J. Am. Chem. Soc. **1983**, *105*, 4942-4950

Alkylidene Hydride Complexes of Tantalum and the Polymerization of Ethylene by $Ta(CHCMe_3)(H)(PMe_3)_3I_2$

H. W. Turner, R. R. Schrock,* J. D. Fellmann, and S. J. Holmes

Contribution from the Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received November 30, 1982*

Abstract: Addition of HX (X = Cl, O_2CCF_3) to $Ta(CHCMe_3)(dmpe)_2Cl$ produces $[Ta(CHCMe_3)(H)(dmpe)_2Cl]^+X^-$, but addition of HCl to $Ta(CHCMe_3)(PMe_3)_4Cl$ gives $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ (in poor yield). $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ can be prepared in good yield by reducing $Ta(CH_2CMe_3)Cl_4$ with 2 equiv of sodium amalgam in the presence of PMe_3. $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(H)(Cl)(PMe_3)$ can be prepared similarly from $Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)Cl_3$. Addition of 2 equiv of Me_3SiX (X = I, O_3SCF_3) to $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ yields $Ta(CHCMe_3)(H)(PMe_3)_3X_2$. Several related species such as $[NEt_4][Ta(CHCMe_3)(H)(PMe_3)_3Cl_3]$ have also been prepared. In all cases the $Ta{=}C_\alpha{-}C_\beta$ angle in the neopentylidene ligand is large ($J_{CH_\alpha} \approx 70$ Hz and $\nu_{CH_\alpha} \approx 2500$ cm^{-1}). Although there is no evidence that H_α and TaH exchange on the ^1H NMR time scale, magnetization transfer studies show that they do exchange readily on the chemical time scale at ~320 K in each of five complexes examined, probably by formation of a tantalum(III) neopentyl complex. Addition of ethylene to $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ produces $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$ in the presence of PMe_3. In the absence of added PMe_3 a new alkylidene hydride complex, $Ta[CH(CH_2CH_2)_nCH_3](H)(PMe_3)_3I_2$, is formed along with tantalum-free even- and odd-carbon organic polymers which are mixtures of internal and terminal olefins. Field desorption mass spectra show that only the odd-carbon organic polymers contain the original C_5 ligand. These and other results suggest that ethylene reacts with the neopentylidene ligand in $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ to form a tantallacyclobutane hydride complex. This species decomposes to give a new alkyl complex, and finally a new alkylidene hydride complex by α-hydride elimination. In contrast, propylene and styrene react faster with the hydride ligand in $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ than with the neopentylidene ligand to give first $Ta(CHR)(R')(PMe_3)_3I_2$ (proposed), then R'H and $Ta(CR)(PMe_3)_3I_2$, and finally $Ta(CHR)(CH_2PMe_3)(PMe_3)_2I_2$. $Ta(CHR)(CH_2PMe_3)(PMe_3)_2I_2$ and $Ta(PMe_3)_3I_2$ are observable decomposition products in the system in which ethylene is polymerized by $Ta(CHCMe_3)(H)(PMe_3)_3I_2$. Neither polymerizes ethylene. We have also prepared $Ta(C_2H_4)Et(PMe_3)_2I_2$, a logical potential intermediate in a classical Cossee-type polymerization reaction, but it too does not polymerize ethylene.

α-Hydride elimination is the name given to the process of forming an alkylidene hydride complex from an alkyl complex. For years the evidence for it was only circumstantial.[1] However, in 1974 Cooper and Green produced firm evidence for an equilibrium between a tungsten(IV) methyl complex and a tungsten(VI) methylene hydride complex.[2] More recently, we have noted that tantalum(V) neopentylidene hydride complexes can be prepared by reducing tantalum(V) neopentyl complexes by two electrons,[3] and Bercaw has observed exchange of an alkylidene α-hydrogen atom with a hydride ligand in a niobium(V) "zirconoxy carbene" hydride complex.[4] Several examples of a related α-hydride elimination reaction, formation of an alkylidyne hydride complex from an alkylidene complex, are also known.[3] Recently, equilibria between d^2 alkylidene complexes and d^0 alkylidyne hydride complexes have been observed directly where the alkylidene ligand is neopentylidene or methylene and the metal is either tantalum ($CHCMe_3$)[5] or tungsten ($CHCMe_3$ and CH_2).[6]

α-Hydride elimination (alkyl → alkylidene hydride) was placed in a new light when Ivin, Rooney, and Green proposed that an alkylidene hydride complex could be a catalyst for the stereospecific polymerization of propylene.[7] This proposal ran counter to the overwhelming evidence that ethylene and propylene are polymerized by rapid sequential insertions into a transition metal–carbon *single* bond.[8] The overall result is, of course, identical, and in a situation where an alkyl complex might be in equilibrium with an alkylidene hydride complex the question reduces to which is the more reactive species. The issue is further complicated by the possibility that an alkyl ligand can be distorted significantly toward an alkylidene hydride system, even when the metal has the d^0 configuration.[9,10] (Related distortions of alkylidene ligands have been known for several years.[11]) The implication is that an alkyl complex may behave as if it were an alkylidene hydride complex without structurally being discretely so, i.e., without complete cleavage of the CH_α bond.

As mentioned earlier, we have been able to prepare well-characterized d^0 neopentylidene hydride complexes of tantalum. We recently discovered that one of these $[Ta(CHCMe_3)(H)(PMe_3)_3I_2]$ will polymerize ethylene.[12] What we report here is the synthesis and characterization of several neopentylidene hydride complexes and a detailed study of how ethylene is polymerized by $Ta(CHCMe_3)(H)(PMe_3)_3I_2$. We feel this study fairly convincingly illustrates that an alkylidene hydride mechanism for polymerizing ethylene *is* possible. Some relatively rapid but less well-defined and therefore virtually undetectable version of it could operate in at least some, if not many, other systems, including some of the more classical Ziegler–Natta catalyst systems.

---

[1] (a) D'yachkovsky, F. S.; Khrushch, N. E. *Zh. Obshch. Khim.* **1971**, *41*, 1779. (b) Farády, L.; Markó, L. *J. Organomet. Chem.* **1972**, *43*, 51. (c) Michman, M.; Zeiss, H. H. *Ibid.* **1968**, *13*, 23. (d) Light, J. R. C.; Zeiss, H. H. *Ibid.* **1970**, *21*, 391. (e) Michman, M.; Zeiss, H. H. *Ibid.* **1968**, *15*, 139. (f) Ikariya, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1974**, 720. (g) Hérrison, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161. (h) Soufflet, J.-P.; Commereuc, D.; Chauvin, Y. *C. R. Acad. Sci., Ser. C* **1973**, *276*, 169.

[2] (a) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 209; **1974**, 761. (b) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

[3] Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608.

[4] Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650.

[5] Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.

[6] (a) Holmes, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 4599. (b) Holmes, S. J.; Clark, D. J.; Turner, H. W.; Schrock, R. R. *Ibid.* **1982**, *104*, 6332.

[7] Ivin, R. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604.

[8] (a) Boor, J., Jr. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979. (b) Cossee, P. *J. Catal.* **1964**, *3*, 80. (c) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.

[9] Fellmann, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481.

[10] Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1410.

[11] (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Schrock, R. R. In "Reactions of Coordinated Ligands"; Braterman, P. S., Ed.; Plenum Press: New York, in press.

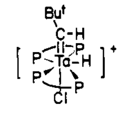
[12] Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331.

0002-7863/83/1505-4942$01.50/0

Results

A Cationic Neopentylidene Hydride Complex. A tantalum(III) neopentylidene complex of the type $Ta(CHCMe_3)(dmpe)_2Cl$ is known.[5] In it the neopentylidene ligand is grossly distorted so that it is closer to what may more accurately be called a neopentylidyne hydride complex. It could in principle be protonated, to yield either $[Ta(CH_2CMe_3)(dmpe)_2Cl]^+$ or, we thought less likely, $[Ta(CHCMe_3)(H)(dmpe)_2Cl]^+$. In fact, the latter is the product when $Ta(CHCMe_3)(dmpe)_2Cl$ reacts with HX (X = Cl, O_2CCF_3) in diethyl ether at −30 °C. These complexes can be obtained as ivory needles from a mixture of dichloromethane and ether. They are stable at room temperature indefinitely.

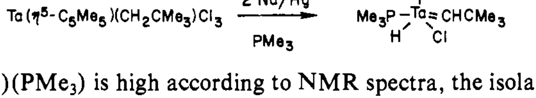
NMR studies suggest that the structure of $[Ta(CHCMe_3)(H)(dmpe)_2Cl]^+$ is closely related to that of $Ta(CCMe_3)(H)(dmpe)_2X$ (X = I, triflate, $AlMe_3Cl$),[5] i.e., a pentagonal bipyramid (**1**). The neopentylidene ligand is still grossly distorted, as evidenced[11] by the relatively high-field shift of H_α (−4.95 ppm for X = Cl), low value for J_{CH_α} (70 Hz for X = Cl), and low value for ν_{CH_α} (2280 cm^{-1}). Therefore, the neopentylidene ligand probably is not fixed in one orientation but "rotates" by virtue of the mobility of H_α about the upper half of the molecule. (A similar process was proposed for "rotation" of the neopentylidene ligand in $Ta(CHCMe_3)(dmpe)_2Cl$.[5]) A triplet signal for the hydride ligand is found at relatively low field (6.33 ppm for X = Cl; J_{HP} = 78 Hz). We see no evidence for an exchange of the hydride ligand with H_α at a rate that is rapid on the NMR time scale.



1

Addition of HCl to $Ta(CHCMe_3)(PMe_3)_4Cl$,[3] a complex that is closely related to $Ta(CHCMe_3)(dmpe)_2Cl$, does not yield $Ta(CHCMe_3)(H)(PMe_3)_4Cl^+Cl^-$. A PMe_3 ligand is lost and replaced by chloride to give $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ in poor yield. This result is not unexpected since although $W(CCMe_3)(dmpe)_2Cl$ reacts with HCl to give $[W(CCMe_3)(H)(dmpe)_2Cl]^+Cl^-$, $W(CCMe_3)(PMe_3)_4Cl$ reacts with HCl to give $W(CCMe_3)(H)(PMe_3)_3Cl_2$.[6b] $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ has been prepared in higher yield by another route and will be described in detail below.

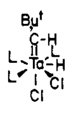
Preparation of $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(H)(Cl)(PMe_3)$. We felt that a possible alternative method of preparing a neopentylidene hydride complex would be to reduce a tantalum(V) neopentyl complex by two electrons. We were confident that a pentamethylcyclopentadienyl complex would be stable since we had been able to prepare $TaCp^*(CCMe_3)(H)(PMe_3)_2$ (Cp^* = $\eta^5\text{-}C_5Me_5$) by reducing $TaCp^*(CHCMe_3)Br_2$ with sodium amalgam in the presence of PMe_3.[3] This approach was successful as shown in eq 1. Although the yield of $TaCp^*(CHCMe_3)(H)(Cl)(PMe_3)$ is high according to NMR spectra, the isolated yield on a relatively small scale is limited to ~30% due to the high solubility of the product in pentane. The neopentylidene ligand is again highly distorted (J_{CH_α} = 72 Hz, ν_{CH_α} = 2525 cm^{-1}, $\delta(H_\alpha)$ 2.44), and the hydride resonance is found at low field (7.53 ppm). The hydride ligand in $TaCp^*(CHCMe_3)(H)(Cl)(PMe_3)$ is coupled to phosphorus (74 Hz) to approximately the same extent as the hydride ligand in $TaCp^*(CCMe_3)(H)(PMe_3)_2$ (J_{HP} = 86 Hz). If we assume that the structure of $TaCp^*(CCMe_3)(H)(PMe_3)_2$ is analogous to that of *trans*-$TaCp^*(CPh)(Cl)(PMe_3)_2$,[13] then the hydride ligand in $TaCp^*(CHCMe_3)(H)(Cl)(PMe_3)$ is most likely also trans to the neopentylidene ligand.



$$Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)Cl_3 \xrightarrow[PMe_3]{2\ Na/Hg} Me_3P\text{-}\overset{Cp^*}{Ta}(H)(Cl){=}CHCMe_3 \quad (1)$$

$TaCp^*(CHCMe_3)(H)(Cl)(PMe_3)$ is stable in solution at 25 °C. At 60 °C it decomposes in the presence of PMe_3 to give a high yield of $TaCp^*(CCMe_3)(Cl)(PMe_3)_2$. It has previously been observed[14] that $TaCp^*(CHR)(CH_2R)Cl$ reacts with PMe_3 to give $TaCp^*(CR)(Cl)(PMe_3)_2$ (R = CMe_3 or Ph), an example of α-hydrogen atom abstraction. Although we have not studied the reaction of $TaCp^*(CHCMe_3)(H)(Cl)(PMe_3)$ with PMe_3 in detail, it is likely that the reaction is another type of α-abstraction reaction in which a hydride ligand is the abstracting group instead of an alkyl ligand. This postulate is sensible for another reason; the reverse reaction (addition of H_2 to an alkylidyne ligand) has been observed under mild conditions.[15,16]

Preparation of $Ta(CHCMe_3)(H)(PMe_3)_3X_2$ (X = Cl, I, OTf) and Related Complexes. $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ can be prepared by reducing $Ta(CH_2CMe_3)Cl_4$ with sodium amalgam in the presence of PMe_3. NMR studies suggest that $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ has a structure with three inequivalent PMe_3 ligands, probably a pentagonal bipyramid (**2**) by analogy with the structure of $Ta(CCMe_3)(H)(dmpe)_2(AlMe_3Cl)$.[5] The neopentylidene ligand is distorted (J_{CH_α} = 72 Hz, ν_{CH_α} = 2440 cm^{-1}) and again "rotating" rapidly about the "Ta=C" bond axis. The hydride ligand gives rise to a signal at 10.0 ppm in the ^1H NMR spectrum and a peak at 1730 cm^{-1} in the IR spectrum. Again there is no evidence for exchange of the hydride ligand with H_α at a rate which is rapid on the ^1H NMR time scale up to 350 K. $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ is thermally stable in the solid state (12 h at 330 K) but decomposes rapidly ($t_{1/2} \approx 6$ h) at 300 K in toluene to give dark brown oily solids. One of the decomposition products is $Ta(PMe_3)_3Cl_3$,[17] according to NMR spectra. $Ta(PMe_3)_3Cl_3$ is nearly always present in trace amounts in a given sample, even those which are analytically pure. $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ is stable in chlorobenzene but decomposes in chloroform or dichloromethane to give as yet uncharacterized products. Protolysis of $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ with HCl or CF_3CO_2H produces neopentane quantitatively.



L = PMe_3

2

We carried out a few experiments that were designed to determine whether $Ta(CHCMe_3)(H)L_3Cl_2$ (L = PMe_3) is formed from $Ta(CH_2CMe_3)L_xCl_2$ (plus or minus the required amount of PMe_3) by an intramolecular α-hydride elimination reaction. The reduction of $Ta(CD_2CMe_3)Cl_4$ to give only $Ta(CDCMe_3)(D)(PMe_3)_3Cl_2$ (ν_{CD_α} = 1805 cm^{-1}, ν_{TaD} = 1270 cm^{-1}) suggests that only the α protons of the neopentyl group are involved. However, reduction of $Ta(CHDCMe_3)Cl_4$ did *not* yield only $Ta(CHCMe_3)(D)L_3Cl_2$ and $Ta(CDCMe_3)(H)L_3Cl_2$. $Ta(CHCMe_3)(H)L_3Cl_2$ was identified by the characteristic octet signal for its hydride ligand in the ^1H NMR spectrum; the ratio of $Ta(CHCMe_3)(H)L_3Cl_2$ to $Ta(CDCMe_3)(H)L_3Cl_2$ was ~1:2. Since mixing $Ta(CHCMe_3)(H)L_3Cl_2$ with $Ta(CDCMe_3)(D)L_3Cl_2$ produces no $Ta(CDCMe_3)(H)L_3Cl_2$, $Ta(CHCMe_3)(H)L_3Cl_2$ must form during the reduction process. There are many possibilities. For example, $Ta(CHCMe_3)(D)L_3Cl_2$ might lose D to some intermediate—a complex such as $Ta(CHDCMe_3)Cl_3L_x$ would seem reasonable—and gain H· in return from some other species. The main point is that we cannot tell if $Ta(CHCMe_3)(H)L_3Cl_2$ is formed from $Ta(CH_2CMe_3)L_3Cl_2$ by an intramolecular α-hydride elimination. It may also be formed to some extent (or

---

(13) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171.

(14) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962.

(15) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739.

(16) Messerle, L. W. Ph.D. Thesis, Massachusetts Institute of Technology, 1979.

(17) Rocklage, S. M.; Turner, H. W.; Fellmann, J. D.; Schrock, R. R. *Organometallics* **1982**, *1*, 703.

Chart I. Complexes in Which Magnetization Is Transferred between H_α and TaH at 315–320 K (Minimum)

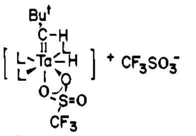
$[Ta(CHCMe_3)(H)(dmpe)_2Cl]^+X^-$ ($X = Cl, O_2CCF_3$)
$Ta(CHCMe_3)(H)(PMe_3)_3I_2$
$Ta(CHCMe_3)(H)(PMe_3)_3(OTf)_2$
$Ta(CHCMe_3)(H)(PMe_3)_2(py)(OTf)_2$
$Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$[a]

[a] Rapidly decomposing at this temperature.

exclusively) by a series of more complex intermolecular reactions.

$Ta(CHCMe_3)(H)L_3Cl_2$ reacts with excess Me_3SiI to give green $Ta(CHCMe_3)(H)L_3I_2$. $Ta(CHCMe_3)(H)L_3I_2$ readily dissolves in toluene, tetrahydrofuran, and chlorobenzene. It is only slightly soluble in ether, and it decomposes slowly in chloroform. $Ta(CHCMe_3)(H)L_3I_2$ is significantly more stable in solution than $Ta(CHCMe_3)(H)L_3Cl_2$. Little has decomposed after 4 h at 330 K in toluene. Nevertheless, we observe trace amounts of TaL_3I_3 (see later) in the ^1H NMR spectrum of analytically pure $Ta(CHCMe_3)(H)L_3I_2$. NMR studies suggest that the structure of $Ta(CHCMe_3)(H)L_3I_2$ is analogous to that proposed for $Ta(CHCMe_3)(H)L_3Cl_2$.

$Ta(CHCMe_3)(H)L_3Cl_2$ reacts with excess Me_3SiOTf in toluene to give a compound with the formula $Ta(CHCMe_3)(H)L_3(OTf)_2$. $Ta(CHCMe_3)(H)L_3(OTf)_2$ is insoluble in ether and aromatic or aliphatic hydrocarbons, but it is soluble and stable in chloroform or dichloromethane. The fact that it conducts slightly in dichloromethane suggests that it must be partially ionized in polar solvents. If so, the triflate which remains bound to the metal would probably be bidentate (**3**). If pyridine is added to a solution of $Ta(CHCMe_3)(H)L_3(OTf)_2$ in dichloromethane, one PMe_3 ligand is replaced by pyridine. Since the hydride signal in the ^1H NMR spectrum of $Ta(CHCMe_3)(H)L_2(py)(OTf)_2$ shows couplings to phosphorus of 85 and 78 Hz, we propose that pyridine has replaced the phosphine ligand closest to the hydride ligand. $Ta(CHCMe_3)(H)L_3(OTf)_2$ also reacts with tetrahydrofuran to give what appear to be at least two isomers of $Ta(CHCMe_3)(H)L_2(THF)(OTf)_2$. The two isomers interconvert rapidly on the NMR time scale at 340 K, probably by loss of THF.



3

$Ta(CHCMe_3)(H)L_3Cl_2$ reacts with NEt_4Cl in tetrahydrofuran to give $[NEt_4][Ta(CHCMe_3)(H)L_2Cl_3]$ as light tan plates in 80% yield after recrystallization from a mixture of toluene and pentane. $[NEt_4][Ta(CHCMe_3)(H)L_2Cl_3]$ is thermally stable in solution for 5 h at 330 K in the presence or absence of PMe_3. NMR data suggest that $[NEt_4][Ta(CHCMe_3)(H)L_2Cl_3]$ is a symmetric pentagonal bipyramid formed by replacing the phosphine ligand that is next to H with a chloride ligand. Surprisingly, $[NEt_4][Ta(CHCMe_3)(H)L_2Cl_3]$ is soluble in toluene and does not conduct well in polar solvents. Evidently the ammonium cation is strongly associated with the anion in solution.

Magnetization Transfer Experiments. Direct Observation of H_α Elimination from Ta(III) Neopentyl Complexes. As noted several times in the previous sections, we have never seen H_α exchange with TaH at a rate that is rapid on the NMR time scale. We were especially interested in whether such an exchange occurs since formation of a Ta(III) neopentyl complex is the most likely way in which it would be accomplished. In this situation magnetization transfer experiments[18,19] are helpful. The magnetization transfer experiment is uncomplicated for each alkylidene hydride complex we have prepared here since the downfield signal for TaH is well separated from the upfield signal for H_α.

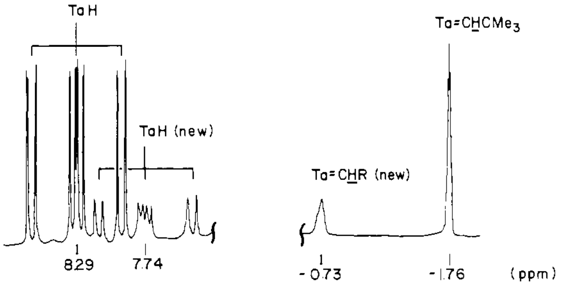
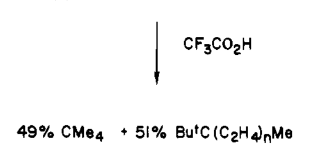
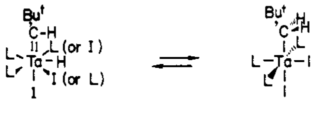


Figure 1. The partial 270-MHz ^1H NMR spectrum of a sample of $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ in C_6D_6 after reaction with 1 equiv of ethylene in toluene at 0 °C.

Scheme I. Results of an ^1H NMR and Protonolysis Experiment Using 0.41 mmol of Catalyst and 2 Equiv of Ethylene



We begin to observe magnetization transfer at ~315–320 K in the five complexes examined (Chart I). The minimum temperature at which the rate of exchange of TaH with H_α becomes sufficiently rapid to transfer magnetization is virtually the same in each case, i.e., *relatively* insensitive to whether the complex is cationic or neutral or to the identity of other ligands. Therefore, the exchange process most likely is well-behaved and intramolecular. The most likely intermediate in the exchange process is a six-coordinate Ta(III) neopentyl complex that has a plane of symmetry which passes through the methylene carbon atom of the neopentyl group. An example is shown in eq 2. Although the exact rate of exchange can be determined by magnetization transfer techniques, qualitative results are sufficient for our purposes here; the rate of exchange is clearly faster than the rate of polymerization of ethylene by $Ta(CHCMe_3)(H)L_3I_2$ (see below). Therefore, $Ta(CH_2CMe_3)L_3I_2$ must also be considered as a possible catalyst for the polymerizaton reaction.



(2)

Reaction of $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ with Ethylene. Synthesis and Characterization of $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$. $Ta(CHCMe_3)(H)L_3I_2$ reacts rapidly with 1–5 equiv of ethylene to give a ca. 20–50% yield of a new alkylidene hydride complex, $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ (Figure 1). In the ^{13}C NMR spectrum of a similarly prepared sample a signal for the new alkylidene α-carbon atom is found at 209 ppm with $J_{CH} = 90$ Hz (cf. 221 ppm and 71 Hz in $Ta(CHCMe_3)(H)L_3I_2$). The fact that we see only "one" new alkylidene hydride complex, when in fact a mixture must be present ($n = 1, 2, 3, ...$), suggests that all chemical shifts in $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ at the field strengths employed are essentially identical for values of $n \geq 1$. This fortuitous result greatly simplifies NMR studies. The fact that $J_{CH} \approx 90$ Hz in $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ suggests that the $Ta{=}C_\alpha{-}C_\beta$ angle is smaller in $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ than it is in $Ta(CHCMe_3)(H)L_3I_2$, possibly in part because of fewer steric problems. The reaction between $Ta(CDCMe_3)(D)L_3I_2$ and ethylene was totally consistent with the formation of only $Ta[CH(CH_2CH_2)_{n-1}CH_2CD_2CMe_3](H)L_3I_2$.

Protonolysis of mixtures of $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ and $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$ ($n = 1, 2, 3, ...$) gives neopentane and $CH_3(CH_2CH_2)_nCMe_3$ in yields that can be

---

(18) Forsén, S.; Hoffman, R. A. *J. Chem. Phys.* **1964**, *40*, 1189; **1963**, *39*, 2892.

(19) Morris, G. A.; Freeman, R. *J. Magn. Reson.* **1978**, *29*, 433.

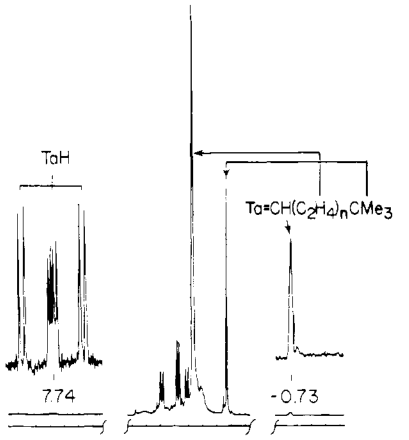


Figure 2. The 270-MHz ^1H NMR spectrum of pure $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$ ($n \approx 1-17$) in C_6D_6.

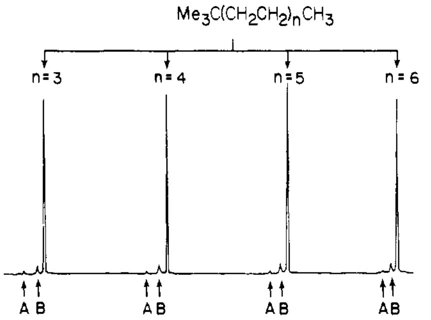


Figure 3. The partial capillary GLC trace of the organic products obtained on hydrolyzing the pentane insoluble products of the reaction of $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ in ether with excess ethylene at 0 °C for 5 min (see text).

predicted by integration of the H_α signals in the ^1H NMR spectrum of each mixture before hydrolysis. The results of a typical hydrolysis experiment are shown in Scheme I. The identity of the first four new alkanes (C_7, C_9, C_{11}, and C_{13}) were confirmed by GLC/MS studies; the mass spectra of the first two were identical with those of authentic samples. The experiment was repeated several times using different amounts of ethylene. In all cases the ^1H NMR spectrum before hydrolysis successfully predicted the relative amounts of neopentane and $CH_3(CH_2CH_2)_nCMe_3$.

Essentially pure $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ (<5% $Ta(CHCMe_3)(H)L_3I_2$) can be prepared by reacting $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ with *excess* ethylene (15 psi) in the presence of 3 equiv of PMe_3 at 0 °C. This noncrystalline "living oligomer" is soluble in pentane, ether, and aromatic solvents. It is stable in the absence of PMe_3 for several hours at 25 °C, but thereafter decomposition is marked ($t_{1/2} \approx 12$ h). Integration of the signals for the methylene protons and the *tert*-butyl protons in the ^1H NMR spectrum of $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ (Figure 2) indicates that approximately 15 equiv of ethylene are present in this sample. Magnetization transfer studies on $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ at 335 K confirmed that TaH and H_α are exchanging rapidly on the chemical time scale.

A solution of $Ta(CHCMe_3)(H)L_3I_2$ was treated with 1 atm of excess ethylene at 0 °C in the absence of PMe_3 for 5 min. The reaction mixture was then diluted with pentane and cooled to −78 °C. The resulting light green precipitate of $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ was isolated by decanting the solution away from it. The precipitate was dissolved in ether at 25 °C and hydrolyzed with 3 N HCl. The hydrolysis products were examined by capillary GLC in the range of C_{11}–C_{17} oligomers (Figure 3). The major products are the alkanes $CH_3(CH_2CH_2)_nCMe_3$. Two minor products are observed, B (~5% of each $CH_3(CH_2CH_2)_nCMe_3$ peak) and A (a trace). B is hydrogenated by Pd on charcoal; A is not. High-field ^1H NMR spectra of the hydrolysis product mixture show olefinic proton signals. Finally, $Me_3CCH_2CH{=}CH_2$ coinjects with one of the lower molecular weight B peaks. These data suggest that B is $CH_2{=}CH(CH_2CH_2)_{n-1}CH_2CMe_3$ while A is an unidentified alkane. (It is not $CH_3(CH_2CH_2)_nCH_3$.) The most plausible source of the terminal olefins are traces trapped in the green precipitate. However, a recent discovery that treatment of $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ with DCl yields alkanes having only one deuterium atom[20] suggests that an alkyl hydride complex may be formed in the first step of the protonolysis reaction, followed by reductive elimination of the alkane (Scheme II; other ligands omitted). A competitive β-hydride elimination (or direct formation of H_2 by a β-abstraction process) is a plausible means of forming traces of the terminal olefin during hydrolysis.

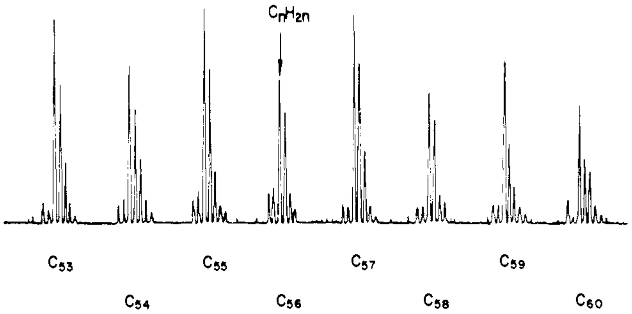
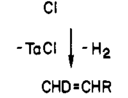


Figure 4. The partial field-desorption mass spectrum of the hydrolysis product of the polymer obtained by treating $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ with excess ethylene (1 atm) for 2 days.

Scheme II. Proposed Mechanism of Deuterolysis of $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$



$$\overset{H}{Ta}{=}CHCH_2R + DCl \longrightarrow \underset{Cl}{\overset{H}{Ta}}CHDCH_2R \xrightarrow{-TaCl} CH_2DCH_2R$$

$$\underset{Cl}{\overset{H}{Ta}}CHDCH_2R \xrightarrow{-TaCl,\ -H_2} CHD{=}CHR$$

We designed a deuterium labeling experiment in order to be certain that no significant amount of branched alkylidene hydride complexes are present. A sample of $Ta(CDCMe_3)(D)L_3I_2$ was treated with 2 equiv of CD_2CD_2 in toluene-d_8 in the absence of added PMe_3. Half of the product was hydrolyzed with HCl gas and other half with DCl gas. In the 250-MHz ^1H NMR spectrum of the organic DCl hydrolysis products only the *tert*-butyl and PMe_3 protons could be seen. In the NMR spectrum of the organic HCl hydrolysis products we observed an identical, flat base line in the region of the methylene protons. We concluded that only $CH_xD_{3-x}(CD_2CD_2)_nCMe_3$ species are present and that the living oligomer contains less than 5% branched (Ta=CRR′) alkylidene ligands. The fact that we can predict the relative amount of $CH_3(CH_2CH_2)_nCMe_3$ formed upon hydrolysis of mixtures of $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ and $Ta(CHCMe_3)(H)L_3I_2$ by integration of the Ta=C*H*R signals has been from the beginning good evidence that few Ta=CRR′ complexes (R and R′ ≠ H) are present.

Preparation of Low Molecular Weight Living Polymer and Polyethylene. When $Ta(CHCMe_3)(H)L_3I_2$ is treated with ethylene at 0 °C in toluene, a precipitate forms after approximately 15 min. After 2 days a 0.30-g sample of $Ta(CHCMe_3)(H)L_3I_2$ yielded a pale green precipitate weighing 1.05 g. The deep green filtrate absorbed little additional ethylene but a significant absorption was observed when the thoroughly rinsed pale green precipitate was suspended in toluene and exposed to ethylene at 0 °C. After 2 days the weight of the pale green precipitate had increased to 1.20 g. A sample prepared under similar conditions (20 psi ethylene, 0 °C, 10 h) analyzed for 7.00% tantalum, 67.85% carbon, and 11.61% hydrogen. A portion of this sample was treated with HCl gas in toluene to give a white polymer which

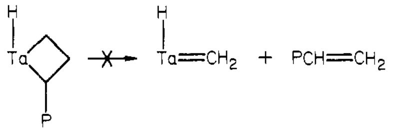
---

[20] Soto, J.; Grubbs, R., unpublished results.

was recrystallized from hot toluene and shown to be tantalum free (84.49% carbon, 14.49% hydrogen).

The field-desorption mass spectrum[21] of the white organic polymer prepared above shows a distribution of molecular ions (C_{40}–C_{200}) separated by 14 mass units. The C_{53}–C_{60} region of a typical FD mass spectrum is shown in Figure 4. The largest molecular ion in each pattern is due to an olefin, C_nH_{2n}; the M + 1 signal is assigned to the molecular ion of an olefin that contains one ^{13}C atom. The relatively high intensity of the M + 2 ion suggests that 10–20% of alkane oligomers are present in addition to the expected molecular ion of an olefin that contains two ^{13}C atoms. We interpret these results in the following manner. After several hours most of the initially formed $Ta[CH_2(CH_2CH_2)_nCMe_3](H)L_3I_2$ decomposes to give odd-carbon, *tert*-butyl-capped olefins and a tantalum hydride complex that reacts with ethylene to produce $Ta[CH_2(CH_2CH_2)_nCH_3](H)L_3I_2$. This non-*tert*-butyl-capped living oligomer also decomposes to give even-carbon olefins. Some low molecular weight living polymer of each type survives although most of the tantalum is by that time present as unreactive decomposition products (see later). Therefore, hydrolysis yields some alkanes in addition to primarily odd- and even-carbon low molecular weight olefin polymers.

In order to be certain that only the odd carbon chains contain the initial C_5 fragment, we prepared a white organic polymer by the above method from $Ta(CDCMe_3)(D)L_3I_2$ and CH_2CH_2. The FD mass spectrum of this labeled polymer in the range C_{50}–C_{60} was qualitatively the same as that shown in Figure 4 except *all the odd-carbon patterns were shifted up by two mass units.* We conclude that only the odd-carbon chains contain the five carbon atoms of the original neopentylidene ligand and, in the case of the labeling experiment, both the original deuteride ligand and the α-deuterium atom on the neopentylidene ligand. Since we do not see *tert*-butyl-capped even-carbon polymers, we can say that chain transfer does *not* consist of any significant extent of metathesis of intermediate metallacyclobutane rings (eq 3; P = polymer).



(3)

A ^1H NMR spectrum of the organic polymer in toluene at 360 K showed multiplets characteristic of terminal and internal olefinic protons at 5.00 ppm and 5.40 ppm, respectively. Integration of these signals indicates that only ~40% of the olefins are terminal. Although it is possible that the internal olefins are exclusively the 2-olefins, we think it more likely that other internal olefins are formed through isomerization reactions. As we show in the next section, the complex decomposition of the living oligomer results in isomerization of terminal olefins. Since the catalyst decomposes with time, even in the presence of ethylene, it is likely that some terminal olefins are isomerized to internal olefins during polymerization of ethylene. However, the fact that not all olefins are the thermodynamically more stable internal isomers suggests that isomerization is relatively slow.

Thermal Decomposition of the Living Oligomer. $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ slowly decomposes at room temperature ($t_{1/2} \approx 12$ h) to give a complex mixture of organic and organometallic products. A ^1H NMR spectrum of a sample in C_6D_6 that had been allowed to decompose in the absence of ethylene for 18 h at 300 K showed none of the characteristic resonances of the alkylidene hydride complex. Resonances at 5.4 and 5.0 ppm suggest the presence of terminal and internal olefins in approximately a 1:1 ratio. $Ta(PMe_3)_3I_3$ was the major identifiable inorganic product. Hydrolysis with 3 N HCl of a similar sample that had been allowed to decompose for 24 h yielded a complex mixture of organic products (Figure 5a). The percentage of new products vs. $CH_3(CH_2CH_2)_nCMe_3$ increases with retention time (~30% of C_{11} to ~200% of C_{21}). When this sample is hydrogenated, the distribution of new alkane products is greatly simplified (Figure 5b). In Figure 5c we show the product distribution in an experiment analogous to the above but in which 4,4-dimethyl-1-pentene had been added. Significant enhancement of the peaks for the new alkane products suggests that they are formed by coupling *tert*-butyl-containing olefins formed in the decomposition process with alkylidene ligands of the type $Ta{=}CH(CH_2CH_2)_nCMe_3$ to give initially various olefin isomers of compounds having primarily three different carbon backbones. Tantalum alkylidene complexes are known to react with olefins to give products of rearrangement of tantallacyclobutane intermediates in the manner shown (for example) in Scheme III.[22] Therefore, we propose that the "coupled" decomposition products arise in this fashion. It is important to note that hydrolysis of a living oligomer before decomposition produces a distribution of products which maximizes in the region C_{11}–C_{13}, while de-

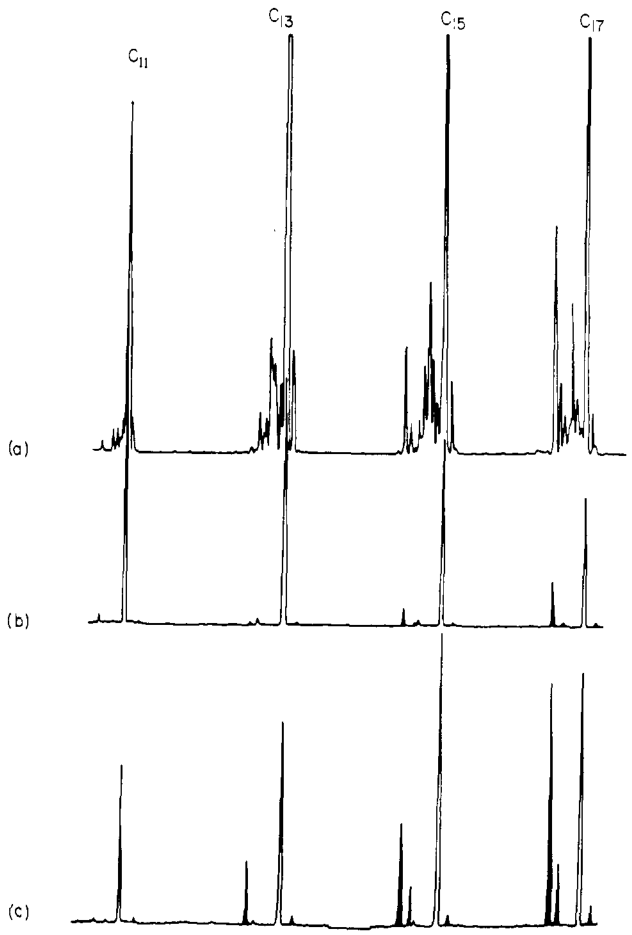
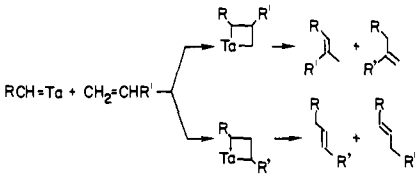


Figure 5. (a) Hydrolysis products of a decomposed sample of $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$. (b) Hydrolysis products of the sample in (a) after hydrogenation using Pd/C. (c) Hydrolyzed and hydrogenated products after decomposition of $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$ in the presence of 4,4-dimethyl-1-pentene. The filled-in peaks are ascribed to products formed by coupling $Ta[CH(CH_2CH_2)_nCMe_3]$ with $Me_3CCH_2CH{=}CH_2$ and higher terminal and internal olefins.

Scheme III



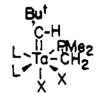
---

[21] Beckey, H. D. "Principles of Field Ionization and Field Desorption Mass Spectroscopy"; Pergamon Press: New York, 1977.

[22] Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440.

composition of this same living polymer produces a distribution of products which maximizes at approximately C_{28}. This is consistent with decomposition of the living polymer to give olefins (probably primarily terminal) which are then hydrogenated, isomerized, or coupled with remaining alkylidene ligands to give a variety of even-carbon dimers containing two *tert*-butyl groups. Such coupled products do not form to any significant extent in the presence of ethylene since ethylene reacts with the alkylidene complexes most rapidly.

Other Results Bearing on Olefin Polymerization. $Ta(CHCMe_3)(H)L_3I_2$ reacts with styrene over a period of ~12 h to give ethylbenzene and a single product which can be identified by its characteristic ^1H, ^{13}C, and ^{31}P NMR spectra as $Ta(CHCMe_3)(CH_2PMe_2)(PMe_3)_2I_2$. An analogous dichloride complex has been prepared by allowing the "equilibrium mixture"[9] of $Ta(CHCMe_3)EtL_2Cl_2$ and $Ta(C_2H_4)NpL_2Cl_2$ to decompose in solution at 25 °C in the presence of PMe_3. A dibromide complex has also been prepared by treating $Ta(CH_2CMe_3)_3Br_2$ with excess PMe_3.[23] The three are likely to have the same structure, perhaps a pentagonal bipyramid or a distorted version thereof (**4**). We postulate that styrene reacts more quickly with the hydride ligand in $Ta(CHCMe_3)(H)L_3I_2$ than it does with the neopentylidene ligand, perhaps for steric reasons, and that intermediate $Ta(CCMe_3)L_3X_2$ is formed from $Ta(CHCMe_3)(alkyl)L_2X_2$ in the presence of L, a type of α-hydrogen atom abstraction reaction that has been observed before.[14] However, the neopentylidyne α-carbon atom in $Ta(CCMe_3)L_3X_2$ is apparently so basic that a proton transfers to it from a PMe_3 ligand. An alternative, less likely possibility is that the alkyl ligand removes a proton from the methyl group of the phosphine ligand directly.



L = PMe_3, X = Cl, Br, I

4

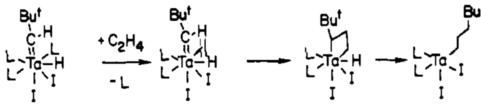
Propylene does not react readily with $Ta(CHCMe_3)(H)L_3I_2$. It reacts more readily with $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ but few oligomers are formed. NMR spectra suggest that the major organometallic product is $Ta[CH(CH_2CH_2)_nCMe_3](CH_2PMe_2)(PMe_3)_2I_2$, probably formed in a manner analogous to that which gives $Ta(CHCMe_3)(CH_2PMe_2)(PMe_3)_2I_2$ above.

There is good NMR evidence that considerable amounts of $Ta[CH(CH_2CH_2)_nCMe_3](CH_2PMe_2)(PMe_3)_2I_2$ are formed in the reaction of $Ta(CHCMe_3)(H)L_3I_3$ with ethylene, but slowly relative to the rate at which $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ forms. Evidently ethylene only occasionally reacts with the hydride ligand instead of the neopentylidene ligand in $Ta(CHR)(H)L_3I_2$ to give $Ta(CHR)EtL_2I_2$ (cf. $Ta(CHCMe_3)EtL_2Cl_2$[9]) and free L. An attempt to prepare $Ta(CHCMe_3)EtL_2I_2$ by reacting the mixture[9] containing $Ta(CHCMe_3)EtL_2Cl_2$ and $Ta(C_2H_4)(CH_2CMe_3)L_2Cl_2$ with Me_3SiI produced only unidentifiable species or, after addition of PMe_3, moderate yields of $Ta(CHCMe_3)(CH_2PMe_2)L_2I_2$. $Ta[CH(CH_2CH_2)_nCMe_3](CH_2PMe_2)(PMe_3)_2I_2$ probably is not a polymerization catalyst since $Ta(CHCMe_3)(CH_2PMe_2)(PMe_3)_2I_2$ reacts readily with ethylene to give 4,4-dimethyl-1-pentene (30%) and *trans*-4,4-dimethylpent-2-ene (70%).

$Ta(PMe_3)_3I_3$ can be prepared by reacting $Ta(C_2H_4)(PMe_3)_2I_3$ with excess PMe_3. It has characteristic signals for the two types of *mer* PMe_3 ligands at 14.5 ppm (one PMe_3) and −12.2 ppm (two PMe_3 ligands) (cf. 9.6 and −6.2 ppm for $Ta(PMe_3)_3Cl_3$ and 14.9 and −11.5 ppm for $Ta(PMe_3)_3Br_3$[17]). $Ta(PMe_3)_3I_3$ reacts with ethylene to give $Ta(C_2H_4)(PMe_3)_2I_3$. Isolated $Ta(C_2H_4)(PMe_3)_2I_3$ is not a catalyst for polymerizing ethylene under the conditions we have employed here.

We were unable to make what is one of the possible intermediates in the ethylene polymerization system, $Ta(C_2H_4)EtL_2I_2$. $Ta(C_2H_4)EtL_2I_2$ is believed to be analogous to $Ta(C_2H_4)EtL_2Cl_2$.[9] The structure of the latter is still uncertain, although the PMe_3 ligands are trans to one another. In the absence of PMe_3 $Ta(C_2H_4)EtL_2I_2$ will react with ethylene slowly to yield traces of oligomers. Examination of the reaction mixture showed that virtually all of the initial $Ta(C_2H_4)EtL_2I_2$ remained. If 1 equiv of PMe_3 is added to $Ta(C_2H_4)EtL_2I_2$ before ethylene is added, no oligomers are observed during the same time period and again only $Ta(C_2H_4)EtL_2I_2$ can be observed by ^1H NMR spectroscopy. We conclude that alkyl ethylene complexes analogous to $Ta(C_2H_4)EtL_2I_2$ cannot be intermediates in the catalytic reaction, particularly in the presence of 1 equiv of PMe_3. (It should be recalled at this point that $Ta(CHCMe_3)(H)L_3I_2$ will still react with ethylene in the presence of excess PMe_3, albeit somewhat more slowly than without any additional PMe_3 being present, to give essentially pure $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$; see above.) We believe this is some of the best evidence that the chain grows by reaction of ethylene with the alkylidene ligand in $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$, not by reaction of ethylene with the alkyl ligand in $Ta[CH_2(CH_2CH_2)_nCMe_3]L_3I_2$.

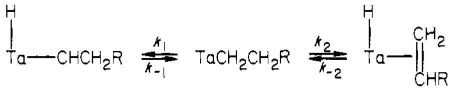
Scheme IV. The Proposed Mechanism of the Reaction between $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ and Ethylene



We have only cursorily studied the reaction between ethylene and other neopentylidene hydride complexes. $Ta(CHCMe_3)(H)L_3Cl_2$ reacts readily with ethylene to yield largely relatively low molecular weight oils. Signals which may be assigned to $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3Cl_2$ can be observed in the ^1H NMR spectra, but the reaction is clearly rather messy, presumably due to rapid catalyst decomposition. The reaction between $Ta(CHCMe_3)(H)L_3(OTf)_2$ and ethylene yields solid polymers, but apparently not as efficiently as in the case of the diiodide catalyst. Deprotonations may be a problem as $Me_3PH^+OTf^-$ has been observed to coprecipitate with the polymer. $[Ta(CHCMe_3)(H)(dmpe)_2(Cl)]^+Cl^-$ does not react with ethylene (40 psi) in 24 h at 25 °C.

Discussion

It would now seem that α-hydride elimination will be the norm when the d^2 metal is one for which d^0 alkylidene or alkylidyne complexes are known[11] (Nb, Ta, Mo,[24] W,[25,26] Re[27]) and when the alkyl ligand does not contain β-hydrogen atoms. It has always been assumed that if β-hydrogen atoms are present, then β-hydride elimination will be faster than α-hydride elimination. What we have discovered in this work is the first example of a preference for α elimination over β elimination. That is not to say that α elimination is necessarily faster ($k_1 > k_2$ in eq 4). It is quite



$$\overset{H}{\overset{|}{Ta}}\!-\!CHCH_2R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TaCH_2CH_2R \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \overset{H}{\overset{|}{Ta}}\!-\!\begin{matrix} CH_2 \\ \| \\ CHR \end{matrix} \qquad (4)$$

possible that $k_1 < k_2$ even though $K_1 > K_2$, as long as the olefin hydride complex does not decompose rapidly or react readily with ethylene. If k_1 *is* greater than k_2, the reason might be that the coordination sphere is crowded enough in the Ta(III) alkyl intermediate to prevent the metal from interacting with a β-hydrogen atom, while at the same time encouraging the metal to interact with an α-hydrogen atom by increasing the Ta–C_α–C_β angle

---

(23) Rupprecht, G. A. Ph.D. Thesis, Massachusetts Institute of Technology, 1979.

(24) McCullough, L., unpublished results.

(25) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

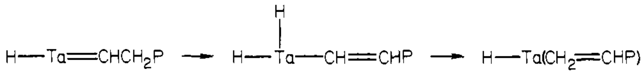
(26) (a) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645. (b) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Ibid.* **1982**, *1*, 1332. (c) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483.

(27) Edwards, D. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6806.

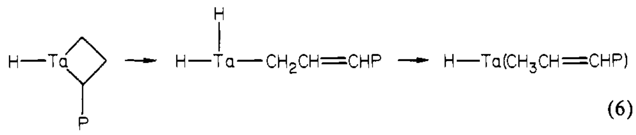
beyond what it would normally be. The stability of $Cr(CMe_3)_4$, a d^2 complex, has been ascribed to a related steric blockage of β-hydride elimination.[28]

The proposed mechanism by which $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ reacts with ethylene to give $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$ is shown in Scheme IV. Loss of one of the PMe_3 ligands as the first step is suggested by the slower rate of reaction of $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ with ethylene in the presence of added PMe_3. The fact that almost pure $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$ can be isolated under these conditions is consistent with the proposal that for steric reasons one PMe_3 ligand is more labile in $Ta(CHCMe_3)(H)L_3I_2$ than in $Ta[CH(CH_2CH_2)_nCMe_3](H)L_3I_2$. It is logical to assume that the ethylene replaces the same PMe_3 ligand that Cl^- replaces in $Ta(CHCMe_3)(H)L_3I_2$ or that pyridine replaces in $Ta(CHCMe_3)(H)L_3(OTf)_2$, i.e., the one adjacent to the hydride ligand. A tantallacyclobutane ring then forms and is subsequently opened when the hydride adds to the substituted α-carbon atom. α-Hydride elimination and readdition of PMe_3 forms (after some molecular rearrangement) $Ta(CHCH_2CH_2CMe_3)(H)L_3I_2$.

There are three plausible ways to transfer the polymer chain. One is β-hydride elimination in $Ta(CH_2CH_2P)L_xI_2$ (P = polymer, x probably 2). A second is rearrangement of an alkylidene ligand (eq 5). A third is rearrangement of a tantallacycle (e.g., eq 6).



$$H{-}Ta{=}CHCH_2P \longrightarrow H{-}\overset{H}{\overset{|}{Ta}}{-}CH{=}CHP \longrightarrow H{-}Ta(CH_2{=}CHP) \qquad (5)$$



(6)

The latter two possibilities have been demonstrated in previous studies of how *trans*-$Ta(CHCMe_3)(PMe_3)_2Cl_3$ reacts with terminal olefins.[22] In all three cases the olefin would be displaced by ethylene to form an ethylene hydride complex which would then be transformed into an ethylidene hydride complex via a Ta(III) ethyl intermediate. An interesting possible alternative way to terminate the chain is to lose a terminal olefin from a tantallacyclobutane hydride complex to produce a methylene hydride complex. This pathway cannot be entirely excluded but must be a relatively minor one for reasons discussed in the Results.

The proposal that it is "$Ta(CHP)(H)L_2I_2$" rather than "$Ta(CH_2P)L_2I_2$" that reacts with ethylene rests on the fact that $Ta(C_2H_4)EtL_2I_2$ can be isolated and that it is catalytically relatively inactive, especially in the presence of 1 equivalent of PMe_3. There is no way to exclude the possibility at this time that "$Ta(CH_2P)L_2I_2$" reacts with ethylene to give intermediate $Ta(C_2H_4)(CH_2P)L_2I_2$ with a structure that is different from that observed for $Ta(C_2H_4)EtL_2I_2$ or that a particular isomer of $Ta(CH_2R)L_3I_2$ reacts readily with ethylene to give $Ta(CH_2CH_2CH_2P)L_3I_2$, each of which would be viewed as a classical "insertion" of ethylene into the Ta–alkyl bond. But we know that α elimination is rapid on the time scale of ethylene polymerization and that alkylidene ligands in labile octahedral d^0 tantalum alkylidene complexes react rapidly with terminal olefins.[22] Therefore we feel that the evidence favors the mechanism shown in Scheme IV.

Experimental Section

General Procedures. All experiments were performed either with use of Schlenk techniques (under argon) or in a Vacuum Atmospheres HE43-2 drybox (under N_2). Solvents were rigorously purified and dried under N_2. ^1H and ^{13}C NMR chemical shifts (in ppm) are referenced to tetramethylsilane and ^{31}P NMR chemical shifts to phosphoric acid. Coupling constants are reported in hertz; CH couplings were obtained from the gated ^1H decoupled spectra. Ethylene was polymerization grade (Phillips). Reagents were obtained from standard sources except where noted.

Preparations. **$[Ta(CHCMe_3)(H)(dmpe)_2Cl]^+CF_3CO_2^-$.** Trifluoroacetic acid (0.2 g, 1.7 mmol) was added to an ether solution of $Ta(CHCMe_3)(dmpe)_2Cl$[5] (1.0 g, 1.7 mmol) at −30 °C. The resulting white powder was recrystallized from a mixture of ether and dichloromethane to give 0.9 g of $[Ta(CHCMe_3)(H)(dmpe)_2Cl]^+CF_3CO_2^-$ as ivory plates: ^1H NMR ($CDCl_3$) δ 6.95 (t, 1, $^2J_{HP} = 78$, TaH), 2.00 (br m, 8, PCH_2CH_2P'), 1.94, 1.86, 1.69, 1.49 (each a d, 6, $^2J_{HP} = 8$–9, PMe groups), 0.89 (s, 9, $CHCMe_3$), −4.92 (m, 1, $CHCMe_3$); the spectrum of a sample at 223 or 323 K is identical; ^{13}C NMR ($CDCl_3$) δ 218.4 (br d, $^1J_{CH} = 65$, $CHCMe_3$), 159.9 (q, $^2J_{CF} = 32$, O_2CCF_3), 117.3 (q, $^1J_{CF} = 298$, O_2CCF_3), 47.0 (s, $CHCMe_3$), 33.1 (s, $^1J_{CH} = 124$, $CHCMe_3$), 22.9 (tm, $^1J_{CH} = 122$, PCH_2CH_2P'), 25.3 (tm, $^1J_{CH} = 122$, PCH_2CH_2P'), 20.7, 16.4, 15.4, 11.5 (each a q, $^1J_{CH} \approx 127$, four PMe groups); $^{31}P\{^1H\}$ NMR ($CHCl_3$) δ 33.7 (m), 12.2 (m); IR (Nujol) 2280 (ν_{CH_α}), 1680 cm^{-1} (ν_{TaH}).

$[Ta(CHCMe_3)(H)(dmpe)_2(Cl)]^+Cl^-$. This compound is prepare straightforwardly by using HCl gas in a manner similar to that used to prepare $[Ta(CHCMe_3)(dmpe)_2(Cl)]^+CF_3CO_2^-$ above: ^1H NMR ($CDCl_3$) δ 6.33 (t, 1, $^2J_{HP} = 78$, TaH), 2.07 (m, 8, PCH_2CH_2P'), 1.93, 1.87, 1.67, 1.50 (each a d, 6, $^2J_{HP} = 8$–9, PMe groups), 0.85 (s, 9, $CHCMe_3$), −4.95 (m, 1, $CHCMe_3$); ^{13}C NMR ($CDCl_3$) δ 217.7 (d, $^1J_{CH} = 70$, $CHCMe_3$), 46.61 (s, $CHCMe_3$), 32.73 (q, $^1J_{CH} = 126$, $CHCMe_3$), 29.49 (tm, $^1J_{CH} = 125$, PCH_2CH_2P'), 25.07 (tm, $^1J_{CH} = 125$, PCH_2CH_2P'), 20.45, 16.12, 15.06, 11.12 (each a q, $^1J_{CH} = 127$, PMe groups); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 34.3 (m), 13.1 (m); IR (Nujol) 2280 (ν_{CH_α}), 1660 cm^{-1} (ν_{TaH}).

$Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(H)(Cl)(PMe_3)$. $Ta(C_5Me_5)(CH_2CMe_3)Cl_3$[29] (3.0 g, 6.1 mmol) was added as a solid to 60 mL of a 1:1 mixture of tetrahydrofuran and ether containing PMe_3 (0.7 ml, 7.3 mmol, excess), sodium amalgam (0.41%, 68.2 g, 12.2 mmol), and 10 mg of naphthalene. The reaction mixture was stirred vigorously for 3 h, filtered through Celite, and stripped. The residue was extracted with pentane (25 mL), and the mixture was filtered. After the filtrate was treated wth Darco, the solvent was removed in vacuo to give a red oil which was >90% $Ta(C_5Me_5)(CHCMe_3)(H)(Cl)(PMe_3)$ by ^1H NMR spectroscopy. The crude product was dissolved in a minimal amount of pentane (~3 mL). After the solution was left standing for 24 h at −30 °C, oily yellw plates (0.9 g) of pure $Ta(C_5Me_5)(CHCMe_3)(H)(Cl)(PMe_3)$ were isolated by decanting away the mother liquor (30% yield): ^1H NMR (toluene-d_8, −30 °C) δ 7.53 (dd, 1, $^3J_{HH_\alpha} = 1.8$, $^3J_{PH} = 74$, TaH), 2.44 (d, 1, $J_{HH_\alpha} = 1.8$, $CHCMe_3$), 2.09 (s, 15, C_5Me_5), 1.18 (d, 9, $^2J_{PH} = 7.3$, PMe_3), 1.11 (s, 9, $CHCMe_3$); ^{13}C NMR (toluene-d_8, −30 °C) δ 232.4 (dd, $^2J_{CP} = 6.5$, $^1J_{CH} = 72$, $CHCMe_3$), 112.1 (s, C_5Me_5), 47.4 (s, $CHCMe_3$), 33.4 (q, $^1J_{CH} \approx 122$, $CHCMe_3$), 18.4 (qd, $^1J_{CP} = 26$, $^1J_{CH} \approx 125$, PMe_3), 13.0 (q, $^1J_{CH} = 130$, C_5Me_5); ^{31}P NMR (C_6D_6) δ −14.9 (d, $^2J_{PH} = 71$); IR (Nujol/NaCl) 2525 (w, ν_{CH}), 1730 cm^{-1} (m, ν_{TaH}).

$Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$. Freshly recrystallized $Ta(CH_2CMe_3)Cl_4$[29] (1.97 g, 5.00 mmol) was added as a solid to 40 mL of ether which had been cooled to −30 °C and which contained sodium amalgam (0.41%, 56.1 g, 10.0 mmol) and PMe_3 (2.4 mL, 25 mmol). The solution was stirred vigorously as it was warmed to 25 °C. The color changed from red (initially) to green and finally to beige over a period of 20 min. After 12 h, the reaction mixture was filtered through Celite, and the solvent was removed in vacuo. The residue was extracted with ether (~150 mL), and the extract was filtered. Pure product (1.38 g) was obtained upon concentrating the filtrate *in vacuo* to ~20 mL. The volume of the filtrate was reduced in vacuo to ~10 mL, and the sample was kept at −30 °C for 48 h. The mother liquor was decanted away from 0.2 g of additional $Ta(CHCMe_3)(H)Cl_2(PMe_3)_3$ (57% total yield): ^1H NMR ($C_6D_5CD_3$) δ 10.00 (ddd, 1, $^3J_{HH_\alpha} = 1.5$, $^2J_{HP_A} = 18$, $^2J_{HP_B} = 102$, $^2J_{HP_C} = 91$, TaH), 1.52, 1.38, and 1.26 (each a d, 9, $^2J_{HP} = 7$–9, three PMe_3 ligands), 0.97 (s, 9, $CHCMe_3$), 0.24 (br, 1, $^3J_{HH_\alpha} = 1.5$, $CHCMe_3$); ^{13}C NMR ($C_6D_6CD_3$) δ 216.0 (d of octet, $^2J_{CP} = 6.4$, $^1J_{CH} = 72$, $CHCMe_3$), 46.2 (s, $CHCMe_3$), 34.1 (q, $^1J_{CH} = 124$, $CHCMe_3$), 22.8, 18.8, 16.3 (each a qd, $^1J_{CP} \approx 25$, $^1J_{CH} \approx 130$, three PMe_3 ligands); ^{31}P NMR ($C_6D_5CD_3$) δ −4.1 (8-line pattern, $^2J_{HP_C} = 91$, $^2J_{P_AP_C} = 115$, $^2J_{P_BP_C} = 50$, PMe_3(C)), −17.5 (8-line pattern, $^2J_{HP_B} = 101$, $^2J_{P_AP_B} = 29$, $^2J_{P_CP_B} = 51$, PMe_3(B)), −26.5 (8-line pattern, $^2J_{HP_A} = 17$, $^2J_{P_BP_A} = 29$, $^2J_{P_CP_A} = 115$, PMe_3(A)); IR (Nujol/NaCl) 2440 (m, ν_{CH_α}), 1730 cm^{-1} (m, ν_{TaH}). Anal. Calcd for $TaC_{14}H_{38}Cl_2P_3$: C, 30.51; H, 6.95. Found: C, 30.37; H, 7.01.

$Ta(CDCMe_3)(D)(PMe_3)_3Cl_2$. $Ta(CDCMe_3)(D)Cl_2(PMe_3)_3$ was prepared as above from $Ta(CD_2CMe_3)Cl_4$ (1.98 g, 5.00 mmol) in ~30 mL of a mixture of ether and THF (3:2) containing sodium amalgam (0.41%, 56.1 g, 10.0 mmol) and PMe_3 (2.4 mL, 25 mmol). $Ta(CDCMe_3)(D)(PMe_3)_3Cl_2$ (1.3 g) was obtained in 47% yield: IR (Nujol/NaCl) 1805 (m, ν_{CD_α}), 1270 cm^{-1} (m, ν_{TaD}).

---

[28] Kruse, W. *J. Organomet. Chem.* **1972**, *42*, C39.

[29] Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.

Ta(CXCMe$_3$)(X)(PMe$_3$)$_3$Cl$_2$ (X = H or D). Ta(CHDCMe$_3$)Cl$_4$ (1.98 g, 5.00 mmol) was stirred with sodium amalgam (0.41%, 56.1 g, 10.0 mmol) and PMe$_3$ (2.4 mL, 25 mmol) in a mixture of ether and tetrahydrofuran (~30 mL) for 1.5 h. Ta(CXCMe$_3$)(X)Cl$_2$(PMe$_3$)$_3$ (X = H or D) was isolated by the above procedure in 41% yield (1.14 g).

Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$. Me$_3$SiI (2.28 g, 11.40 mmol) was added to a solution of Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$Cl$_2$ in toluene (20 mL). After 2 h the solvents were removed in vacuo and the residue was recrystallized from a mixture of toluene and pentane to give 3.5 g (88% yield) of yellow-green microcrystals: ^{1}H NMR (C$_6$D$_6$) δ 8.29 (dddd, 1, $^2J_{HP}$ = 18, 92, 104, $^3J_{HH_\alpha}$ = 1.5, TaH), 1.82, 1.54, 1.51 (each a d, 9, $^2J_{HP} \approx 8$, three PMe$_3$ ligands), 0.95 (s, 9, CHC*Me*$_3$), −1.79 (m, 1, C*H*CMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 221.1 (d, $^1J_{CH}$ = 71, *C*HCMe$_3$), 46.7 (s, CH*C*HMe$_3$), 32.9 (s, $^1J_{CH}$ = 127, CHC*Me*$_3$), 25.4, 23.2, 19.3 (each a q, $J_{CH} \approx 130$, PMe$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ −29.0 (m), −43 (m); IR (Nujol) 2420 (ν_{CH_α}), 1800 cm^{-1} (ν_{TaH}). Anal. Calcd for TaC$_{14}$H$_{38}$I$_2$P$_3$: C, 22.90; H, 5.18. Found: C, 22.44; H, 5.24.

Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$(OTf)$_2$. Me$_3$SiOTf (1.70 g, 7.60 mmol) was added to a solution of Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$Cl$_2$ (2.00 g, 3.60 mmol) in toluene (20 mL). After 2 h the precipitate was filtered off and recrystallized from a mixture of dichloromethane and ether to give 2.2 g (80%) of white needles: ^{1}H NMR (CD$_2$Cl$_2$) δ 11.0 (dddd, 1, $^2J_{HP}$ = 16, 85, 105, $^3J_{HH}$ = 2, TaH), 1.76, 1.64, 1.58 (each a d, 9, $^2J_{HP} \approx 8$, three PMe$_3$ ligands), 1.12 (s, 9, CHC*Me*$_3$), −3.5 (m, 1, C*H*CMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 238.3 (d, $^1J_{CH}$ = 66, *C*HCMe$_3$), 120.1 (q, $^1J_{CF}$ = 319.8, O$_3$SCF$_3$), 119.82 (s, $^1J_{CF}$ = 317, O$_3$SCF$_3$), 18.61, 16.36 (q, $^1J_{CH} \approx 133$, three PMe$_3$ ligands); ^{31}P NMR (CH$_2$Cl$_2$) δ −2.09 (br d, $^2J_{PH}$ = 95), −14.40 (br m); IR (Nujol) 2300 (ν_{CH_α}), 1770 cm^{-1} (ν_{TaH}); conductivity (CH$_2$Cl$_2$, 1.82 × 10^{-3} M) 8.24 cm^{-1} M^{-1} Ω^{-1}. Anal. Calcd for TaC$_{18}$H$_{42}$P$_4$O$_3$SCF$_3$: C, 30.65; H, 6.00. Found: C, 30.56; H, 6.08.

Ta(CHCMe$_3$)(H)(PMe$_3$)$_2$(py)(OTf)$_2$. Pyridine (0.23 g, 2.9 mmol) was added to Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$(OTf)$_2$ (1.50 g, 1.93 mmol) dissolved in dichloromethane. After 2 h in the reaction mixture was evaporated to dryness, and the residue was recrystallized from a mixture of dichloromethane and ether to give 1.3 g of light yellow needles (86% yield): ^{1}H NMR (CD$_2$Cl$_2$) δ 11.95 (dd, 1, $^2J_{HP}$ = 85, 78, TaH), 7.8–7.1 (m, 5, C$_5$H$_5$N), 1.58 (d, 9, $^2J_{HP}$ = 8, PMe$_3$′), 1.27 (d, 9, $^2J_{HP}$ = 8, PMe$_3$″), 1.09 (s, 9, CHC*Me*$_3$), −2.28 (m, 1, C*H*CMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 236.4 (d, $^1J_{CH}$ = 66, *C*HCMe$_3$), 140.5 (d, $^1J_{CH}$ = 165, py), 125.7 (d, J = 165, py), 120.5 (q, $^1J_{CF}$ = 305, O$_3$SCF$_3$), 49.3 (s, CH*C*Me$_3$), 33.4 (q, $^1J_{CH}$ = 126, CHC*Me*$_3$), 19.0 (q, $^1J_{CH}$ = 125, PMe$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$, 310 K) δ 3.57 (s); ^{31}P NMR (CDCl$_3$, 310 K) δ 3.57 (d, $^2J_{PH}$ = 83).

[NEt$_4$][Ta(CHCMe$_3$)(H)(PMe$_3$)$_2$Cl$_3$]. Tetraethylammonium chloride (1.0 g) was added to Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$Cl$_2$ (3.35 g, 6.10 mmol) in tetrahydrofuran (20 mL), and the mixture was stirred for 2 h. The solution was evaporated to dryness and the residue recrystallized from a mixture of toluene and pentane to give 2.8 g of tan plates (71% yield): ^{1}H NMR (C$_6$D$_6$) δ 11.36 (t, 1, $^2J_{HP}$ = 8.50, TaH), 2.91 (q, 8, $^2J_{HH}$ = 7, (CH$_3$C*H*$_2$)$_4$N), 1.81 (t, 18, $^2J_{HP}$ = 3.4, PMe$_3$), 1.26 (s, 9, CHC*Me*$_3$), 0.93 (t, 12, $^2J_{HH}$ = 7, (C*H*$_3$CH$_2$)$_4$N), 0.85 (m, 1, C*H*CMe$_3$); ^{13}C NMR (C$_6$D$_6$/C$_6$D$_5$Br) δ 212.5 (d, $^1J_{CH}$ = 86, *C*HCMe$_3$), 53.1 (t, $^1J_{CH}$ = 145, (CH$_3$*C*H$_2$)$_4$N), 45.5 (s, CH*C*Me$_3$), 34.6 (s, J_{CH} = 127, CHC*Me*$_3$), 19.8 (q, $^1J_{CH}$ = 129, PMe$_3$), 8.2 (q, $^1J_{CH}$ = 129, (*C*H$_3$CH$_2$)$_4$N); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ −4.6 (s); ^{31}P NMR (C$_6$D$_6$) δ −4.6 (br d, $^2J_{PH}$ = 85); IR (Nujol) 2470 (w, ν_{CH_α}), 1760 cm^{-1} (s, ν_{TaH}). Anal. Calcd for TaC$_{19}$H$_{49}$P$_2$Cl$_3$N: C, 35.61; H, 7.65. Found: C, 36.02; H, 8.25.

Ta(CHCMe$_3$)(CH$_2$PMe$_2$)(PMe$_3$)$_2$Cl$_2$. A sample of the "equilibrium mixture" of Ta(CHCMe$_3$)(CH$_2$CH$_3$)(PMe$_3$)$_2$Cl$_2$ and Ta(CH$_2$CMe$_3$)(CH$_2$CH$_2$)(PMe$_3$)$_2$Cl$_2$ (5.0 g, 9.9 mmol) was dissolved in toluene, and PMe$_3$ (1.50 g, 20 mmol) was added. After 24 h the solvent was removed in vacuo, and the crude product was recrystallized from ether to give off-white microcrystals (3.2 g, 64%): ^{1}H NMR (C$_6$H$_6$) δ 1.54 (d, 3, $^1J_{HP} \approx 10$, CH$_2$P*Me*Me′), 1.50, 1.45 (each a d, 9, $^1J_{HP} \approx 8$, PMe$_3$), 1.40 (d, 3, $^1J_{HP} \approx 10$, CH$_2$PMe*Me*′), 0.87 (s, 9, CHC*Me*$_3$), −0.41 (br m, 1, C*H*CMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 227.2 (d, $^1J_{CH}$ = 68, *C*HCMe$_3$), 46.6 (s, CH*C*Me$_3$), 32.9 (q, J_{CH} = 128, CHC*Me*$_3$), 17.8 (q, $^1J_{CH}$ = 127, PMe$_3$), 16.0 (q, $^1J_{CH}$ = 126, PMe$_3$′), 14.5 (m, *C*H$_2$PMe$_2$), 14.2 (q, $^1J_{CH}$ = 125, CH$_2$P*Me*Me′), 9.6 (q, $^1J_{CH}$ = 130, CH$_2$PMe*Me*′).

Ta(CHCMe$_3$)(CH$_2$PMe$_2$)(PMe$_3$)$_2$I$_2$. (a) From Ta(CHCMe$_3$)(CH$_2$PMe$_2$)(PMe$_3$)$_2$Cl$_2$. Ta(CHCMe$_3$)(CH$_2$PMe$_2$)(PMe$_3$)$_2$Cl$_2$ (0.70 g, 1.30 mmol) was dissolved in toluene, and Me$_3$SiI (0.55 g, 2.70 mmol) was added. After 4 h the solution was evaporated to dryness, and the crude product was recrystallized from ether to give 0.80 g of yellow-green crystals (84% yield): ^{1}H NMR (C$_6$D$_6$) δ 1.80, 1.74 (each a d, 9, $^1J_{HP} \approx 8$, PMe$_3$), 1.64 (d, $^1J_{HP} \approx 11$, PMe$_3$ and CH$_2$P*Me*Me′), 1.28 (d, 3, $^1J_{HP} \approx 11$, CH$_2$PMe*Me*′), 0.84 (s, 9, CHC*Me*$_3$), −2.13 (br d, 1, $J_{HP} \approx 8$, C*H*CMe$_3$); signals due to the methylene protons of the CH$_2$PMe$_2$ ligand could not be identified; ^{31}P{^{1}H} NMR (C$_6$H$_6$) δ −33.5 (m), −40.3 (m), −63.9 (m).

(b) From Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$. Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$ (0.05 g, 0.07 mmol) and styrene (0.013 g, 0.13 mmol) were dissolved in benzene-d_6 in a 5-mm NMR tube. Signals due to ethyl benzene and Ta(CHCMe$_3$)(CH$_2$PMe$_2$)(PMe$_3$)$_2$I$_2$ grew in over a period of 12 h. The solvent was removed in vacuo. A ^{1}H NMR spectrum of nonvolatile components showed only signals due to Ta(CHCMe$_3$)(CH$_2$PMe$_2$)(PMe$_3$)$_2$I$_2$.

Ta[CH(CH$_2$CH$_2$)$_n$CMe$_3$](H)(PMe$_3$)$_3$I$_2$ (*n* = 0, 1, 2, ..., 20). Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$ (0.50 g, 0.68 mmol) was dissolved in toluene containing PMe$_3$ (0.20 g, 2.64 mmol), and the mixture was stirred under ethylene (15 psi) at 0 °C for 5 h. All volatile components were removed in vacuo, yielding 0.51 g of a toluene-soluble green oil, the ^{1}H NMR spectrum of which showed it to consist of >95% Ta[CH(CH$_2$CH$_2$)$_n$CMe$_3$](H)(PMe$_3$)$_3$I$_2$ and <5% Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$: ^{1}H NMR (C$_6$D$_6$) δ 7.72 (m, 1, TaH), 1.75, 1.56, 1.45 (each a d, 9, $J_{HP} \approx 8$, three PMe$_3$ ligands), 1.35 (br s, 40, CH$_2$ groups) 0.90 (s, 9, CMe$_3$), −0.77 (br s, 1, =C*H*R); selective irradiation (345 K) of the signal centered at δ −0.77 caused complete collapse of the multiplet at 7.72 ppm; ^{31}P{^{1}H} NMR (C$_6$H$_6$) δ −29.0 (m, AB part of ABX pattern), −43.0 (m, X part); ^{13}C NMR (C$_6$D$_6$) δ 208.9 (d, $^1J_{CH}$ = 90, *C*H(CH$_2$CH$_2$)$_n$CMe$_3$), 30.2 (9, $^1J_{CH}$ ~ 125, CH(CH$_2$CH$_2$)$_n$C*Me*$_3$), 30.2 (t, $^1J_{CH}$ = 125, CH(*C*H$_2$*C*H$_2$)$_n$CMe$_3$), 25.3, 23.4, 19.5 (all quartets with $^1J_{CP} \approx 128$, PMe$_3$).

Mass Balance Experiments. Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$ (0.30 g, 0.41 mmol) was dissolved in toluene and 2,2-dimethylbutane (0.18 g, 0.20 mmol) followed by 1–2 equiv of ethylene with use of standard vacuum line techniques. After 2 h, a sample was removed, and a 250-MHz ^{1}H NMR spectrum was recorded. It showed 52% of starting material and 48% of a new alkylidene hydride complex. The remaining reaction mixture was hydrolyzed by using 0.7 equiv of CF$_3$CO$_2$H. The volatile organic products were passed down to a short alumina column and analyzed on a 100/120 Gas Chrom Q column. The hydrolysis products consisted of neopentane (0.17 mmol), 2,2-dimethylpentane (0.05 mmol), 2,2-dimethylheptane (~0.02 mmol), 2,2-dimethylnonane (0.05 mmol), 2,2-dimethylundecane (0.05 mmol), and 2,2-dimethyltridecane (0.02 mmol). The quantity of 2,2-dimethylheptane is inaccurate due to the overlap of the peak with the toluene peak. the identity of the first four oligomers was confirmed by GLC/mass spectroscopy. This experiment was repeated several times by using different amounts of ethylene, and in all cases the ^{1}H NMR spectrum (before hydrolysis) successfully predicted the amounts of neopentane and higher alkanes in the hydrolysis product mixture.

Ta(C$_2$H$_4$)(PMe$_3$)$_2$I$_3$. Ta(CHCMe$_3$)(PMe$_3$)$_2$I$_3$ (3.0 g, 3.8 mmol; prepared by treating Ta(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$[30] with 3 equiv of Me$_3$SiI) was dissolved in 10 mL of toluene, and the solution was exposed to 30 psi of ethylene for 1 day. The toluene was removed in vacuo, and the green-brown residue was recrystallized from dichloromethane by adding ether and cooling to −30 °C for 1 day (total yield 2.5 g, 88%): ^{1}H NMR (C$_6$D$_6$) δ 3.10 (t, 4, $^1J_{HP}$ = 2.5, C$_2$H$_4$), 1.81 (virtual t, 18, $^1J_{HP} \approx 4$, PMe$_3$); ^{13}C NMR (CDCl$_3$) δ 67.9 (t, $^1J_{CH}$ = 154, C$_2$H$_4$), 20.3 (tq, $^1J_{CP}$ = 14.5, $^1J_{CH}$ = 131, PMe$_3$); ^{31}P NMR (C$_6$D$_6$) δ −13.2 (s). Anal. Calcd for TaC$_8$H$_{22}$I$_3$P$_2$: C, 12.94; H, 2.98. Found: C, 12.98; H, 3.08.

Ta(PMe$_3$)$_3$I$_3$. A mixture of Ta(C$_2$H$_4$)(PMe$_3$)$_2$I$_3$ (1.04 g, 1.40 mmol), and PMe$_3$ (0.67 ml, 7 mmol) in 20 mL in toluene in a flask equipped with a dry ice condenser was refluxed for 8 h. The yellow-brown solution was filtered, and all solvents were removed from the filtrate in vacuo. The residue was recrystallized from THF (2 mL) by adding ether (3 mL) and cooling to −30 °C for 1 day to give 0.51 g of brown-black crystals (46% yield): ^{1}H NMR (C$_6$D$_6$) δ 14.5 (br s, 9, PMe$_3$), −12.2 (br s, 18, 2 PMe$_3$). Anal. Calcd for TaC$_9$H$_{27}$I$_3$P$_3$: C, 13.68; H, 3.42. Found: C, 14.03; H, 3.39.

Exposing a solution of Ta(PMe$_3$)$_3$I$_3$ to ethylene at 30 psi produces Ta(C$_2$H$_4$)(PMe$_3$)$_2$I$_3$ quantitatively. Treatment of the solution after 16 h with CF$_3$CO$_2$H and analysis of the volatile components by GLC showed no evidence of any ethylene oligomers.

Ta(C$_2$H$_4$)Et(PMe$_3$)$_2$I$_2$. Ta(C$_2$H$_4$)Et(PMe$_3$)$_2$Cl$_2$[22] (1.5 g, 3.25 mmol) and Me$_3$SiI (2 g, 10 mmol) were combined in 30 mL of toluene. After 3.5 h the volatile components were removed from the green solution in vacuo. The residue was redissolved in 30 mL of toluene and treated two more times with 2 g of Me$_3$SiI for 3 h. The second time the solution was concentrated to 2 mL and 3 mL of ether added. After the mixture had stood for 1 day at −30 °C, 0.8 g (38%) of pure, green, crystalline Ta(C$_2$H$_4$)Et(PMe$_3$)$_2$I$_2$ was filtered off: ^{1}H NMR (C$_6$D$_6$) δ 2.11 (br m, 2, C$_2$*H*$_2$H′$_2$), 1.62 (virt t, 18, PMe$_3$), 1.20 (br m, 2, C$_2$H$_2$*H*′$_2$), 0.02 (m, 3, TaCH$_2$C*H*$_3$), −2.05 (br q, J_{HH} = 7.8, TaC*H*$_2$CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 75.8 (t, J_{CH} = 133, Ta*C*H$_2$CH$_3$), 60.3 (t, J_{CH} = 151, C$_2$H$_4$), 17.4 (virt t of q, J_{CP} = 14, J_{CH} = 129, PMe$_3$), 2.9 (q, J_{CH} = 124, TaCH$_2$*C*H$_3$); ^{31}P NMR (toluene) δ −24.3 (s). Anal. Calcd for TaC$_{10}$H$_{27}$I$_2$P$_2$: C, 18.63;

---

(30) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

4950 *J. Am. Chem. Soc.* **1983**, *105*, 4950–4954

H, 4.19. Found: C, 18.94; H, 4.19.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 81-21282 to R.R.S.) and, in part, the National Institutes of Health (Research Grant RR00317 to Professor Klaus Biemann). We thank Dr. Catherine Costello for obtaining FD mass spectra, Professor Satoru Masamune for use of his capillary GLC equipment, and Professor Robert H. Grubbs for permission to quote unpublished results.

Registry No. **1**$^+$$CF_3CO_2^-$, 86024-14-8; **1**$^+$$Cl^-$, 86024-15-9; **2** (X = Cl), 86087-44-7; **2** (X = I), 86087-47-0; **3**, 86024-18-2; **4** (X = Cl), 86024-24-0; **4** (X = I), 86045-49-0; $TaCp^*(CHCMe_3)(H)(Cl)(PMe_3)$, 86087-43-6; $Ta(CDCMe_3)(D)(PMe_3)_3Cl_2$, 86087-45-8; $Ta(CHCMe_3)(D)(PMe_3)_3Cl_2$, 86024-16-0; $Ta(CDMe_3)(H)(PMe_3)_3Cl_2$, 86087-46-9; $Ta(CHCMe_3)(H)(PMe_3)_2(py)(OTF)_2$, 86024-20-6; $[NEt_4][Ta(CHCMe_3)(H)(PMe_3)_2Cl_3]$, 86024-23-9; $Ta(C_2H_4)(PMe_3)_2I_3$, 86024-25-1; $Ta(PMe_3)_3I_3$, 86024-26-2; $Ta(C_2H_4)Et(PMe_3)_2I_2$, 86024-27-3; $Ta(CHCMe_3)(dmpe)_2Cl$, 80559-92-8; $Ta(C_5Me_5)(CH_2CMe_3)Cl_3$, 68087-41-2; $Ta(CH_2CMe_3)Cl_4$, 71201-79-1; $Ta(CD_2CMe_3)Cl_4$, 75349-01-8; $Ta(CHDMe_3)Cl_4$, 86024-28-4; $Ta(CHCMe_3)(CH_2CH_3)(PMe_3)_2Cl_2$, 79839-93-3; $Ta(CH_2CMe_3)(CH_2CH_2)(PMe_3)_2Cl_2$, 79839-94-4; $Ta(CHCMe_3)(PMe_3)_2CD_3$, 70083-62-4; $Ta(C_2H_4)Et(PMe_3)_2Cl_2$, 79855-21-3; Me_3SiI, 16029-98-4; Me_3SiOTf, 27607-77-8; C_2H_4, 74-85-1; trifluoroacetic acid, 76-05-1; tetraethylammonium chloride, 56-34-8; neopentane, 463-82-1; 2,2-dimethylpentane, 590-35-2; 2,2-dimethylheptane, 1071-26-7; 2,2-dimethylnonane, 17302-14-6; 2,2-dimethylundecane, 17312-64-0; 2,2-dimethyltridecane, 61869-04-3; 2,2-dimethylbutane, 75-83-2.

Synthesis and Structural Characterization of $[Re_2Cl_4(PMe_2Ph)_4]^{n+}$ (n = 0, 1, or 2): A Series of Complexes Possessing Metal–Metal Bond Orders of 4, 3.5, and 3 and the Dependence of Bond Length upon Bond Order

F. Albert Cotton,*[1a] Kim R. Dunbar,[1b] Larry R. Falvello,[1a] Milagros Tomas,[1a] and Richard A. Walton*[1b]

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received November 26, 1982*

Abstract: The following three compounds have been prepared in crystalline form and thoroughly characterized by chemical, electrochemical, magnetic, spectroscopic, and structural methods: $Re_2Cl_4(PMe_2Ph)_4$, **1**; $[Re_2Cl_4(PMe_2Ph)_4](PF_6)$, **2**; $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$, **3**. Compound **1** forms crystals in space group $C2/c$ with a = 17.571 (2) Å, b = 9.991 (1) Å, c = 22.316 (3) Å, β = 107.47 (1)°, V = 3737 (1) Å^3, and Z = 4. Olive green **2**, obtained by oxidation of **1** with $NOPF_6$, crystallizes in space group $P2_1/c$ with a = 10.596 (2) Å, b = 33.129 (6) Å, c = 13.801 (2) Å, β = 111.16 (1)°, V = 4518 (2) Å^3, and Z = 4. Compound **3**, also green and also obtained from **1** by oxidation with $NOPF_6$, crystallizes in space group $P2_1/c$ with a = 24.317 (8) Å, b = 10.485 (4) Å, c = 20.284 (7) Å, β = 111.61 (3)°, V = 4808 (3) Å^3, and Z = 4. Compounds **1–3** are reversibly electrochemically interconvertible with $E_{1/2}$ values of +0.85 and −0.26 V vs. SCE. **1** and **3** are diamagnetic while **2** has a magnetic moment of 1.35 μ_B (per Re_2 unit) and exhibits an ESR spectrum with $g_\parallel$ = 2.19 and $g_\perp$ = 2.24. Compound **2** has its $\delta \rightarrow \delta^*$ transition at 1360 nm. In going through the series **1** to **2** to **3**, the Re–Cl distances decrease (ca. 0.048 Å at each step), the Re–P distances increase (ca. 0.045 Å at each step), and the Re–Re distances change by −0.023 (2) Å from **1** to **2** and by −0.003 (2) Å (i.e., not significantly) from **2** to **3**. These bond length changes, which do not correlate simply with the bond order, are discussed and explanations proposed.

Introduction

A fundamental question in the chemistry of dimetal species containing metal–metal multiple bonds[2] is not only how strong, in a thermodynamic sense, are such bonds, but how does the δ component affect the M–M bond length in compounds containing quadruple bonds (i.e., those possessing the $\sigma^2\pi^4\delta^2$ configuration)? While the presence or absence of the δ component is often critical in dictating the rotational conformation (eclipsed versus staggered) that may be present in such dimetal species, it is clear that this contribution is much weaker than the σ or π contributions to the M–M bond and thus its effect on the bond length is not easy to forecast.

In efforts over the years to elucidate this matter, structural studies have been carried out on pairs of complexes that possess *identical* ligand sets but differ in the population of the δ and δ^* orbitals. Of particular note in this regard are studies on the $[Tc_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$ anions,[3,4] possessing $\sigma^2\pi^4\delta^2$ and $\sigma^2\pi^4\delta^2\delta^{*1}$ configurations, respectively, and the sulfate- or phosphate-bridged anions $[Mo_2(SO_4)_4]^{4-}$, $[Mo_2(SO_4)_4]^{3-}$, and $[Mo_2(HPO_4)_4]^{2-}$[5,6] for which the ground-state electronic configurations are $\sigma^2\pi^4\delta^2$, $\sigma^2\pi^4\delta^1$, and $\sigma^2\pi^4$, respectively.

For the first time we have synthesized, and herein report the structural characterization of, a series of three complexes possessing M–M bonds of orders 4, 3.5, and 3 and identical sets of *monodentate* ligands. The isolation of the complexes $Re_2Cl_4(PMe_2Ph)_4$, $[Re_2Cl_4(PMe_2Ph)_4]PF_6$, and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ provides an ideal opportunity to study the variation of M–M bond length with changes in δ contribution to the bond in the absence of any special bonding constraints engendered by sets of *bridging* ligands.

Experimental Section

Starting Materials. The complexes $(n\text{-}Bu_4N)_2Re_2Cl_8$ and $Re_2Cl_4(PMe_2Ph)_4$ were prepared by previously reported methods.[7,8] The ligand

---

(1) (a) Texas A&M University. (b) Purdue University.

(2) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley; New York, 1982.

(3) Cotton, F. A.; Daniels, L.; Davison, A.; Orvig, C. *Inorg. Chem.* **1981**, *20*, 3051.

(4) Cotton, F. A.; Davison, A.; Day, V. W.; Fredrich, M. F.; Orvig, C.; Swanson, R. *Inorg. Chem.* **1982**, *21*, 1211.

(5) Cotton, F. A.; Frenz, B. A.; Pedersen, E.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 391. Cotton, F. A.; Frenz, B. A.; Webb, T. R. *J. Am. Chem. Soc.* **1973**, *95*, 4431.

(6) Bino, A.; Cotton, F. A. *Inorg. Chem.* **1979**, *18*, 3562.