also grateful to Dr. B. Gimarc (University of South Carolina) for a helpful discussion. This work was supported by PHS Grant GM 26390 from the National Institute of General Medical Sciences.

Supplementary Material Available: Tables of structure factor amplitudes for 7-[(Hyp)$(NH_3)_5$Ru]Cl_3·$3H_2O$ and 9-[(7-MeHyp)$(NH_3)_5$Ru]Cl_3, of thermal parameters, of k_{obsd} as a function of pH, and of data for ΔpK_a and ΔE vs. r^{-2} free energy correlations, a plot of k_{obsd} vs. T^{-1}, and a plot of ΔpK_a vs. ΔE (37 pages). Ordering information is given on any current masthead page.

Trigonal-Bipyramidal Bis(neopentylidene), Neopentylidene/Ethylene, and Bis(ethylene) Complexes of Tantalum and How They React with Ethylene. A Catalyst for Rapidly Dimerizing Ethylene to 1-Butene

J. D. Fellmann, R. R. Schrock,* and G. A. Rupprecht

Contribution from the Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received January 29, 1981*

Abstract: We have prepared trigonal-bipyramidal bis(neopentylidene) complexes [$Ta(CHCMe_3)_2(R)L_2$, R = Cl, Me, Et, Bu, Np (Np = CH_2CMe_3), or mesityl, L = PMe_3], neopentylidene/ethylene complexes [$Ta(CHCMe_3)(C_2H_4)(R)L_2$, R = Et or Np], and bis(ethylene) complexes [$Ta(C_2H_4)_2(R)L_2$, R = Et or Np] by reactions involving abstraction of an α- or β-hydrogen atom from one alkyl group by another alkyl group. The PMe_3 ligands in these TBP molecules are found in the axial positions, the neopentylidene ligands lie in the trigonal plane, and the ethylene ligands line up along the L–Ta–L axis. Every complex which contains an ethyl or neopentyl ligand reacts with ethylene to give a catalyst which rapidly dimerizes ethylene to 1-butene. We propose that tantalacyclobutane complexes can form only when ethylene adds to the metal and that rearrangement of a TaC_3 ring by a β-hydride process is slow relative to the rate of opening a TaC_3 ring by migration of an α-hydrogen atom (from neopentyl) or a β-hydrogen atom (from ethyl or neoheptyl) to C_α of the ring. The final product of these reactions is postulated to be $Ta(C_2H_4)_2(Bu)L_2$. The butyl ring forms in the last step when a β-hydrogen atom from another ligand transfers to C_α of a tantalacyclopentane ring. We believe ethylene is dimerized by $Ta(C_2H_4)_2(Bu)L_2$ via a related "tantalacyclopentane" mechanism and not by a mechanism which involves insertion of ethylene into a tantalum–ethyl bond. Some variation of this "metallacyclopentane mechanism" for dimerizing ethylene is a valid, mechanistically indistinguishable alternative to the "insertion mechanism" which has dominated proposals in the literature to date.

Some time ago we found that $Ta(CHCMe_3)Np_3$ (Np = CH_2CMe_3) in the presence of at least 2 equiv of PMe_3 in pentane at 25 °C will dimerize ethylene rapidly and selectively to 1-butene. Since such selectivity is rare,[1] we set out to learn more about this reaction. In the process we discovered trigonal-bipyramidal (TBP) complexes which contain two neopentylidene ligands,[2] one neopentylidene and one ethylene ligand, and two ethylene ligands. Some of these complexes react rapidly with ethylene to give the dimerization catalysts.[3] Others give catalytically inactive products. Since we can identify the predominant species in a catalyst solution, we can propose a mechanism for dimerizing ethylene to 1-butene. Our proposal differs significantly from the usual one in that the C–C bond is postulated to form via a metallacyclopentane complex and not by insertion of ethylene into a metal–ethyl bond. This paper reports the full details of this work.

Results

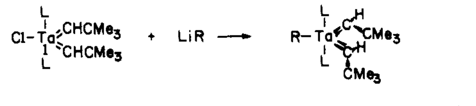
Bis(neopentylidene) Complexes. $TaNp_4Cl$ decomposes at ca. 0 °C to give transient $Ta(CHCMe_3)Np_2Cl$.[4] In the presence of PMe_3, another equivalent of neopentane is formed and yellow $Ta(CHCMe_3)_2(Cl)L_2$ (L = PMe_3) can be isolated in high yield (eq 1). $Ta(CHCMe_3)_2(Cl)L_2$ also can be prepared (but in lower

$$TaNp_4Cl \xrightarrow{-CMe_4} \text{“}Ta(CHCMe_3)Np_2Cl\text{”} \xrightarrow[2PMe_3]{-CMe_4} Ta(CHCMe_3)_2(Cl)(PMe_3)_2 \quad (1)$$

yield) as shown in eq 2. $Ta(CHCMe_3)_2(Cl)L_2$ is moderately soluble in pentane, can be sublimed (with some decomposition), is a monomer in cyclohexane, and shows a parent ion peak in its mass spectrum.

$$Ta(CHCMe_3)Cl_3L_2{}^5 + MgNp_2(dioxane) \xrightarrow[ether]{-30\ °C} Ta(CHCMe_3)_2(Cl)L_2 \quad (2)$$

$Ta(CHCMe_3)_2(Cl)L_2$ reacts with lithium alkyls to give the derivatives shown in eq 3 in high yield. $Ta(CHCMe_3)_2(Np)L_2$ also can be prepared directly from $Ta(CHCMe_3)Np_3$ by addition of PMe_3 (eq 4).



(3)

R = CH_2CMe_3, CD_2CMe_3, Me, Et, Bu, mesityl

$$Ta(CHCMe_3)Np_3 + 2L \xrightarrow{-CMe_4} Ta(CHCMe_3)_2(Np)L_2 \quad (4)$$

---

[1] Lefebvre, G.; Chauvin, Y. In "Aspects of Homogeneous Catalysis"; R. Ugo, Ed.; Carlo Manfredi: Editore-Milano, 1970; Vol. 1, pp 107–201, and references therein.

[2] Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964–5966.

[3] Fellmann, J. D.; Rupprecht, G. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5099–5101.

[4] Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370.

[5] Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236–6244.

0002-7863/81/1503-5752$01.25/0

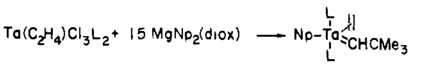
The structure of $Ta(CHCMe_3)_2(mesityl)L_2$ has been determined by Churchill and Youngs.[6] As shown in eq 3, it is a trigonal-bipyramidal molecule with axial PMe_3 ligands. The planes of the neopentylidene ligands coincide with the trigonal plane, the *tert*-butyl groups point in the same direction, and one neopentylidene ligand is more distorted ($Ta{=}C_\alpha{-}C_\beta$ angle = 168.9 (6)°) than the other ($Ta{=}C_\alpha{-}C_\beta$ angle = 154.0 (6)°). The $C_\alpha{=}Ta{=}C_\alpha$ angle is 109°. All indications are that the structures of other derivatives (R = Cl, CH_2CMe_3, Me, Et, and Bu; eq 3) are analogous to that of $Ta(CHCMe_3)_2(mesityl)L_2$.

The ^1H, ^{13}C, and ^{31}P NMR data are all consistent with the trigonal-bipyramidal structure. For example, the ^1H NMR spectrum of $Ta(CHCMe_3)_2(Np)L_2$ shows a "virtually coupled" triplet pattern for the PMe_3 protons, three *tert*-butyl resonances, and two neopentylidene H_α resonances at 6.93 and 2.08 ppm. In the ^{13}C NMR spectrum the two resonances for the neopentylidene α-carbon atoms are found at 274 (J_{CH} = 95 Hz) and 246 ppm (J_{CH} = 85 Hz). Selective irradiation of the ^1H resonance found at 6.93 ppm in the ^1H NMR spectrum shows that it is bound to the α-carbon atom which gives rise to the lower field resonance in the ^{13}C NMR spectrum. Similarly, we can show that the proton whose resonance is at 2.08 ppm is the one bound to the α-carbon atom whose resonance is at 246 ppm. These experiments suggest that the C_α and H_α resonances for the more distorted neopentylidene ligand (J_{CH} = 85 Hz) are found upfield from the resonances for C_α and H_α in the less distorted neopentylidene ligand. This seems to be a general trend for Nb and Ta alkylidene complexes.[7]

The NMR spectra of all derivatives vary with temperature. The overall process is equilibration of the neopentylidene ligands. At least one PMe_3 ligand must be lost from $Ta(CHCMe_3)_2(Np)L_2$ during the equilibration process since the "virtual triplet" patterns become singlets and coupling of the methylene protons in the neopentyl group to ^{31}P is lost. In the 60-MHz ^1H NMR spectrum the two neopentylidene H_α resonances coalesce at ~390 K. $Ta(CHCMe_3)_2(Me)L_2$ behaves similarly. In $Ta(CHCMe_3)_2(Cl)L_2$, however, the neopentylidene ligands equilibrate by a process which does *not* involve loss of PMe_3 ($T_c \simeq 300$ K for the C_α resonances in the 15-MHz ^{13}C NMR spectrum; $\Delta G^\ddagger = 13 \pm 1$ kcal mol^{-1}).

Two interesting pieces of NMR data should be pointed out. First, although neopentylidene α-protons are only weakly coupled to ^{31}P, α-protons in an alkyl group are strongly coupled. In $Ta(CHCMe_3)_2(Np)L_2$, for example, the resonance for the neopentyl α-protons is found at 0.61 ppm with $^3J_{HP}$ = 19 Hz. Second, J_{CH_α} in the neopentyl ligand in $Ta(CHCMe_3)_2(Np)L_2$ is only 108 Hz. Such a low $C{-}H_\alpha$ coupling constant could be ascribed to a relatively large $M{-}C_\alpha{-}C_\beta$ angle and correspondingly less s character in the $C{-}H_\alpha$ bond (cf. low J_{CH_α} values for the distorted neopentylidene ligands). So far, however, no structural evidence is in fact available which suggests that $M{-}C_\alpha{-}C_\beta$ angles in neopentyl ligands under some circumstances are abnormally large.

Neopentylidene/Ethylene Complexes. $Ta(C_2H_4)Cl_3L_2$[8] in ether reacts with 1.5 equiv of $MgNp_2(dioxane)$ to give a yellow crystalline complex which decomposes in solution above ~40 °C. At −20 °C its ^{13}C NMR spectrum is similar to that of $Ta(CHCMe_3)_2(Np)L_2$ except a single ethylene carbon resonance (J_{CH} = 145 Hz) replaces the resonances for one of the neopentylidene ligands. Since two sets of ethylene proton resonances are found in the ^1H NMR spectrum at 1.27 and −0.15 ppm, we believe the product is a TBP molecule analogous to $Ta(CHCMe_3)_2(Np)L_2$ in which the ethylene ligand is aligned along the L—Ta—L axis as shown in eq 5. The chemical shifts for



$$Ta(C_2H_4)Cl_3L_2 + 1.5\,MgNp_2(diox) \longrightarrow Np{-}\overset{L}{\underset{L}{Ta}}(C_2H_4){=}CHCMe_3 \qquad (5)$$

C_α (247 ppm) and H_α (0.816 ppm) of the neopentylidene ligand suggest that the $M{=}C_\alpha{-}C_\beta$ angle is still of the order of 170°.

$Ta(CHCMe_3)Cl_3L_2$ reacts with 1.5 equiv of $MgEt_2(diox)$ to give a red oil which contains three species. About 30% of the mixture is $Ta(C_2H_4)_2(Et)L_2$ (see next section); the remainder consists of two isomers of $Ta(CHCMe_3)(C_2H_4)(Et)L_2$ (eq 6).

$$Ta(CHCMe_3)Cl_3L_2 + 1.5MgEt_2(diox) \rightarrow Ta(CHCMe_3)(C_2H_4)(Et)L_2 + Ta(C_2H_4)_2(Et)L_2 \qquad (6)$$

$Ta(C_2H_4)_2(Et)L_2$ crystallizes from the reaction mixture leaving a red oil enriched in $Ta(CHCMe_3)(C_2H_4)(Et)L_2$. The ^{13}C NMR spectrum of this red oil at −50 °C shows a complete set of resonances for each of the two isomers of $Ta(CHCMe_3)(C_2H_4)(Et)L_2$. Each set is similar to that observed for $Ta(CHCMe_3)(C_2H_4)(Np)L_2$. At 50 °C the two isomers interconvert rapidly on the NMR time scale *without* loss of coordinated PMe_3 ($\Delta G \simeq 13$ kcal mol^{-1}). We proposed that the two isomers are those shown in eq 7. The greater steric bulk of Np vs. Et may explain why

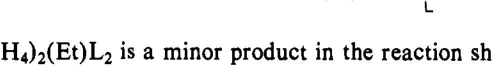

(7)

only one isomer of $Ta(CHCMe_3)(C_2H_4)(Np)L_2$ is found and why it loses PMe_3 so much more readily than $Ta(CHCMe_3)(C_2H_4)(Et)L_2$ does.

It is interesting to note that $Ta(CHCMe_3)(C_2H_4)(Np)L_2$ is a tautomer of $Ta(CHCMe_3)_2(Et)L_2$. We have seen no evidence that they interconvert under conditions where they are stable (eq 8).

$$Ta(CHCMe_3)(C_2H_4)(Np)L_2 \not\rightleftharpoons Ta(CHCMe_3)_2(Et)L_2 \qquad (8)$$

Bis(ethylene) Complexes. The reaction between $Ta(C_2H_4)Cl_3L_2$ and 1.5 equiv of $MgEt_2(diox)$ at −30 °C in ether gives thermally sensitive, red, crystalline $Ta(C_2H_4)_2(Et)L_2$ in ~50% yield (eq 9).



$$Ta(C_2H_4)Cl_3L_2 + 1.5\,MgEt_2(diox) \xrightarrow[ether]{-30°} Et{-}\overset{L}{\underset{L}{Ta}}(C_2H_4)_2 \qquad (9)$$

($Ta(C_2H_4)_2(Et)L_2$ is a minor product in the reaction shown in eq 6.) It also can be prepared directly from $TaCl_5$ in ~40% yield (eq 10). A third way to prepare $Ta(C_2H_4)_2(Et)L_2$ is to treat

$$TaCl_5 + 2L + 2.5MgEt_2(diox) \rightarrow \underset{\sim 40\%}{Ta(C_2H_4)_2(Et)L_2} \qquad (10)$$

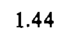
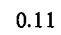
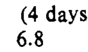
$TaNp_2Et_3$ with PMe_3 (eq 11); $Ta(C_2H_4)_2(Et)L_2$ crystallizes out

$$TaNp_2Et_3 + 2L \rightarrow \underset{75\%(50\%\ \text{isolated})}{Ta(C_2H_4)_2(Et)L_2} + \underset{25\%}{Ta(CHCMe_3)(C_2H_4)(Et)L_2} \qquad (11)$$

selectively in the presence of more soluble $Ta(CHCMe_3)(C_2H_4)(Et)L_2$. All ^1H, ^{31}P, and ^{13}C NMR data suggest that the geometry of $Ta(C_2H_4)_2(Et)L_2$ is closely related to the other molecules we have been discussing, as shown in eq 9.

Reactions of TBP Complexes with Ethylene. $Ta(CHCMe_3)_2(Cl)L_2$ reacts slowly with ethylene (35 psi) at 40 °C to give red, crystalline $Ta(1,3\text{-butadiene})(C_2H_4)(Cl)L_2$ (eq 12) and predom-

Table I. Organic Products from the Reactions of TBP Complexes with Ethylene[a]

complex	T, °C	t			
$Ta(CHCMe_3)_2(Cl)L_2$	40	48 h	1.75	0.14	6.5 (4 days)[b]
$Ta(CHCMe_3)_2(Me)L_2$	25	48 h	1.44	0.11	6.8
$Ta(CHCMe_3)_2(Mes)L_2$	50	1 h		no reaction	
$Ta(CHCMe_3)_2(Np)L_2$	25	30 min	2.99		~2 min^{-1}
$Ta(CHCMe_3)_2(Et)L_2$	25	1.5 h	1.60	0.30	~2 min^{-1}
$Ta(CHCMe_3)(C_2H_4)(Np)L_2$	25	1 h	1.80		~2 min^{-1}
$Ta(C_2H_4)_2(Et)L_2$		0			~0.5 min^{-1} [c]

[a] All reactions were done in hydrocarbon solvents at 30–50 psi of ethylene; L = PMe_3. [b] 2-Ethyl-1-pentene = 0.34 after 4 days. [c] 2-Ethyl-1-pentene = 0.32, C_8 products = 0.14, after 3 h.

---

[6] Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930–1935.
[7] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.
[8] Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440–1447.

$$\mathrm{Ta(CHCMe_3)_2(Cl)L_2 + C_2H_4 \xrightarrow[24\ h]{40\ °C} Ta(1,3\text{-butadiene})(C_2H_4)(Cl)L_2} \quad (12)$$

inantly 4,4-dimethyl-1-pentene (Table I). Ta(1,3-butadiene)(C_2H_4)(Cl)L_2 also can be prepared by reacting Ta($CHCMe_3$)(Cl)L_4[9] with ethylene or by reducing Ta(C_2H_4)Cl_3L_2 with 2 equiv of sodium amalgam under ethylene. An ethyl derivative can be prepared straightforwardly. Ta(1,3-butadiene)(C_2H_4)(Cl)L_2 in the presence of ethylene gave only traces of butenes after 6 h at 45 °C; most of the Ta(1,3-butadiene)(C_2H_4)(Cl)L_2 was recovered unchanged.

Samples of Ta(1,3-butadiene)(C_2H_4)(R)L_2 (R = Cl, Et) contain two asymmetric isomers whose ratio varies with temperature and solvent. Since the phosphorus nuclei in each isomer are not coupled to one another, we can at least state that the PMe_3 ligands are mutually cis. The number of possible octahedral structures is still large since we must include various possible orientations of ethylene and the possibility that butadiene is in the trans form.[10] Both the chloro and the ethyl derivatives decompose above ~100 °C, but before they do, only one symmetric molecule is observed on the NMR time scale, probably the result of losing coordinated PMe_3.

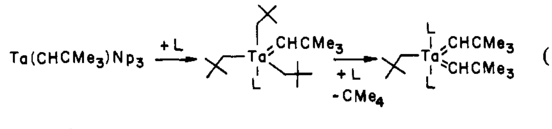
Ta($CHCMe_3$)$_2$(Me)L_2 also reacts slowly with ethylene to give the expected organic products but no recognizable product containing butadiene. Ta($CHCMe_3$)$_2$(mesityl)L_2 does not react with ethylene in 1 h at 50 °C.

The last four complexes listed in Table I react rapidly with ethylene to give C_7H_{14} products approximately equal to the sum of all C_5H_x (x = 10 or 11) groups in the starting complex, and a dimerization catalyst which is active for several hours before the activity wanes. When 1-butene begins filling up the reaction vessel (or if the supply of ethylene is shut off), 2-ethyl-1-butene begins to form. Longer reaction times yield small, but increasing amounts of C_8 and higher hydrocarbons. When Ta($CHCMe_3$)$_2$(CD_2CMe_3)L_2 is the starting complex a ca. 1:1 mixture of d_0 and d_1 labeled 4,4-dimethyl-1-pentene is produced.

The catalyst systems were examined carefully by ^{13}C NMR. All contain the same two organometallic products. The major one (~75% of the mix) we can identify as Ta(C_2H_4)$_2$(Bu)L_2 by comparison of its spectrum with that for Ta($CHCMe_3$)$_2$(Bu)L_2 and that for Ta(C_2H_4)$_2$(Et)L_2. Ta(C_2H_4)$_2$(Bu)L_2 could be isolated from pentane at −78 °C only in low yield and with great difficulty because of its high solubility. The minor product was still present in this isolated material. The minor product cannot be identified unambiguously although its ^{13}C NMR spectrum is consistent with it being Ta(C_2H_4)(1-butene)(Bu)L_2.

Discussion

Neopentylidene ligands in the complexes we have prepared here probably arise when an ethyl or neopentyl group abstracts an α-hydrogen atom from a neighboring neopentyl group[7] (e.g., eq 13). While it is almost certainly true that the alkyl group which leaves must be in a coordination position ~90° to the neopentyl group which donates the α-hydrogen atom,[4,11] it is not yet clear whether the optimum coordination number is five, six, or even seven.[5] Any one coordination number could be sufficient in a given situation. Formation of ethylene probably involves a related β-hydrogen abstraction process (e.g., eq 9). In some situations α-hydrogen abstraction and α-hydrogen abstraction are competitive (eq 11).



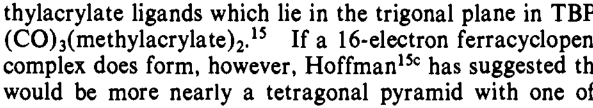
(13)

We were at first surprised that the neopentylidene/ethylene complexes could be isolated. One might think they would decompose via formation and rearrangement of a tantalacyclobutane (TaC_3) ring[8] by β-hydride elimination. Either the TaC_3 ring cannot form or it does not rearrange rapidly compared to the rate of reformation of the neopentylidene/ethylene complex. We think the former hypothesis is more reasonable because of the relatively large angle (~110°) between the neopentylidene and ethylene ligands. Only if an ethylene ligand or a neopentylidene ligand occupies one apical position, or a sixth ligand enters the coordination sphere, could a tantalacyclobutane ring form which has a C_α–M–C_α angle close to what it is in known platinacylclobutane complexes (~75°).[12] Although one could also propose that the neopentylidene and ethylene ligands must be able to achieve a relative orientation as shown in eq 14 (exactly opposite to that observed) before a C–C bond can form, we see no reason why this relative orientation should be inaccessible on the chemical time scale. Finally, the results we report here, along with recent structural results[13] for the only other alkylidene/ethylene complex, Ta(η^5-C_5Me_5)($CHCMe_3$)(C_2H_4)(PMe_3), suggest that an ethylene ligand also could be called a dianion. Therefore, all of the TBP species we discuss here could be called Ta(V) complexes. Coupling the neopentylidene and ethylene ligands would amount to a reduction of Ta(V) to Ta(III) and a lowering of the total valence electron from 16 to 14, both of which are likely to be unfavorable.

(14)

If the analogy between an ethylene and an alkylidene ligand is as close as we suspect, then the reasons why a tantalacyclopentane complex does not form in a TBP bis(ethylene) complex should be analogous.[14] It is interesting to note that ferracyclopentane derivatives are proposed to form by coupling two methylacrylate ligands which lie in the trigonal plane in TBP Fe(CO)$_3$(methylacrylate)$_2$.[15] If a 16-electron ferracyclopentane complex does form, however, Hoffman[15c] has suggested that it would be more nearly a tetragonal pyramid with one of the iron–carbon bonds at the apex.

Another unusual finding is that Ta($CHCMe_3$)$_2$(CD_2CMe_3)L_2 is not converted into Ta($CHCMe_3$)($CDCMe_3$)($CHDCMe_3$)L_2 by a process shown in eq 15. Since we have found it useful to view the neopentylidene ligand as a dianion, we would not expect the intermediate shown in eq 15 to be viable. Alkylidene hydride complexes are now known,[9] but only ones in which tantalum (counting the alkylidene ligand as a dianion) is in the 5+ oxidation state. A process related to α-hydrogen abstraction, in this case what amounts to a more or less direct transfer of a neopentyl α-hydrogen atom to a neopentylidene ligand, also would not seem favorable with the neopentyl and neopentylidene ligands so far apart. Similar reasoning could explain why Ta($CHCMe_3$)(C_2H_4)(Np)L_2 and Ta($CHCMe_3$)$_2$(Et)L_2 do not interconvert.



(15)

One of the most important questions is how does ethylene react with TBP neopentylidene complexes? Let us first consider the reaction between ethylene and Ta($CHCMe_3$)$_2$(R)L_2 where R = Cl, methyl, or mesityl (Scheme I). None of these reactions yields a dimerization catalyst. Since L is known to be labile, a likely

---

[9] Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608–6609.

[10] Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344–6346.

[11] Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.

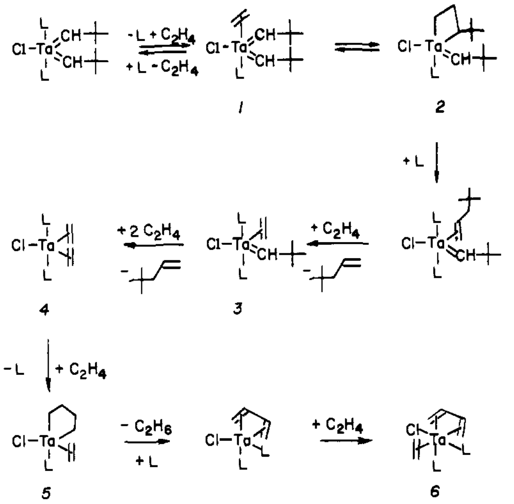
[12] Gillard, R. D.; Keeton, M.; Mason, R.; Pilbrow, M. F.; Russell, D. R. *J. Organomet. Chem.* **1971**, *33*, 247.

[13] Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169–176.

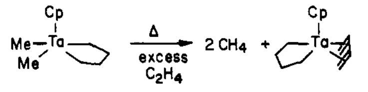
[14] The C_α–Ta–C_α angles in known tantalacyclopentane complexes are 70–75 °C: Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1980**, *19*, 3106–3112.

[15] (a) Grevels, F.-W.; Schulz, D.; Koerner v. Gustorf, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 534–536. (b) Krüger, C.; Tsay, Y.-H. *Cryst. Struct. Commun.* **1976**, *5*, 215–218. (c) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952–2962.

Scheme I

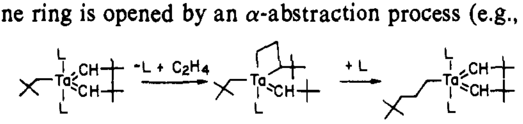


first step is loss of L and coordination of ethylene to give **1**. A tantalacyclobutane complex (**2**) now should be able to form since the ethylene–Ta–neopentylidene angle in **1** is ~90° and the ethylene ligand can orient in the preferred manner shown in eq 14. Rearrangement of the TaC_3 ring to 4,4-dimethyl-1-pentene and displacement of it by ethylene to give **3** is reasonable on the basis of the analogous reaction of $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ with ethylene.[16] Likewise **3** should be converted into **4**. At this point a *tantalacyclopentane* complex can form (**5**),[16] which, through a double β-hydride elimination and loss of ethane, is ultimately converted into the final product, **6**. A related reaction[17] is shown in eq 16 and analogous results have been observed in a titanium system.[18] There are many possible variations of Scheme I involving six-coordinate intermediates, a *trans*-4,4-dimethyl-2-pentene complex, etc., but we feel any detailed discussion of the various possibilities is unjustified. One significant point is that if a methyl or mesityl group is present instead of a chloride, methane or mesitylene would almost certainly be generated at some point and a complex analogous to **6** would not be formed. No product from the reaction of $Ta(CHCMe_3)_2(Me)L_2$ with ethylene could, in fact, be identified. Note that reactions of $Ta(CHCMe_3)_2(R)L_2$ (R = Cl, methyl, or mesityl) are slow.

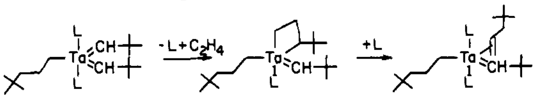


(16)

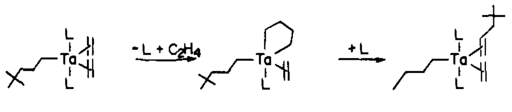
Because $Ta(CHCMe_3)_2(Np)L_2$ reacts virtually instantaneously with ethylene, we have to postulate that the first tantalacyclobutane ring is opened by an α-abstraction process (e.g., eq 17) and the second tantalacyclobutane ring is opened by a β-hydrogen abstraction process (eq 18). Both processes must be fast relative to the rate of rearrangement of the TaC_3 ring. In the final step a tantalacyclopentane ring forms and the immediate precursor to the active catalyst is generated (eq 19). Because this proposal alone does not explain the fact that $Ta(CHCMe_3)_2(CD_2CMe_3)L_2$ reacts with ethylene to give approximately a 1:1 mixture of d_0 and d_1 4,4-dimethyl-1-pentene, we have to postulate a scrambling of H and D, either one between neopentyl and neopentylidene α-carbon atoms *after* reaction with ethylene (but *before* any 4,4-dimethyl-1-pentene is formed) or a more complex one (involving other ligands) which fortuitously gives the observed mixture. In that case we cannot exclude the possibility that *in the presence of ethylene* a neoheptyl ligand may be converted to a 4,4-dimethyl-1-pentene ligand (eq 20; cf. eq 23). The last three complexes listed in Table I should react with ethylene to give $Ta(C_2H_4)_2(Bu)L_2$ by a series of reactions related to those shown in eq 17–20.



(17)

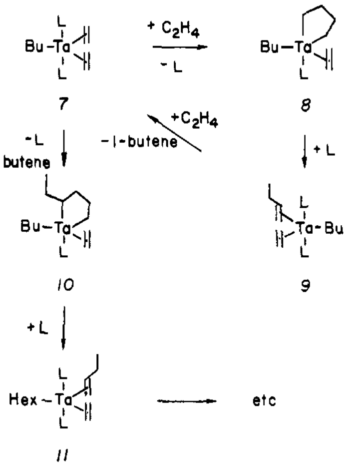


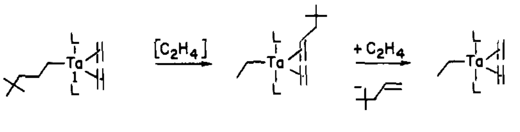
(18)



(19)

Scheme II



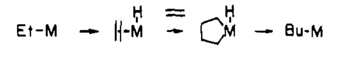


(20)

The proposed mechanism for dimerizing ethylene is shown in Scheme II. It requires no new proposals. The predominate species in solution (**7**) forms a tantalacyclopentane complex (**8**) in which the TaC_4 ring is opened by a β-hydrogen abstraction process to give **9**. The selectivity of forming 1-butene depends on the 1-butene in **9** being displaced rapidly by ethylene to form **7**. No 2-butenes form since no free metal hydride is present which could catalyze the isomerization of 1-butene. As the 1-butene concentration increases some codimerization to give C_6 products via **10** and **11** becomes competitive. Selective formation of 1-butene and some codimerization are also found in the $(\eta^5\text{-}C_5Me_5)\text{-}\overline{Cl_2TaCH_2CH_2CH_2CH_2}$ catalyst system.[19] An important difference between the system we describe here and the $\eta^5\text{-}C_5Me_5$ system is that the rate-limiting step of the dimerization reaction in the $\eta^5\text{-}C_5Me_5$ system is a relatively slow β-hydride elimination. Contraction of the TaC_4 ring to a TaC_3 ring could be rate limiting in some situations.[19] In the system we describe here neither β-elimination nor ring contraction is part of the catalytic process.

The reason why our catalyst eventually becomes inactive remains obscure. Perhaps a double β-hydride elimination process (cf. eq 16) generates a butadiene complex, which is relatively inactive for dimerizing ethylene.

The "metallacycle mechanism" we have proposed here is a reasonable alternative to the often postulated formation of 1-butene by insertion of ethylene into a metal–ethyl bond;[1,20] i.e., the "insertion mechanism" can be broken down into steps which include formation of a metallacyclopentane complex as shown in eq 21. Alternatively, the H which adds to C_α of the MC_4 ring



(21)

---

[16] McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558–4570.

[17] McLain, S. J. Ph.D. Thesis, MIT, May 1979.

[18] Pez, G. P. *J. Chem. Soc., Chem. Commun.* **1977**, 550.

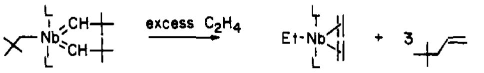
[19] McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610–5618.

[20] Cossee, P. *J. Catal.* **1964**, *3*, 80–88.

could be a proton instead of a hydride. For example, the crucial intermediate in Cramer's ethylene dimerization system[21] could well be a metallacyclopentane complex and the butyl complex, the result of its being protonated (eq 22).

$$[\mathrm{Cl_3(C_2H_4)}\overline{\mathrm{RhCH_2CH_2CH_2CH_2}}]^{2-} \xrightarrow[\mathrm{S\,=\,solvent}]{\mathrm{H^+}} [\mathrm{Cl_3(C_2H_4)Rh(butyl)(S)}]^- \quad (22)$$

It is interesting to note (as we will report separately[22]) that the analogous niobium system utterly fails to dimerize ethylene to 1-butene (eq 23). We believe, as was found in the analogous



(23)

η^5-C$_5$Me$_5$ niobium system,[19] that niobacyclopentane complexes simply do not form readily, and because they cannot, Nb(C$_2$H$_4$)$_2$(Bu)L$_2$ does not form, and ethylene is not dimerized.

Experimental Section

General procedures and techniques can be found elsewhere.[4,5] ^{13}C and ^{1}H NMR data are listed in parts per million Me$_4$Si relative to internal and ^{31}P NMR data in parts per million relative to external 85% H$_3$PO$_4$. Samples were analyzed by Bernhardt or Schwartzkopf.

Elemental Analyses. A peculiar and frustrating aspect of this work is that every complex containing at least one neopentylidene ligand analyzed low for carbon, hydrogen, and phosphorus despite numerous changes in analytical procedure and special experimental techniques by different experimentalists. We believe this is due primarily to the lability and volatility of PMe$_3$ during analysis. We had a similar problem with complexes of the type M(CHCMe$_3$)Cl$_3$L$_2$ (M = Nb or Ta, L = PMe$_3$, PMe$_2$Ph, etc.) but *not* with analogues containing bidentate ligands (dmpe, bpy, diphos, etc.).[5] Complexes in which PMe$_3$ is bound more tightly (as judged by NMR studies), e.g., Ta(C$_2$H$_4$)$_2$(Et)(PMe$_3$)$_2$, did analyze satisfactorily. We have included several unsatisfactory analytical results as examples. An exact mass measurement of the parent ion peak in the mass spectrum of Ta(CHCMe$_3$)$_2$(Cl)(PMe$_3$)$_2$ confirmed its elemental composition.

Preparations. (1) TaNp$_2$Et$_3$. TaNp$_2$Cl$_3$ (1.04 g, 2.42 mmol) was dissolved in ether (~10 mL), and the solution was cooled to −30 °C. A solution of MgEt$_2$(diox) (0.62 g, 3.63 mmol) in ether (10 mL) at −30 °C was added rapidly to the stirred solution containing TaNp$_2$Cl$_3$. The solution was warmed to 25 °C, and the solvent was removed in vacuo. The oily residue was extracted with pentane (15 mL) and filtered. Removal of the solvent gave an orange oil (0.91 g) which rapidly darkened at 25 °C (92% yield). The product was more stable in Et$_2$O than in pentane.

^{13}C NMR (toluene-d_8, −30 °C): 119.7 (t, $^1J_{\mathrm{CH}}$ = 106 Hz, *C*H$_2$CMe$_3$), 92.9 (t, $^1J_{\mathrm{CH}}$ = 116 Hz, *C*H$_2$CH$_3$), 36.0 (s, CH$_2$*C*Me$_3$), 34.9 (q, $^1J_{\mathrm{CH}}$ = 126 Hz, CH$_2$C*Me*$_3$), 15.7 ppm (q, $^1J_{\mathrm{CH}}$ = 126 Hz, CH$_2$*C*H$_3$).

(2) Ta(CHCMe$_3$)$_2$(Cl)(PMe$_3$)$_2$. Ta(CHCMe$_3$)Np$_3$ (4.0 g, 8.61 mmol) was dissolved in 100 mL of toluene, and the solution was cooled to −78 °C. A 1.88-mL sample of HCl in ether (4.58 M, 8.61 mmol), diluted with 10 mL of ether, was slowly added to give yellow TaNp$_4$Cl. (It is important to avoid adding excess acid since it will react with TaNp$_4$Cl to give TaNp$_3$Cl$_2$, which is difficult to separate from the product.) After PMe$_3$ (1.5 g, 19.7 mmol, excess) in toluene (5 mL) was added, the reaction was warmed to room temperature and stirred for 4 h. The solvent was removed in vacuo, and the residue of crude Ta(CHCMe$_3$)$_2$(Cl)(PMe$_3$)$_2$ (4.28 g) was recrystallized from minimal pentane at −30 °C (3.90 g, 89% yield). Ta(CHCMe$_3$)$_2$(Cl)(PMe$_3$)$_2$ can be sublimed with some decomposition at 70 °C and 0.05 μm.

Anal. Calcd for TaC$_{16}$H$_{38}$ClP$_2$: C, 37.78; H, 7.52; Cl, 6.97; P, 12.17. Found: C, 39.15, 39.16; H, 6.85, 6.88; Cl, 7.08; P, 11.82. (See remarks above concerning elemental analyses.) Molecular weight (cyclohexane) calcd: 508. Found: 550. Mass spectrum calcd (M$^+$): 508.16176. Found: 508.16044. ^{1}H NMR (toluene-d_8, 270 MHz, −30 °C): δ 8.200 (s, 1, C*H*CMe$_3$), 1.207 (s, 9, CHC*Me*$_3$), 1.199 (s, 9, CHC*Me*$_3$′), 1.158 (t, 18, J = 3.1 Hz, PMe$_3$), 0.446 (s, 1, C*H*CMe$_3$′). ^{1}H NMR (60 MHz, 0 °C): neopentylidene H$_\alpha$ resonances coalesce [T_c = 0 ± 10 °C, $\Delta\nu$ = 480 ± 10 Hz, $\Delta G^\ddagger$ = 12.2 ± 0.5 kcal mol^{-1}]. ^{1}H NMR (60 MHz, 110 °C): δ 4.74 (br, C*H*CMe$_3$), 1.31 (t, J = 3.3 Hz, PMe$_3$), 1.23 (s, CHC*Me*$_3$). ^{13}C NMR (toluene-d_8, 67.89 MHz, −30 °C): 273.4 (dt, $^2J_{\mathrm{CP}}$ = 5.5 Hz, $^1J_{\mathrm{CH}}$ = 98 Hz, *C*HCMe$_3$), 240.9 (dt, $^2J_{\mathrm{CP}}$ = 7.5 Hz, $^1J_{\mathrm{CH}}$ = 86 Hz, *C*HCMe$_3$′), 47.8 (s, CH*C*Me$_3$′), 44.2 (s, CH*C*Me$_3$), 35.0 (q, $^1J_{\mathrm{CH}}$ = 125 Hz, CHC*Me*$_3$), 34.5 (q, $^1J_{\mathrm{CH}}$ = 130 Hz, CHC*Me*$_3$′), 17.2 ppm (qt, $^1J_{\mathrm{CP}}$= 12.5 Hz, $^1J_{\mathrm{CH}}$ = 128 Hz, PMe$_3$). ^{13}C NMR (22.5 MHz, 25 °C): neopentylidene C$_\alpha$ resonances coalesce [T_c = 25 ± 10 °C, $\Delta\nu$ = 730 ± 20 Hz, $\Delta G^\ddagger$ = 13.2 ± 0.8 kcal mol^{-1}]. ^{13}C NMR (15.0 MHz, 95 °C): 258.0 (br d, $^1J_{\mathrm{CH}}$ = 91 Hz, *C*HCMe$_3$), 45.9 (s, CH*C*Me$_3$), 35.0 (q, $^1J_{\mathrm{CH}}$ = 125 Hz, CHC*Me*$_3$), 17.7 ppm (qt, $^1J_{\mathrm{CP}}$ = 11.7 Hz, $^1J_{\mathrm{CH}} \approx$ 125 Hz, PMe$_3$). ^{31}P NMR (toluene-d_8, 36.4 MHz, 30 °C): δ 2.8 (s). IR (Nujol): 2670 cm^{-1} (w, ν_{CH}).

(3) Ta(CHCMe$_3$)$_2$(Me)(PMe$_3$)$_2$. A 1.29-mL sample of LiMe·LiBr complex in ether (1.69 M, 2.12 mmol), diluted with 10 mL of ether, was added dropwise to an ether solution (15 mL) of Ta(CHCMe$_3$)$_2$(Cl)(PMe$_3$)$_2$ which had been cooled to −78 °C. The reaction was warmed to 25 °C and stirred for 30 min. The solvent was removed in vacuo, and the solid yellow residue was extracted with pentane (20 mL). The extract was filtered and treated with Darco, and all solvent was removed in vacuo. The product sublimed at 70 °C and 1 μm (0.76 g, 73% yield).

Anal. Calcd for TaC$_{17}$H$_{41}$P$_2$: C, 41.81; H, 8.46. Found: C, 40.53, 35.66; H, 8.18, 7.05. (See remarks above concerning elemental analyses.)

^{1}H NMR (toluene-d_8, 60 MHz, 143 °C): δ 4.42 (br, C*H*CMe$_3$), 1.17 (br, PMe$_3$), 1.06 (br, CHC*Me*$_3$), −0.3 (br t, $^3J_{\mathrm{HP}} \approx$ 30 Hz, Me). ^{1}H NMR (72 °C): neopentylidene H$_\alpha$ resonances coalesce [T_c = 345 ± 10 K, $\Delta\nu$ = 279 ± 5 Hz, $\Delta G^\ddagger$ = 16.0 ± 0.5 kcal mol^{-1}]. ^{13}C NMR (toluene-d_8, 15 MHz, 25 °C): 273.3 (br d, $^1J_{\mathrm{CH}}$ = 92 Hz, *C*HCMe$_3$), 246.4 (br d, $^1J_{\mathrm{CH}}$ = 90 Hz, *C*HCMe$_3$′), 47.3 (s, CH*C*Me$_3$′), 44.6 (s, CH*C*Me$_3$), 35.5 (q, $^1J_{\mathrm{CH}}$ = 126 Hz, CHC*Me*$_3$), 18.7 ppm (qt, $^1J_{\mathrm{CP}}$ = 11.7 Hz, $^1J_{\mathrm{CH}}$ = 127 Hz, PMe$_3$). The Ta–Me group was not located.

(4) Ta(CHCMe$_3$)$_2$(Et)(PMe$_3$)$_2$. Ethyl lithium in benzene (0.58 mL of 1.08 M solution, 0.63 mmol) was added slowly to Ta(CHCMe$_3$)$_2$(Cl)(PMe$_3$)$_2$ (0.32 g, 0.63 mmol) in ether (7 mL) at −78 °C. The reaction mixture was warmed to 25 °C and stirred for 30 min. The solvent was removed in vacuo and the residue extracted with 20 mL of pentane. The extract was filtered, and the filtrate was concentrated to 1 mL. Cooling to −30 °C for 16 h yielded 0.24 g of yellow needles (76% yield).

^{1}H NMR (benzene-d_6, 270 MHz, 25 °C): δ 6.92 (br s, 1, C*H*CMe$_3$), 3.32 (br s, 1, C*H*CMe$_3$′), 1.30 (s, 9, CHC*Me*$_3$), 1.27 (s, 9, CHC*Me*$_3$′), 1.18 (t, 18, $^2J_{\mathrm{HP}}$ = 6.6 Hz, PMe$_3$), 0.915 (t, 3, J_{HH} = 8 Hz, CH$_2$C*H*$_3$), 0.538 (qt, 2, J_{HH} = 8 Hz, $^2J_{\mathrm{HP}}$ = 20 Hz, C*H*$_2$CH$_3$). ^{13}C NMR (benzene-d_6, 15 MHz, 25 °C): 271.4 (dt, $^2J_{\mathrm{CP}}$ = 6 Hz, $^1J_{\mathrm{CH}}$ = 97 Hz, *C*HCMe$_3$), 244.4 (dt, $^2J_{\mathrm{CP}}$ = 8 Hz, $^1J_{\mathrm{CH}}$ = 92 Hz, *C*HCMe$_3$′), 46.2 (s, CH*C*Me$_3$′), 44.1 (s, CH*C*Me$_3$), 39.1 (qt, $^2J_{\mathrm{CP}} \approx$ 4 Hz, $^1J_{\mathrm{CH}} \approx$ 125 Hz, *C*H$_2$CH$_3$), 35.0 (q, $^1J_{\mathrm{CH}}$ = 123 Hz, CHC*Me*$_3$), 34.5 (q, $^1J_{\mathrm{CH}}$ = 123 Hz, CHC*Me*$_3$′), 18.8 (qt, $^1J_{\mathrm{CP}}$ = 11 Hz, $^1J_{\mathrm{CH}}$ = 130 Hz, PMe$_3$), 5.6 ppm (q, $^1J_{\mathrm{CH}} \approx$ 125 Hz, CH$_2$*C*H$_3$). ^{31}P NMR (toluene-d_8, 36.4 MHz, 30 °C): δ −2.4 (s). IR (Nujol/NaCl): 2660 cm^{-1} (w, ν_{CH}).

(5) Ta(CHCMe$_3$)$_2$(Bu)(PMe$_3$)$_2$. A solution of Ta(CHCMe$_3$)$_2$(Cl)(PMe$_3$)$_2$ (1.58 g, 3.11 mmol) in pentane (20 mL) at −30 °C was treated dropwise with butyllithium (1.24 mL of 2.54 M hexane solution, 3.15 mmol, diluted with 5 mL of pentane). The reaction mixture was warmed to room temperature, and after 25 min was filtered through Celite. Solvent was removed in vacuo to give a yellow residue which was recrystallized from minimal pentane at −30 °C (two crops, 0.69 g, 42% yield).

^{1}H NMR (benzene-d_6, 270 MHz, 30 °C): δ 6.858 (br s, C*H*CMe$_3$), 2.822 (br s, C*H*CMe$_3$′), 1.593 (br m, J_{HH} = 6.9 Hz), 1.292 (s, CHC*Me*$_3$), 1.265 (s, CHC*Me*$_3$′), 1.116 (br m, J_{HH} = 6.4 Hz), 0.588 (br m). ^{13}C NMR (benzene-d_6, 67.89 MHz, 30 °C): 272.7 (br d, $^1J_{\mathrm{CH}}$ = 92 Hz, *C*HCMe$_3$), 245.6 (br d, $^1J_{\mathrm{CH}}$ = 89 Hz, *C*HCMe$_3$′), 51.2 (t, $^1J_{\mathrm{CH}}$ = 113 Hz, *C*H$_2$CH$_2$CH$_2$CH$_3$), 46.4 (s, CH*C*Me$_3$′), 44.0 (s, CH*C*Me$_3$), 35.1 (q, $^1J_{\mathrm{CH}}$ = 124 Hz, CHC*Me*$_3$), 34.4 (q, $^1J_{\mathrm{CH}}$ = 124 Hz, CHC*Me*$_3$′), 30.1 (t, $^1J_{\mathrm{CH}}$ = 122 Hz, CH$_2$*C*H$_2$CH$_2$CH$_3$), 27.7 (t, $^1J_{\mathrm{CH}}$ = 123 Hz, CH$_2$CH$_2$*C*H$_2$CH$_3$), 19.0 (br q, $^1J_{\mathrm{CH}}$ = 129 Hz, PMe$_3$), 14.4 ppm (q, $^1J_{\mathrm{CH}}$ = 124 Hz, CH$_2$CH$_2$CH$_2$*C*H$_3$). ^{31}P NMR (toluene-d_8, 36.4 MHz, 30 °C): δ −1.9 (s).

(6) Ta(CHCMe$_3$)$_2$(Mes)(PMe$_3$)$_2$. Mesityllithium (0.20 g, 1.6 mmol, 7% excess) was added to Ta(CHCMe$_3$)$_2$(Cl)(PMe$_3$)$_2$ (0.76 g, 1.5 mmol) in ether (25 mL) at −30 °C. The solution was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the yellow residue was extracted with 25 mL of pentane. The extract was filtered and the solvent removed from the filtrate in vacuo. The crude product (0.76 g) was dissolved in minimal ether. Yellow crystals (0.67 g, 75% yield) were isolated after the solution was cooled at −30 °C for 16 h.

^{1}H NMR (benzene-d_6, 60 MHz, 30 °C): δ 6.72 (br s, 1, C*H*CMe$_3$), 2.74 (br s, 3, para-Me), 2.26 (br s, 6, ortho-Me), 2.0 (s, 1, C*H*CMe$_3$′), 1.42 (s, 9, CHC*Me*$_3$), 1.39 (s, 9, CHC*Me*$_3$′), 1.15 (t, 18, $^2J_{\mathrm{HP}}$ = 3.2 Hz, PMe$_3$). ^{13}C NMR (benzene-d_6, 15.0 MHz, 25 °C): 275 (dt, $^2J_{\mathrm{CP}}$ = 6.6 Hz, $^1J_{\mathrm{CH}}$ = 104 Hz, *C*HCMe$_3$), 243 (dt, $^2J_{\mathrm{CP}}$ = 9.9 Hz, $^1J_{\mathrm{CH}}$ = 91 Hz, *C*HCMe$_3$′), 196 (s, C$_{\mathrm{ipso}}$), 141 (br d, $^3J_{\mathrm{CP}}$ = 34 Hz, C$_{\mathrm{ortho}}$), 133 (s, C$_{\mathrm{para}}$), 128 (d, $^1J_{\mathrm{CH}}$ = 157 Hz, C$_{\mathrm{meta}}$), 48.2 (s, CH*C*Me$_3$′), 45.0 (s, CH*C*Me$_3$), 35.0 (q, $^1J_{\mathrm{CH}}$ = 124 Hz, CHC*Me*$_3$) 30.0 (q, $^1J_{\mathrm{CH}} \approx$ 121 Hz, para-

---

(21) Cramer, R. *J. Am. Chem. Soc.* **1965**, *87*, 4717–4727.

(22) Fellmann, J. D.; Schrock, R. R., in press.

methyl), 21.5 (q, $^{1}J_{CH}$ = 125 Hz, ortho-methyl), 19.1 ppm (qt, $^{1}J_{CP}$ = 11.7 Hz, $^{1}J_{CH}$ = 130 Hz, PMe_3). ^{31}P NMR (toluene-d_8, 36.4 MHz, 30 °C): δ 0.9 (s), −1.0 (s).

(7) $Ta(CHCMe_3)_2(CD_2CMe_3)(PMe_3)_2$. $Ta(CHCMe_3)_2(Cl)(PMe_3)_2$ (2.21 g, 4.34 mmol) was dissolved in 15 mL of pentane, and $LiCD_2CMe_3$ (0.35 g, 4.34 mmol) was added slowly as a solid. The reaction mixture was filtered through Celite, and the filtrate was treated with Darco, concentrated, and cooled to −30 °C for 16 h. The solvent was decanted, and 0.86 g of crystals were isolated. Concentrating and cooling the mother liquor to −30 °C gave an additional 0.9 g of pure product (74% yield). $Ta(CHCMe_3)_2(CD_2CMe_3)(PMe_3)_2$ reacted with acetone to give 1.94 equiv of diisobutylene-D_0. No d_1 could be detected. The ^{1}H NMR spectrum showed no neopentyl α-proton signal.

(8) $Ta(CHCMe_3)_2(Np)(PMe_3)_2$. A solution of $Ta(CHCMe_3)Np_3$ (5.00 g, 10.8 mmol) and PMe_3 (1.80 g, 23.8 mmol, 10% excess) in 4 mL of benzene deposited orange crystals of $Ta(CHCMe_3)_2(Np)(PMe_3)_2$ after 4 h at 25 °C. The volume was reduced in vacuo to obtain a second crop. The crops were combined and recrystallized from pentane at −30 °C; yield 5.63 g (96%).

^{1}H NMR (C_6D_6, 270 MHz, 35 °C): δ 6.93 (t, 1, $^{3}J_{HP}$ = 3.0 Hz, $CHCMe_3$), 2.08 (br s, 1, $CHCMe_3'$), 1.32 (t, 18, $^{2}J_{HP}$ = 2.4 Hz, PMe_3), 1.21 (s, 9, CMe_3), 1.20 (s, 9, CMe_3), 1.16 (s, 9, CMe_3), 0.61 (t, 2, $^{3}J_{HP}$ = 19 Hz, CH_2CMe_3). The triplets at 1.32 and 0.61 collapse to singlets on decoupling phosphorus. ^{13}C NMR (toluene-d_8, 67.89 MHz, 35 °C): 274.1 (d, J_{CH} = 95 Hz, $CHCMe_3$), 245.6 (d, J_{CH} = 85 Hz, $CHCMe_3'$), 72.0 (t, J_{CH} = 108 Hz, CH_2CMe_3), 47.3 (s, $CHCMe_3$), 44.5 (s, $CHCMe_3$), 38.4 (s, CH_2CMe_3), 37.4 (q, J_{CH} = 122 Hz, CMe_3), 35.6 (q, J_{CH} = 122 Hz, CMe_3), 34.5 (q, J_{CH} = 125 Hz, CMe_3), 20.2 ppm (q, J_{CH} = 128 Hz, PMe_3). Molecular weight (cyclohexane): calcd 544. Found: 540.

(9) $Ta(CHCMe_3)(C_2H_4)(Np)(PMe_3)_2$. $Ta(C_2H_4)Cl_3(PMe_3)_2$ (1.5 g, 3.22 mmol) in ether (60 mL) at −30 °C was treated with solid $MgNp_2(diox)$ (1.25 g, 4.91 mmol). The reaction mixture was stirred at 25 °C for 30 min and filtered, and the solvent was removed from the filtrate in vacuo. The oily residue was extracted with pentane and filtered. The filtrate was concentrated to ~3 mL, and the concentrate cooled to −30 °C. Two crops of yellow product were collected and recrystallized from a saturated pentane solution at −30 °C to give 1.0 g of large, yellow cubes (59% yield). $Ta(CHCMe_3)(C_2H_4)(Np)(PMe_3)_2$ is indefinitely stable at −30 °C in the solid state, but in aromatic solvents it decomposes above 40 °C.

^{1}H NMR (toluene-d_8, 250 MHz, −30 °C): δ 1.431 (t, 18, $^{2}J_{HP}$ = 2.8 Hz, PMe_3), 1.268 (m, 2, $HHC{=}CHH$), 1.051 (s, 9, CH_2CMe_3), 0.872 (s, 9, $CHCMe_3$), 0.816 (br s, 1, $CHCMe_3$), 0.399 (t, 2, $^{3}J_{HP}$ = 21 Hz, CH_2CMe_3), −0.152 (m, 2, $HHC{=}CHH$). ^{13}C NMR (toluene-d_8, 67.89 MHz, −20 °C): 247.1 (dt, $^{2}J_{CP}$ = 11.3 Hz, $^{1}J_{CH}$ = 93 Hz, $CHCMe_3$), 75.2 (br t, $^{2}J_{CP} \approx$ 3 Hz, $^{1}J_{CH}$ = 108 Hz, CH_2CMe_3), 47.0 (s, $CHCMe_3$), 36.2 (q, $^{1}J_{CH}$ = 125 Hz, CH_2CMe_3), 35.8 (s, CH_2CMe_3), 34.6 (q, $^{1}J_{CH}$ = 125 Hz, $CHCMe_3$), 33.6 (tt, $^{2}J_{CP}$ = 6.6 Hz, $^{1}J_{CH}$ = 145 Hz, C_2H_4), 18.5 ppm (qt, $^{1}J_{CP}$ = 9.5 Hz, $^{1}J_{CH}$ = 126 Hz, PMe_3). ^{31}P NMR (toluene-d_8, 36.2 MHz, 0 °C): δ −1.9 (s).

(10) Observation of $Ta(CHCMe_3)(C_2H_4)(Et)(PMe_3)_2$. $Ta(CHCMe_3)Cl_3(PMe_3)_2$ (2.04 g, 4.00 mmol) in Et_2O (50 mL) at −30 °C was mixed with an ether solution of $MgEt_2(diox)$ (1.02 g, 6.00 mmol) which had been cooled to −30 °C. The reaction mixture was warmed to 25 °C and stirred for 20 min. The mixture was filtered, and the filtrate was stripped to an oil which was extracted with 40 mL of pentane. The pentane solution was treated with Darco and filtered. Evaporation of the solvent gave 1.44 g of a red oil which was a 7:3 mixture of $Ta(CHCMe_3)(C_2H_4)(Et)(PMe_3)_2$ and $Ta(C_2H_4)_2(Et)(PMe_3)_2$ by ^{1}H and ^{13}C NMR. At −30 °C crystals of $Ta(C_2H_4)_2(Et)(PMe_3)_2$ slowly formed in the oil which could thereby be enriched in $Ta(CHCMe_3)(C_2H_4)(Et)(PMe_3)_2$.

^{1}H NMR (benzene, 60 MHz, 25 °C): δ 1.35 (t, $^{2}J_{HP} \approx$ 3 Hz, PMe_3), 1.10 (s, $CHCMe_3$), 0.0 (br q, $J_{HH} \approx$ 9 Hz, CH_2CH_3), −0.90 (t, $J_{HH} \approx$ 9Hz, CH_2CH_3). ^{13}C NMR (toluene-d_8, 67.89 MHz, −50 °C): major isomer, 238.2 (dt, $^{2}J_{CP}$ = 10.3 Hz, $^{1}J_{CH}$ = 92 Hz, $CHCMe_3$), 47.1 (s, $CHCMe_3$), 40.3 (br t, $^{1}J_{CH}$ = 123 Hz, CH_2CH_3), 34.5 (q, $^{1}J_{CH}$ = 127 Hz, $CHCMe_3$), 28.8 (tt, $^{2}J_{CP} \approx$ 7 Hz, $^{1}J_{CH}$ = 147 Hz, C_2H_4), 16.73 (qt, $^{1}J_{CP}$ = 11.6 Hz, $^{1}J_{CH}$ = 127 Hz, PMe_3), −2.41 ppm (br q, $^{1}J_{CH}$ = 124 Hz, CH_2CH_3); minor isomer, 260.2 (dt, $^{2}J_{CP}$ = 10.2 Hz, $^{1}J_{CH}$ = 80 Hz, $CHCMe_3$), 46.5 (s, $CHCMe_3$), 30.3 (br t, $^{1}J_{CH}$ = 122 Hz, CH_2CH_3), 34.0 (q, $^{1}J_{CH} \approx$ 127 Hz, $CHCMe_3$), 31.1 (br t, $^{1}J_{CH} \approx$ 147 Hz, C_2H_4), 16.6 (qt, $^{1}J_{CP}$ = 11.7 Hz, $^{1}J_{CH} \approx$ 127 Hz, PMe_3), 1.34 ppm (br q, $^{1}J_{CH}$ = 126 Hz, CH_2CH_3). ^{13}C NMR (5 °C): neopentylidene C_α signals coalesce [$\Delta\nu$ = 330 ± 20 Hz; $\Delta G^{\ddagger} \approx$ 13 kcal mol^{-1}]. ^{31}P NMR (toluene-d_8, 36.2 MHz, −60 °C): major isomer, δ 0.0 (s); minor isomer, δ −7.8 (s).

(11) $Ta(C_2H_4)_2(Et)(PMe_3)_2$. (a) From $Ta(C_2H_4)Cl_3(PMe_3)_2$. $Ta(C_2H_4)Cl_3(PMe_3)_2$ (2.0 g, 4.3 mmol) in 50 mL of ether was mixed with a solution of $MgEt_2(diox)$ (1.2 g, 7.03 mmol, 10% excess) in ether (10 mL) at −30 °C. As the reaction warmed to 25 °C gas evolved and the color changed from blue to orange at ~0 °C. Volatiles were removed in vacuo, and the residue was extracted with pentane (~50 mL). Brown insolubles (1.51 g) were filtered off. Concentrating and cooling the filtrate gave 0.97 g of orange irregular crystals (54% yield). EtMgBr can be substituted for $MgEt_2(diox)$.

(b) From $TaCl_5$. PMe_3 (0.4 mL, excess) was added to $TaCl_5$ (0.72 g, 2.0 mmol) in 30 mL of ether at −30 °C to give an orange precipitate of $TaCl_5(PMe_3)_2$. The reaction mixture was cooled to −78 °C, and $MgEt_2(diox)$ (0.85 g, 5.0 mmol) in 20 mL of Et_2O was added dropwise. The mixture was stirred for 45 min, warmed to 25 °C, and filtered. Removal of the solvent in vacuo left a brown solid which was extracted with 25 mL of pentane. The extract was filtered and stripped. The product was dissolved in 5 mL of a 3:2 ether/pentane solution which was then cooled to −30 °C for 12 h. Crystals (0.34 g) were isolated by decanting the mother liquor. Larger scale reactions gave poorer yields.

(c) From $TaNp_2Et_3$. $TaNp_2Et_3$ (1 mmol) in 5 mL of ether or pentane reacts with PMe_3 (2 mmol) in 3 h to give 0.2 g (48%) of $Ta(C_2H_4)_2(Et)(PMe_3)_2$. The complex was isolated by stripping the solvent and recrystallizing the residue from ether/pentane mixtures (see above). By $^{13}C\{^{1}H\}$ NMR, the reaction mixture consisted of ~20% $TaNp_2Et_3$, ~20% $Ta(CHCMe_3)(C_2H_4)(Et)(PMe_3)_2$, and ~60% $Ta(C_2H_4)_2(Et)(PMe_3)_2$.

Anal. Calcd for $TaC_{12}H_{31}P_2$: C, 34.46; H, 7.46. Found: C, 34.58; H, 7.68. Molecular weight (cyclohexane) calcd: 418. Found: 372. ^{1}H NMR (benzene-d_6, 270 MHz, 25 °C): δ 1.150 (t, 18, $^{2}J_{HP}$ = 2.4 Hz, PMe_3), 0.870 (qt, 2, $^{2}J_{HP}$ = 23.8 Hz, J_{HH} = 8.1 Hz, CH_2CH_3), 0.530 (m, 2, $HHC{=}CHH$), −0.294 (m, 2, $HHC{=}CHH$), −0.999 (t, 3, J_{HH} = 7.9 Hz, CH_2CH_3). $^{1}H\{^{31}P\}$ NMR (90 MHz, f_1 = 36.350 65 MHz): δ 1.15 (s, PMe_3), 0.87 (q, $J_{HH} \approx$ 8 Hz, CH_2CH_3), 0.53, −0.29 (br, olefinic H), −1.00 (t, $J_{HH} \approx$ 8 Hz, CH_2CH_3). ^{13}C NMR (benzene-d_6, 67.89 MHz, −20 °C): 36.89 (t, $^{1}J_{CH}$ = 128 Hz, PMe_3), 36.41 (tt, $^{2}J_{CP}$ = 7.3 Hz, $^{1}J_{CH}$ = 150 Hz, C_2H_4), 14.04 (qt, $^{1}J_{CP}$ = 9.5 Hz, $^{1}J_{CH}$ = 128 Hz), −2.28 ppm (q, $^{1}J_{CH}$ = 123 Hz, CH_2CH_3). ^{31}P NMR (toluene-d_8, 36.4 MHz, 0 °C): δ 1.1 (s).

(12) Observation of $Ta(C_2H_4)_2(Bu)(PMe_3)_2$ and "$Ta(C_2H_4)$(1-butene)(Bu)$(PMe)_2$". $Ta(C_2H_4)_2(Et)(PMe_3)_2$ dissolved in toluene-d_8 was reacted with C_2H_4 (30 psi) at 0 °C for 3 h. A $^{13}C\{^{1}H\}$ NMR spectrum at −20 °C showed $Ta(C_2H_4)_2(Bu)(PMe_3)_2$, 1-butene, and a minor component which is tentatively identified as $Ta(C_2H_4)$(1-butene)(Bu)$(PMe_3)_2$. A sample of $Ta(C_2H_4)_2(Bu)(PMe_3)_2$ was isolated in low yield from a concentrated pentane solution at −78 °C after several hours. It was still contaminated with the minor product. The mixture of these two products can be prepared from any other complex which reacts with ethylene to give the dimerization catalyst.

^{13}C NMR (toluene-d_8, 67.89 MHz, −20 °C): $Ta(C_2H_4)_2(Bu)(PMe_3)_2$, 52.6 (tt, $^{2}J_{CP}$ = 4.4 Hz, $^{1}J_{CH}$ = 118 Hz, $CH_2CH_2CH_2CH_3$), 39.4 (tt, $^{2}J_{CP}$ = 7.3 Hz, $^{1}J_{CH}$ = 145 Hz, C_2H_4), 33.5 (t, $^{1}J_{CH}$ = 124 Hz, $CH_2CH_2CH_2CH_3$), 28.2 (t, $^{1}J_{CH}$ = 124 Hz, $CH_2CH_2CH_2CH_3$), 14.7 (qt, $^{1}J_{CP} \approx$ 11 Hz, $^{1}J_{CH}$ = 128 Hz, PMe_3), 12.7 ppm (q, $^{1}J_{CH}$ = 124 Hz, $CH_2CH_2CH_2CH_3$); "$Ta(C_2H_4)$(1-butene)(Bu)$(PMe_3)_2$", 56.3 (br d, $^{1}J_{CH}$ = 146 Hz, $CH_2{=}CHCH_2CH_3$), 54.3 (br t, $^{1}J_{CH}$ = 147 Hz, $CH_2{=}CHCH_2CH_3$), 51.0 (br t, $^{1}J_{CH}$ = 117 Hz, $CH_2CH_2CH_2CH_3$), 36.0 (br t, $^{1}J_{CH} \approx$ 133 Hz, $-CH_2-$), 29.3 (t, $^{1}J_{CH} \approx$ 120 Hz, $-CH_2-$), 28.8 (t, $^{1}J_{CH} \approx$ 120 Hz, $-CH_2-$), 22.2 (q, $^{1}J_{CH} \approx$ 120 Hz, $-CH_3$), 20.3 (t, $^{1}J_{CH} \approx$ 120 Hz, $-CH_2-$), 15.9 (qt, $^{1}J_{CP} \approx$ 11 Hz, $^{1}J_{CH} \approx$ 128 Hz, PMe_3), 8.8 ppm (q, $^{1}J_{CH}$ = 124 Hz, $-CH_3$). ^{31}P NMR (toluene-d_8, 36.4 MHz, −20 °C): $Ta(C_2H_4)_2Bu(PMe_3)_2$, 6.2 (s); "$Ta(C_2H_4)$(1-butene)$Bu(PMe_3)_2$", δ 7.5 (s).

(13) Ta(1,3-butadiene)$(C_2H_4)(Cl)(PMe_3)_2$. (a) From $Ta(C_2H_4)Cl_3(PMe_3)_2$. $Ta(C_2H_4)Cl_3(PMe_3)_2$ (1.40 g, 3.00 mmol) and Na/Hg (0.41%, 33.6 g, 6.0 mmol) were placed in a pressure vessel, and the vessel was flushed with C_2H_4. A solution of ether/THF (1:1, 30 mL) containing PMe_3 (0.6 mL, 6.3 mmol, excess) was added by syringe. The reaction mixture was pressurized with C_2H_4 (30 psi) and stirred for 16 h at 25 °C. The solution was filtered through Celite, and the solvent was removed in vacuo. The residue was extracted with pentane (50 mL) and filtered. The filtrate was stripped to red crystals which were dissolved in ether (~5 mL). Cooling to −30 °C for 12 h gave 0.9 g of irregularly shaped, red crystals (67% yield).

(b) From $Ta(CHCMe_3)_2(Cl)(PMe_3)_2$. $Ta(CHCMe_3)_2(Cl)(PMe_3)_2$ (4.28 g, 8.41 mmol) was dissolved in pentane (~40 mL), and the solution was pressurized with C_2H_4 (35 psi) for 24 h at 40 °C. The yellow solution became deep red (~4 h) and a red powder precipitated. The reaction mixture was cooled to 25 °C, 60 mL of pentane was added, and the solution was filtered. Removal of the solvent in vacuo gave 3.37 g of red microcrystalline product which was pure by ^{1}H NMR (yield 89%).

Anal. Calcd for $TaC_{12}H_{28}ClP_2$: C, 31.98; H, 6.26. Found: C, 30.73; H, 6.96. ^{1}H NMR (toluene-d_8, 270 MHz, −30 °C): δ 4.826 (m, 1,

$\mathrm{CH_2{=}\mathit{CH}{-}CH{=}CH_2}$), 4.600 (m, 1, $\mathrm{CH_2{=}CH{-}\mathit{CH}{=}CH_2}$), 1.380 (d, 9, $^2J_{HP}$ = 7.3 Hz, $\mathrm{PMe_3}$), 0.957 (d, 9, $^2J_{HP}$ = 6.7 Hz, $\mathrm{PMe_3'}$), 2.23, 1.44, 1.15, 1.00, 0.842, –0.161, –0.807, –0.919 (m, 1, olefinic resonances). The 4.826- and 4.600-ppm resonances coalesce at 75 ± 10 °C [$\Delta\nu$ = 62 ± 5 Hz, $\Delta G^\ddagger$ = 17 ± 1 kcal mol^{-1}]. ^{13}C NMR (toluene-d_8, 67.89 MHz, –30 °C): 94.87 (d, $^1J_{CH}$ = 160 Hz, $\mathrm{CH_2{=}\mathit{C}H{-}CH{=}CH_2}$), 92.57 (d, $^1J_{CH}$ = 163 Hz, $\mathrm{CH_2{=}CH{-}\mathit{CH}{=}CH_2}$), 51.79 (tt, $^2J_{CP}$ = 5.6 Hz, $^1J_{CH}$ = 147 Hz, $\mathrm{\mathit{C}H_2{=}CH_2}$), 43.40 (ddd, $^2J_{CP}$ = 5.7 Hz, $^1J_{CH}$ = 155 and 148 Hz, $\mathrm{CH_2{=}\mathit{C}H_2}$), 34.75 (ddd, $^2J_{CP}$ = 7.8 Hz, $^1J_{CH}$ = 141 and 149 Hz, $\mathrm{\mathit{C}H_2{=}CH{-}CH{=}CH_2}$), 30.19 (tt, $^2J_{CP}$ = 8.2 Hz, $^1J_{CH}$ ≈ 150 Hz, $\mathrm{CH_2{=}CH{-}CH{=}\mathit{C}H_2}$), 14.92 (qd, $^1J_{CP}$ = 21.6 Hz, $^1J_{CH}$ = 130 Hz, $\mathrm{PMe_3}$), 13.54 (qd, $^1J_{CP}$ = 23.3 Hz, $^1J_{CH}$ = 130 Hz, $\mathrm{PMe_3'}$). ^{13}C NMR (15.0 Hz, 60 °C): ethylene carbon atom resonances coalesce [T_c = 60 ± 10 °C, $\Delta\nu$ = 129 ± 5 Hz, $\Delta G^\ddagger$ = 16 ± 1 kcal mol^{-1}]. ^{13}C NMR (15.0 MHz, 100 °C): 93.95 (s, $\mathrm{CH_2{=}\mathit{C}H{-}\mathit{C}H{=}CH_2}$), 47.8 (br s, $\mathrm{\mathit{C}H_2{=}\mathit{C}H_2}$), 33.1 (s, $\mathrm{\mathit{C}H_2{=}CH{-}CH{=}\mathit{C}H_2}$), 14.9 ppm (d, $^1J_{CP}$ ≈ 12 Hz, $\mathrm{PMe_3}$). ^{31}P NMR ($\mathrm{CDCl_3}$, 109.3 MHz, –30 °C): δ 2.0 (s) and –8.3 (s) (major isomer), 2.5 (s) and –7.8 (s) (minor isomer). The ratio of the major to minor isomer was 2:1 at –30 °C for this sample in this solvent.

(14) Ta(1,3-butadiene)($\mathbf{C_2H_4}$)(Et)($\mathbf{PMe_3}$)$_2$. $\mathrm{Ta(C_4H_6)(C_2H_4)(Cl)(PMe_3)_2}$ (1.25 g, 2.77 mmol) was dissolved in ether (25 mL), and the solution was cooled to –78 °C. A 4.7-mL sample of a 1.18 M $\mathrm{LiC_2H_5}$ (excess) in benzene solution was added slowly by syringe. The reaction mixture was warmed to 25 °C, stirred for 30 min, and filtered. The solvent was removed in vacuo, and the residue was recrystallized from minimal pentane; yield 0.6 g (49%).

Anal. Calcd for $\mathrm{TaC_{14}H_{33}P_2}$: C, 37.84; H, 7.48. Found: C, 37.23; H, 7.32. ^{1}H NMR (toluene-d_8, 270 MHz, –40 °C): δ 4.92 (m, $\mathrm{CH_2{=}\mathit{CH}{-}CH{=}CH_2}$), 3.46 (m, $\mathrm{CH_2{=}CH{-}\mathit{CH}{=}CH_2}$), 1.30 (d, $^2J_{HP}$ ≈ 6 Hz, $\mathrm{PMe_3}$), 0.87 (d, $^2J_{HP}$ ≈ 6 Hz, $\mathrm{PMe_3'}$), 1.55, 1.16, 0.76, –0.16, and –0.37 (m, olefinic and $\mathrm{CH_2}$ resonances), –0.05 (t, $^3J_{HH}$ = 7.7 Hz, $\mathrm{CH_2\mathit{CH}_3}$). ^{13}C NMR (toluene-$d_8$, 67.89 MHz, –40 °C): major isomer, 102.3 (d, $^1J_{CH}$ = 157 Hz, $\mathrm{CH_2{=}\mathit{C}H{-}CH{=}CH_2}$), 89.0 (d, $^1J_{CH}$ = 163 Hz, $\mathrm{CH_2{=}CH{-}\mathit{C}H{=}CH_2}$), 48.6 ppm (tt, $^2J_{CP}$ = 5.7 Hz, $^1J_{CH}$ = 146 Hz, $\mathrm{\mathit{C}H_2{=}CH_2}$), 42.1 (td, $^2J_{CP}$ = 4.8 Hz, $^1J_{CH}$ = 149 Hz, $\mathrm{CH_2{=}\mathit{C}H_2}$), 33.9 (td, $^2J_{CP}$ = 5.8 Hz, $^1J_{CH}$ = 150 Hz, $\mathrm{\mathit{C}H_2{-}CH{-}CH{=}CH_2}$), 33.6 (t, $^1J_{CH}$ = 116 Hz, $\mathrm{\mathit{C}H_2CH_3}$), 25.1 (td, $^2J_{CP}$ = 9.0 Hz, $^1J_{CH}$ = 149 Hz, $\mathrm{CH_2{=}CH{-}CH{=}\mathit{C}H_2}$), 15.0 (qd, $^1J_{CP}$ = 17.7 Hz, $^1J_{CH}$ ≈ 130 Hz, $\mathrm{PMe_3}$), 13.5 (qd, $^1J_{CP}$ = 19.4 Hz, $^1J_{CH}$ ≈ 130 Hz, $\mathrm{PMe_3'}$), 5.8 ppm (q, $^1J_{CH}$ = 123 Hz, $\mathrm{CH_2\mathit{C}H_3}$); minor isomer, 94.4 ($\mathrm{CH_2{=}\mathit{C}H{-}CH{=}CH_2}$), 92.3 ($\mathrm{CH_2{=}CH{=}\mathit{C}H{=}CH_2}$), 51.7 ($\mathrm{\mathit{C}H_2{=}CH_2}$), 43.2 ($\mathrm{CH_2{=}\mathit{C}H_2}$), 1.55 ppm ($\mathrm{CH_2\mathit{C}H_3}$). (Other signals could not be found in this sample.) ^{31}P NMR (toluene-d_8, 109.3 MHz, –47 °C): δ –6.4 (s) and –11.4 (s) (major isomer), –6.0 (s) and –11.9 (s) (minor isomer). The ratio of the major to minor isomer was 3:1 at –47 °C and 1:1 at 30 °C.

Acknowledgment. We thank the National Science Foundation for support (Grant CHE 79-05307), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support in the form of a fellowship to G.A.R. We also want to thank D. Traficante for helpful discussions, and Andrew Schkuta of Professor K. Biemann's group for determining the exact mass of $\mathrm{Ta(CHCMe_3)_2(Cl)(PMe_3)_2}$ at the NIH Mass Spectroscopy Facility (Grant No. RR00317).

Thioether Ligation in Iron–Porphyrin Complexes: Models for Cytochrome *c*

Toshio Mashiko,[1] Christopher A. Reed,*[1] Kenneth J. Haller,[2] Margaret E. Kastner,[2] and W. Robert Scheidt*[2]

Contribution from the Departments of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and University of Southern California, Los Angeles, California 90007.

Received December 22, 1980. Revised Manuscript Received May 20, 1981

Abstract: Iron-*meso*-tetraphenylporphyrin complexes having thioether ligation have been synthesized and investigated as models for cytochrome *c*. Using a 5-(*N*-imidazoyl)valeramido-derivatized "tail porphyrin" of iron(II) and tetrahydrothiophene, it was possible to isolate a mixed-ligand complex having thioether imidazole coordination, [*meso*-mono[*o*-(5-(*N*-imidazolyl)-valeramido)phenyl]triphenylporphinato](tetrahydrothiophene)iron(II) (**1**). The crystal structure of **1** was determined. An analogous iron(III) model for ferricytochrome *c* was characterized by EPR in solution (g = 2.90, 2.37, 1.48). A structural comparison between the iron(II)/iron(III) redox pair of complexes bis(tetrahydrothiophene)(*meso*-tetraphenylporphinato)iron(II) (**5**) and bis(pentamethylene sulfide)(*meso*-tetraphenylporphinato)iron(III) perchlorate (**7**) was made by X-ray analysis and reveals Fe–S bond lengths which are notably insensitive to oxidation state change. The structural analysis for bis(tetrahydrothiophene)(*meso*-tetraphenylporphinato)iron(III) perchlorate (**6**) is also briefly reported. All complexes have low-spin ground states. The main implications for cytochrome *c* are as follows: (i) Fe–S bond lengths in methionine-ligated hemoproteins are expected to be about 2.33 Å and rather insensitive to oxidation state change, (ii) coordinate bond length changes are unlikely to contribute to Franck–Condon barriers of electron transfer, and (iii) the intrinsic stability of the Fe(III)–S(thioether) bond is sufficiently high that a protein conformation-enforced methionine–iron contact need not be invoked. Crystal data: **1**, a = 13.170 (4) Å, b = 15.037 (11) Å, c = 25.422 (8) Å, β = 90.29 (2)°, monoclinic, space group $P2_1/c$, Z = 4; **5**, a = 13.225 (3) Å, b = 17.967 (5) Å, c = 10.283 (2) Å, α = 91.07 (2)°, β = 99.22 (2)°, γ = 76.59 (2)°, triclinic, space group $P\bar{1}$, Z = 2; **7**, a = 17.830 (3) Å, b = 18.781 (3) Å, c = 18.187 (3) Å, orthorhombic, space group $P2_12_12_1$, Z = 4; **6**, a = 13.007 (7) Å, b = 19.188 (9) Å, c = 11.256 (5) Å, α = 93.99 (3)°, β = 107.17 (4)°, γ = 95.01 (4)°, triclinic, space group $P1$, Z = 2.

The cytochromes are a widely distributed class of electron carriers having heme prosthetic groups. The reversible iron(II)/iron(III) valency change enables the cytochromes to function in numerous biological redox processes, and the prototypical cytochromes *c* have commanded much attention. Following the elucidation of the first crystal structure of a cytochrome *c* in 1971, the problem of understanding its mechanism of electron transfer became the central focus of cytochrome research.[3,4] The two most contentious issues, the pathway of electron transfer and the factors affecting the rate, remain incompletely resolved although considerable progress has been made.[5,6] Intimately related to these

---

(1) University of Southern California.

(2) University of Notre Dame.

(3) Dickerson, R. E.; Timkovich, R. "The Enzymes"; Boyer, P., Ed.; Academic Press: New York, 1975, Vol XI; pp 397–547.

(4) Salemme, F. R. *Annu. Rev. Biochem.* **1977**, *46*, 327–386.

0002-7863/81/1503-5758$01.25/0