$, 90 MHz, −50 °C) 10.395 (br s, 1, MH), 10.297 (br s, 1, MH), 3.3 (br q, 2, $MC\mathit{H}_2CH_3$), 2.35 (m, 4, ring-$C\mathit{H}_2CH_3$), 2.18 and 1.89 (s, ring-Me), 0.86 ppm (m, 9, $MCH_2C\mathit{H}_3$ and ring-$CH_2C\mathit{H}_3$).

**Preparation of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_5H$.** 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 ~1 g of the product would not dissolve in ether. This brown solid was recrystallized from toluene/pentane to give ~25 mg of $Ta_2Cp'_2Cl_5H$.

A mixture of $TaCp'Cl_3Np$ (0.5 g) and $TaCp'Cl_2Np_2$ (0.5 g) was dissolved in 75 mL of pentane, and the solution was stirred under 45 psi of $H_2$ for 1 h at 25 °C. The pentane insolubles (0.38 g) were shown to contain $[TaCp'Cl_2H]_2$ and $Ta_2Cp'_2Cl_5H$ by $^1$H NMR. Recrystallization from toluene/pentane gave 0.13 g of less soluble, red-orange $Ta_2Cp'_2Cl_5H$ (20% yield): $^1$H NMR ($C_6D_6$) 6.08 (s, 1, hydride), 2.6 (q, 4, $J$ = 8 Hz, ring-$C\mathit{H}_2CH_3$), 2.2 (s, 12, ring-$CH_3$), 2.15 (s, 12, ring-$CH_3$), 0.93 ppm (t, 6, $J$ = 12 Hz, ring-$CH_2C\mathit{H}_3$). Anal. Calcd for $Ta_2C_{22}H_{35}Cl_5$: C, 31.50; H, 4.20. Found: C, 31.16; H, 4.44.

**Preparation of $Ta(\eta^5\text{-}C_5Me_5)Cl_2(CH_2CMe_3)(H)$.** Butane (distilled from lithium butyl) was condensed onto $TaCp''Cl_2Np_2$ (0.26 g, 0.5 mmol) in a 50-mL flask and 20 mL of $H_2$ added by syringe after the solution was cooled to −78 °C. The temperature was slowly raised to −30 °C as the solution was stirred. After 0.5 h at −30 °C the color of the solution was orange. The solvent was removed in vacuo at −30 °C, leaving a yellow solid which was characterized by NMR and IR methods: $^1$H NMR (toluene-$d_8$, −30 °C) 22.87 (s, 1, Ta-H), 1.779 (s, 15, $C_5Me_5$), 1.421 (s, 9, $CMe_3$), 0.921 ppm (s, 2, $C\mathit{H}_2CMe_3$); $^{13}$C NMR (toluene-$d_8$, −50 °C) ~120 (ring carbon signals), 94.7 (t, $C\mathit{H}_2CMe_3$), 35.6 (q, $CH_2C\mathit{Me}_3$), 12.4 ppm (q, ring-$CH_3$ groups); IR (neat oil on NaCl, 35 °C) 1750 cm$^{-1}$ (w br, Ta-H).

**Reaction of $Ta(\eta^5\text{-}C_5Me_5)Cl_2(CH_2CMe_3)(H)$ with Chloroform.** A 0.53-g (1.0-mmol) sample of $TaCp''Cl_2Np_2$ was dissolved in 50 mL of pentane containing ~3 mL of chloroform. The reaction was cooled to −78 °C, and 25 mL (1.1 mmol) of $H_2$ was added by syringe. The reaction was warmed slowly to 25 °C. The deep red color lightened to orange at −10 °C 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 $TaCp''Cl_3Np$. It was identified by NMR comparison with an authentic sample.[9b]

**Reaction of $Ta(\eta^5\text{-}C_5Me_5)Cl_2$(propylene) with $H_2$ in the Presence of Chloroform.** A reaction analogous to that above starting with $TaCp''Cl_2$(propylene) (0.43 g, 1 mmol) under excess $H_2$ gave an orange solution from which yellow-orange needles of $TaCp''Cl_3$(propyl) (0.29 g, 0.61 mmol) could be isolated by concentrating and cooling the solution: $^1$H NMR ($C_6D_6$) 2.551 (sextet, 2, $J$ = 6.7 Hz, $-CH_2C\mathit{H}_2CH_3$), 1.970 (s, 15, $C_5\mathit{Me}_5$), 1.162 (t, 3, $J$ = 6.7 Hz, $-CH_2CH_2C\mathit{H}_3$), 0.985 ppm (t, 2, $J$ = 6.5 Hz, $-C\mathit{H}_2CH_2CH_3$); $^{13}$C NMR ($CDCl_3$) ~127 (ring carbons), 90.5 (t, $-\mathit{C}H_2CH_2CH_3$), 21.5 (t, $-CH_2\mathit{C}H_2CH_3$), 15.2 (q, $-CH_2CH_2\mathit{C}H_3$), 13.14 ppm (q, ring methyl groups). Anal. Calcd for $TaC_{13}H_{22}Cl_3$: C, 33.53; H, 4.76. Found: C, 33.54; H, 4.58.

**X-ray Crystallographic Study of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$.** 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),[27] with $a$ = 20.084 (6) Å, $b$ = 16.972 (4) Å, $c$ = 15.869 (4) Å, $\beta$ = 96.86 (2)°, and $Z$ = 8 (dimeric species) at 20 ± 1 °C.

Intensity measurements were made on a Nicolet P$\bar{1}$ autodiffractometer using 1.0° wide $\omega$ scans and graphite-monochromated Mo K$\bar{\alpha}$ 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 $2\theta_{MoK\bar{\alpha}} < 55.0°$ (the equivalent of 1.0 limiting Cu K$\bar{\alpha}$ spheres) were measured in two concentric shells of increasing $2\theta$. A scanning rate of 6.0°/min was employed for the scan between $\omega$ settings at 0.50° respectively above and below the calculated K$\bar{\alpha}$ doublet value ($\lambda_{K\bar{\alpha}}$ = 0.71073 Å) for those reflections having $3° < 2\theta_{MoK\bar{\alpha}} < 43°$; a scanning rate of 4.0°/min was used for those reflections having $43° < 2\theta_{MoK\bar{\alpha}} < 55.0°$. Each of these 1° 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° above and below the calculated value for each reflection. The intensity data were corrected empirically for absorption effects ($\mu_a{}^{28a}$(Mo K$\bar{\alpha}$) = 8.86 mm$^{-1}$) using psi scans for four reflections having $2\theta$ values between 7° and 22° and were then reduced to relative squared amplitudes, $|F_o|^2$, 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 $R_1$ (unweighted, based on F)[29] = 0.182 for those 4339 reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. The remaining nonhydrogen atoms were located from a series of difference Fourier syntheses using more complete structural models. While these remaining nonhydrogen atoms were located, 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 ($R_1$ = 0.049 for 4339 reflections) as $Ta_2Cp'_2Cl_4H_2$ with anisotropic thermal parameters for all 56 nonhydrogen atoms, the occupancies of all eight "chlorine" sites were allowed to vary. After

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(27) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. 1, p 99.

(28) (a) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974, Vol. IV, pp 55–56; (b) pp 99–101; (c) pp 149–150.

(29) The $R$ values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, 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.

convergence, two of the "chlorine" sites on each dimer ($Cl_a$ and $Cl_b$ in Figure 1) had refined occupancies near 1.00, while the other two ($Cl/C_a$ and $Cl/C_b$ 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 $R_1 = 0.048$ and $R_2$ (weighted, based on F)[29] = 0.052 for 4339 independent reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$; similar refinement cycles with the more complete ($2\theta_{MoK\bar{\alpha}} < 55°$) data set gave $R_1 = 0.056$ and $R_2 = 0.061$ for 6542 absorption-corrected reflections having $I > 3\sigma(I)$. These and all subsequent structure factor calculations employed recent tabulations of atomic form factors[28b] and anomalous dispersion corrections[28c] to the scattering factors of the Ta and Cl atoms. The final cycles[10] of empirically weighted[30] 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 $2\theta_{MoK\bar{\alpha}} < 55°$ 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 Co.

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**Registry No.** $[TaCp''Cl_2H]_2$, 74153-79-0; $[TaCp'Cl_2H]_2$, 74153-80-3; $[TaCp'Br_2H]_2$, 81389-10-8; $Ta_2Cp'_2Cl_3Hz_2(CH_2CMe_3)$, 81389-09-5; $Ta_2Cp''_2Cl_3H_2(CH_2CMe_3)$, 81389-08-4; $Ta_2Cp'_2Cl_3H_2(CH_2SiMe_3)$, 81389-07-3; $Ta_2Cp'_2Cl_3H_2(Me)$, 81389-06-2; $Ta_2Cp''_2Cl_3H_2(Me)$, 81389-05-1; $Ta_2Cp'_2Cl_3H_2(CH_2CH_3)$, 81389-04-0; $Ta_2Cp'_2Cl_5H$, 74153-82-5; $TaCp''Cl_2(CH_2CMe_3)(H)$, 81389-03-9; $TaCp''Cl_2$(propylene), 71453-85-5; $TaCp''Cl_2$(styrene), 71414-50-1; $TaCp''Cl_2Np_2$, 71228-87-0; $TaCp'Cl_2Np_2$, 81389-02-8; $TaCp'Br_2$(propylene), 81389-01-7; $TaCp'Cl_2$(propylene), 81389-00-6; $TaCp'Cl_3Np$, 81388-99-0; $TaCp''Cl_3Np$, 68087-41-2; $TaCp''Cl_3$(propyl), 81388-98-9.

**Supplementary Material Available:** Crystal structure analysis report and 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 $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3H_2(Me)$ (38 pages). Ordering information is given on any current masthead page.

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[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 $||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$, where the $F_c$ values were calculated from the fully-refined model using unit weighting and an $I > 3\sigma(I)$ rejection criterion.

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# Synthesis and Crystal Structure of an Analogue of 2-($\alpha$-Lactyl)thiamin, Racemic Methyl 2-Hydroxy-2-(2-thiamin)ethylphosphonate Chloride Trihydrate. A Conformation for a Least-Motion, Maximum-Overlap Mechanism for Thiamin Catalysis[1]

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*Contribution from the Biocrystallography Lab, VA Medical Center, Box 12055, Pittsburgh, Pennsylvania 15240, the Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.* *Received July 23, 1981*

**Abstract:** Methyl 2-hydroxy-2-(2-thiamin)ethylphosphonate, phosphalactylthiamin, is a phosphonate analogue of 2-(1-carboxy-1-hydroxyethyl)thiamin, the initial intermediate in the thiamin-catalyzed decarboxylation of pyruvic acid. Crystal-structure analysis of phosphalactylthiamin reveals that the thiamin portion of the molecule assumes the S conformation that is characteristic of other C(2)-substituted thiamins. However, in contrast to previously studied derivatives the conformation of the phosphalactyl substituent is unique in that its hydroxyl is in close contact with the bridging methylene instead of the thiazolium ring sulfur and the bond to the phosphonate is oriented perpendicular to the ring plane. This structural feature is also consistent with the NMR spectrum. The structure suggests that the principles of least motion and maximum orbital overlap can be applied to thiamin catalysis of the decarboxylation of pyruvate since the observed structure conforms to theoretical expectations for 2-($\alpha$-lactyl)thiamin diphosphate. Phosphalactylthiamin has the empirical formula $C_{15}H_{24}N_4O_5PS{\cdot}Cl{\cdot}3H_2O$. The crystal examined was monoclinic, $P2_1/c$, $a = 9.916$ (8) Å, $b = 16.840$ (1) Å, $c = 15.786$ (1) Å, $\beta = 119.45$ (4)°, $V = 2295$ Å$^3$, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least squares to an $R$ value of 0.067 for 1587 structure factor amplitudes measured with Mo K$\alpha$ radiation on an Enraf-Nonius automatic diffractometer.

Thiamin (TH), in the form of the diphosphate ester, is a coenzyme in a number of metabolically important enzymes that catalyze the decarboxylation of $\alpha$-keto acids and the transfer of aldehyde or acyl groups.[2] Although the general outline of the catalytic mechanism has been known for over two decades,[3] many details of the mechanism in both enzymatic and nonenzymatic systems remain to be elucidated. In an effort to obtain information pertaining to these details, structures have been determined for thiamin and its derivatives and analogues. The derivatives that have been of particular interest are the C(2)-substituted thiamins,

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[1] The crystal structure analysis was done by August Turano in partial fulfilment of the Ph.D. degree, University of Pittsburgh, Pittsburgh, PA.

[2] For a general review of thiamin catalysis, see: Krampitz, L. O. *Annu. Rev. Biochem.* **1969**, *38*, 213. A detailed review of the structural and mechanistic aspects of thiamin catalysis is given by Gallo et al., (Gallo, A. A.; Mieyal, J. J.; Sable, H. Z. *Bioorg. Chem.* **1978**, *4*, 147-177).

[3] Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719-3726.

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