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Supplementary Material Available: Tables of structure factor

amplitudes for 7-[(Hyp)(NH₃)₅Ru]Cl₃·3H₂O and 9-[(7-MeHyp)(NH₃)₅Ru]Cl₃, of thermal parameters, of k_{obsd} as a function of pH, and of data for $\Delta p K_a$ and ΔE vs. r^{-2} free energy correlations, a plot of k_{obsd} vs. T^{-1} , and a plot of $\Delta p K_a$ 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

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Abstract: We have prepared trigonal-bipyramidal bis(neopentylidene) complexes $[Ta(CHCMe_3)_2(R)L_2, R = Cl, Me, Et, Bu, Np (Np = CH_2CMe_3), or mesityl, L = PMe_3], neopentylidene/ethylene complexes <math>[Ta(CHCMe_3)(C_2H_4)(R)L_2, R = Et \text{ or } Np]$, and bis(ethylene) complexes $[Ta(C_2H_4)_2(R)L_2, R = Et \text{ or } Np]$ 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 -hydrogen atom (from ethyl or neoheptyl) to C $_\alpha$ of the ring. The final product of these reactions is postulated to be Ta(C_2H_4)₂(Bu)L₂. The butyl ring forms in the last step when a β -hydrogen atom from another ligand transfers to C $_\alpha$ of a tantalacyclopentane ring. We believe ethylene is dimerized by Ta(C_2H_4)₂(Bu)L₂ via a related "tantalacyclopentane" 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. TaNp₄Cl decomposes at ca. 0 °C to give transient Ta(CHCMe₃)Np₂Cl.⁴ In the presence of PMe₃, another equivalent of neopentane is formed and yellow Ta(CHCMe₃)₂(Cl)L₂ (L = PMe₃) can be isolated in high yield (eq 1). $Ta(CHCMe_3)_2(Cl)L_2$ also can be prepared (but in lower

TaNp₄Cl
$$\xrightarrow{-CMe_4}$$
 "Ta(CHCMe₃)Np₂Cl" $\xrightarrow{-CMe_4}$
Ta(CHCMe₃)_{2PMe₃}
Ta(CHCMe₃)₂(Cl)(PMe₃)₂ (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.

$$T_{a}(CHCMe_{3})Cl_{3}L_{2}^{5} + MgNp_{2}(dioxane) \xrightarrow[ether]{-30 °C} T_{a}(CHCMe_{3})_{2}(Cl)L_{2} (2)$$

 $Ta(CHCMe_3)_2(Cl)L_2$ 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 PMe₃ (eq 4).

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

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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 PMe₃ 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_{α} - C_{β} angle = 168.9 (6)°) than the other (Ta= C_{α} - C_{β} angle = 154.0 (6)°). The C_{α} = Ta = C_{α} 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, ¹³C, and ³¹P NMR data are all consistent with the trigonal-bipyramidal structure. For example, the ¹H NMR spectrum of Ta(CHCMe₃)₂(Np)L₂ shows a "virtually coupled" triplet pattern for the PMe₃ protons, three *tert*-butyl resonances, and two neopentylidene H_{α} resonances at 6.93 and 2.08 ppm. In the ¹³C NMR spectrum the two resonances for the neopentylidene α -carbon atoms are found at 274 ($J_{CH} = 95$ Hz) and 246 ppm $(J_{CH} = 85 \text{ Hz})$. 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 ¹³C 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 ($J_{CH} = 85 \text{ Hz}$) 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 PMe₃ 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 ³¹P 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 PMe₃ ($T_c \simeq 300$ K for the C_{α} resonances in the 15-MHz ¹³C NMR spectrum; $\Delta G^* = 13 \pm$ 1 kcal mol⁻¹).

Two interesting pieces of NMR data should be pointed out. First, although neopentylidene α -protons are only weakly coupled to ³¹P, 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 ${}^{3}J_{HP} = 19$ Hz. Second, $J_{CH_{\alpha}}$ in the neopentyl ligand in Ta(CHCMe₃)₂(Np)L₂ is only 108 Hz. Such a low C-H_{α} coupling constant could be ascribed to a relatively large M-C_{α}-C_{β} angle and correspondingly less s character in the C-H_{α} bond (cf. low $J_{CH_{\alpha}}$ 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 MgNp₂(dioxane) to give a yellow crystalline complex which decomposes in solution above ~ 40 °C. At -20 °C its ¹³C NMR spectrum is similar to that of Ta- $(CHCMe_3)_2(Np)L_2$ except a single ethylene carbon resonance $(J_{CH} = 145 \text{ Hz})$ 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

$$T_{\alpha}(C_{2}H_{4})C_{1_{3}L_{2}} + 15 MgNp_{2}(diox) \longrightarrow Np-T_{\alpha} + CCHCMe_{3}$$
(5)

 C_{α} (247 ppm) and H_{α} (0.816 ppm) of the neopentylidene ligand

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

complex	<i>T</i> , ℃	t //	\sim	\sim	\sim
$Ta(CHCMe_3)_2(Cl)L_2$	40	48 h	1.75	0.14	6.5 (4 days) ^b
Ta(CHCMe,),(Me)L,	25	48 h	1.44	0.11	6.8
Ta(CHCMe,), (Mes)L,	50	1 h		no reaction	
Ta(CHCMe,),(Np)L,	25	30 min	2.99		$\sim 2 \min^{-1}$
Ta(CHCMe,),(Et)L,	25	1.5 h	1.60	0.30	$\sim 2 \min^{-1}$
$Ta(CHCMe_3)(C_2H_4)-$ (Np)L ₂	25	1 h	1.80		$\sim 2 \text{ min}^{-1}$
$Ta(C_2H_4)_2(Et)L_2$		0			$\sim 0.5 \text{ min}^{-1} c$

^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_s products = 0.14, after 3 h.

suggest that the M= C_{α} - C_{β} angle is still of the order of 170°. $Ta(CHCMe_3)Cl_3L_2$ reacts with 1.5 equiv of MgEt₂(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).

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

 $Ta(C_2H_4)_2(Et)L_2$ crystallizes from the reaction mixture leaving a red oil enriched in Ta(CHCMe₃)(C_2H_4)(Et)L₂. The ¹³C NMR spectrum of this red oil at -50 °C shows a complete set of resonances for each of the two isomers of $T_a(CHCMe_3)(C_2H_4)(Et)L_2$. 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 PMe₃ ($\Delta G \simeq 13$ 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

$$E_{1} - M_{H} \xrightarrow{\downarrow} H \xrightarrow{\downarrow} E_{1} - M_{H} \xrightarrow{\downarrow} H$$

$$(7)$$

only one isomer of $Ta(CHCMe_3)(C_2H_4)(Np)L_2$ is found and why it loses PMe₃ 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).

$$Ta(CHCMe_3)(C_2H_4)(Np)L_2 \neq Ta(CHCMe_3)_2(Et)L_2$$
(8)

Bis(ethylene) Complexes. The reaction between $Ta(C_2H_4)Cl_3L_2$ and 1.5 equiv of MgEt₂(diox) at -30 °C in ether gives thermally sensitive, red, crystalline $Ta(C_2H_4)_2(Et)L_2$ in ~50% yield (eq 9).

$$Ta(C_2H_4)Cl_3L_2 + 1.5 MgEt_2(diox) \xrightarrow{-30^{\circ}}_{ether} Et - Ta \downarrow \qquad (9)$$

 $(Ta(C_2H_4)_2(Et)L_2$ is a minor product in the reaction shown in eq 6.) It also can be prepared directly from TaCl₅ in \sim 40% yield (eq 10). A third way to prepare $Ta(C_2H_4)_2(Et)L_2$ is to treat $TaCl_5 + 2L + 2.5MgEt_2(diox) \rightarrow Ta(C_2H_4)_2(Et)L_2$ (10)

 $TaNp_2Et_3$ with PMe₃ (eq 11); $Ta(C_2H_4)_2(Et)L_2$ crystallizes out $TaNp_2Et_3 + 2L \rightarrow$

$$T_a(C_2H_4)_2(Et)L_2 + T_a(CHCMe_3)(C_2H_4)(Et)L_2$$
 (11)
75%(50% isolated) 25%

selectively in the presence of more soluble Ta-(CHCMe₃)(C_2H_4)(Et)L₂. All ¹H, ³¹P, and ¹³C 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(CHCMe₃)₂-(Cl)L₂ reacts slowly with ethylene (35 psi) at 40 °C to give red, crystalline Ta(1,3-butadiene)(C_2H_4)(Cl)L₂ (eq 12) and predom-

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$$Ta(CHCMe_{3})_{2}(Cl)L_{2} + C_{2}H_{4} \xrightarrow{40 \ C} Ta(1,3-butadiene)(C_{2}H_{4})(Cl)L_{2}$$

$$24 h \qquad (12)$$

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-(CHCMe₃) $(Cl)L_4^9$ 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 PMe₃ 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 PMe₃.

 $Ta(CHCMe_3)_2(Me)L_2$ also reacts slowly with ethylene to give the expected organic products but no recognizable product containing butadiene. Ta(CHCMe₃)₂(mesityl)L₂ 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 ¹³C 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 ¹³C 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 group⁷ (e.g., eq 13). While it is almost certainly true that the alkyl group which

$$T_{\alpha}(CHCMe_{3})Np_{3} \xrightarrow{+L} \times T_{\alpha}^{CHCMe_{3}} \xrightarrow{L} CHCMe_{3} \xrightarrow{L} CHCMP_{3} \xrightarrow{L} CHCMP_{3}$$

leaves must be in a coordination position $\sim 90^{\circ}$ 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).

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) ring⁸ by β -hydride elimination. Either the TaC₃ 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 ($\sim 110^{\circ}$) 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 $(\sim 75^\circ)$.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

$$\begin{array}{cccc} \mathsf{T}^{\alpha} & \overset{\bullet}{\overset{\bullet}} & \overset{\bullet}{\overset{\bullet}} & \overset{\bullet}{\overset{\bullet}} & \overset{\bullet}{\overset{\bullet}} & \overset{\bullet}{\overset{\bullet}} & (14) \\ & + & \overset{\bullet}{\overset{\bullet}} & \overset{\bullet}{\overset{\bullet}} & \end{array}$$

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 results¹³ for the only other alkylidene/ethylene complex, $Ta(\eta^5 - C_5Me_5)(CHCMe_3)(C_2H_4)(PMe_3)$, 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.

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(CHCMe₃)(CDCMe₃)(CHDCMe₃)L₂ by a process shown in eq 15. Since we have found it useful to view

$$Me_{3}CCD_{2}-T_{4} \overset{\uparrow}{\underset{\downarrow}{\overset{\leftarrow}{\overset{\leftarrow}{\leftarrow}{\leftarrow}}}} CHCMe_{3}} \xrightarrow{ \begin{tabular}{c} & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & &$$

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 Similar reasoning could explain why Taapart. $(CHCMe_3)(C_2H_4)(Np)L_2$ and $Ta(CHCMe_3)_2(Et)L_2$ do not interconvert.

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

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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 TaC₃ 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(η^5 -C₃H₃)(CHCMe₃)Cl₂ 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 reaction¹⁷ is shown in eq 16 and analogous results have been observed in a titanium

$$Me \xrightarrow{Cp} \qquad \underbrace{\Delta}_{excess} 2 CH_4 + \underbrace{T_0}_{T_0} \qquad (16)$$

system.¹⁸ There are many possible variations of Scheme I involving six-coordinate intermediates, a *trans*-4,4-dimethyl-2pentene 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(CHCMe₃)₂(Me)L₂ with ethylene could, in fact, be identified. Note that reactions of Ta(CHCMe₃)₂(R)L₂ (R = Cl, methyl, or mesityl) are slow.

Because Ta(CHCMe₃)₂(Np)L₂ 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)

$$\times \overset{L}{\underset{c}{\overset{c}}_{CH+}} \overset{CH+}{\xrightarrow{}} \overset{L+C_{2H_{4}}}{\xrightarrow{}} \overset{T_{0}}{\underset{c}{\overset{c}}_{CH+}} \overset{+L}{\xrightarrow{}} \overset{L}{\underset{c}{\overset{c}}_{CH+}} \overset{L}{\xrightarrow{}} \overset{L}{\underset{c}{\overset{c}}_{CH+}} (17)$$

and the second tantalacyclobutane ring is opened by a β -hydrogen abstraction process (eq 18). Both processes must be fast relative

$$\times \overset{L}{\xrightarrow{}}_{L^{2}CH^{+}}^{L^{2}CH^{+}} \overset{-L^{+}C_{2}H_{4}}{\times} \overset{\uparrow}{\xrightarrow{}}_{L^{2}CH^{+}}^{I^{2}CH^{+}} \overset{+L}{\xrightarrow{}} \overset{\downarrow}{\xrightarrow{}}_{L^{2}CH^{+}}^{I^{2}CH^{+}} (18)$$

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

(16) McLain, S. J.; Wood, C. D.; Schrock, R. R. J. Am. Chem. Soc. 1979, 101, 4558-4570.

Scheme II



alone does not explain the fact that Ta(CHCMe₃)₂(CD₂CMe₃)L₂ 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.

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 TaC₄ ring is opened by a β -hydrogen abstraction process to give 9. The selectivity of forming 1-butene depends on the 1butene 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 $(\eta^5-C_5Me_5)$ -Cl₂TaCH₂CH₂CH₂CH₂ catalyst system.¹⁹ An important difference between the system we describe here and the η^{5} -C₅Me₅ system is that the rate-limiting step of the dimerization reaction in the η^5 -C₅Me₅ 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 MC₄ ring

(20) Cossee, P. J. Catal. 1964, 3, 80-88.

⁽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.

could be a proton instead of a hydride. For example, the crucial intermediate in Cramer's ethylene dimerization system²¹ could well be a metallacyclopentane complex and the butyl complex, the result of its being protonated (eq 22).

$$[Cl_{3}(C_{2}H_{4})\overset{\dagger}{R}hCH_{2}CH_{2}CH_{2}\overset{\dagger}{C}H_{2}]^{2-} \xrightarrow{H^{*}}_{S = solvent} \\ [Cl_{3}(C_{2}H_{4})Rh(butyl)(S)]^{-} (22)$$

It is interesting to note (as we will report separately²²) that the analogous niobium system utterly fails to dimerize ethylene to 1-butene (eq 23). We believe, as was found in the analogous

$$\times \stackrel{\text{Top}}{\underset{L}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}}}}}}}}}}}}}}}}}}}}}}}}}$$

 η^5 -C₅Me₅ niobium system,¹⁹ that niobacyclopentane complexes simply do not form readily, and because they cannot, Nb-(C₂H₄)₂(Bu)L₂ does not form, and ethylene is not dimerized.

Experimental Section

General procedures and techniques can be found elsewhere.^{4,5} ¹³C and ¹H NMR data are listed in parts per million Me₄Si relative to internal and ³¹P NMR data in parts per million relative to external 85% H_3PO_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 PMe₃ during analysis. We had a similar problem with complexes of the type $M(CHCMe_3)Cl_3L_2$ (M = Nb or Ta, $L = PMe_3$, PMe_2Ph , etc.) but not with analogues containing bidentate ligands (dmpe, by, diphos, etc.).⁵ Complexes in which PMe₃ is bound more tightly (as judged by NMR studies), e.g., $Ta(C_2H_4)_2(Et)(PMe_3)_2$, 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) TaNp₂Et₃. TaNp₂Cl₃ (1.04 g, 2.42 mmol) was dissolved in ether (~10 mL), and the solution was cooled to -30 °C. A solution of MgEt₂(diox) (0.62 g, 3.63 mmol) in ether (10 mL) at -30 °C was added rapidly to the stirred solution containing TaNp₂Cl₃. 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 Et₂O than in pentane.

¹³C NMR (toluene- d_8 , -30 °C): 119.7 (t, ¹ J_{CH} = 106 Hz, CH₂CMe₃), 92.9 (t, ¹ J_{CH} = 116 Hz, CH₂CH₃), 36.0 (s, CH₂CMe₃), 34.9 (q, ¹ J_{CH} = 126 Hz, CH₂CMe₃), 15.7 ppm (q, ¹ J_{CH} = 126 Hz, CH₂CH₃). (2) Ta(CHCMe₃)₂(CI)(PMe₃)₂. Ta(CHCMe₃)Np₃ (4.0 g, 8.61 mea)) was disensed in 10° FL scheme distance of the second secon

(2) Ta(CHCMe₃)₂(Cl)(PMe₃)₂. Ta(CHCMe₃)Np₃ (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 TaNp₄Cl. (It is important to avoid adding excess acid since it will react with TaNp₄Cl to give TaNp₃Cl₂, which is difficult to separate from the product.) After PMe₃ (1.5 g, 19.7 mmol, excess) in toluene (5 mL) was added, the reaction was varmed to room temperature and stirred for 4 h. The solvent was removed in vacuo, and the residue of crude Ta-(CHCMe₃)₂(Cl)(PMe₃)₂ (4.28 g) was recrystallized from minimal pentane at -30 °C (3.90 g, 89% yield). Ta(CHCMe₃)₂(Cl)(PMe₃)₂ can be sublimed with some decomposition at 70 °C and 0.05 μ m.

Anal. Calcd for TaC₁₆H₃₈ClP₂: 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. ¹H NMR (toluene-d₈, 270 MHz, -30 °C): δ 8.200 (s, 1, CHCMe₃), 1.207 (s, 9, CHCMe₃), 1.199 (s, 9, CHCMe₃), 1.158 (t, 18, J = 3.1 Hz, PMe₃), 0.446 (s, 1, CHCMe₃'). ¹H NMR (60 MHz, 0 °C): neopentylidene H_a resonances coalesce [$T_c = 0 \pm 10$ °C, $\Delta \nu = 480 \pm 10$ Hz, $\Delta G^{\bullet} = 12.2 \pm 0.5$ kcal mol⁻¹]. ¹H NMR (60 MHz, 110 °C): δ 4.74 (br, CHCMe₃), 1.31 (t, J = 3.3 Hz, PMe₃), 1.23 (s, CHCMe₃). ¹³C NMR (toluene-d₈, 67.89 MHz, -30 °C): 273.4 (dt, ²_J_{CH} = 55 Hz, ¹_J_{CH} = 98 Hz, CHCMe₃), 240.9 (dt, ²_J_{CP} = 7.5 Hz, ¹_J_{CH} = 86 Hz, CHCMe₃'), 44.2 (s, CHCMe₃), 3.5.0 (q, ¹_J_{CH} = 125 Hz, CHCMe₃), 34.5 (q, ¹_J_{CH} = 130 Hz, CHCMe₃'), 17.2 ppm (qt, ¹J_{CP}= 12.5 Hz, ¹J_{CH} = 128 Hz, PMe₃). ¹³C NMR (22.5 MHz, 25 °C): neopentylidene C_α resonances coalesce [$T_c = 25 \pm 10$ °C, $\Delta \nu = 730 \pm 20$ Hz, $\Delta G^* = 13.2 \pm 0.8$ kcal mol⁻¹]. ¹³C NMR (15.0 MHz, 95 °C): 258.0 (br d, ¹J_{CH} = 91 Hz, CHCMe₃), 45.9 (s, CHCMe₃), 35.0 (q, ¹J_{CH} = 125 Hz, CHCMe₃), 17.7 ppm (qt, ¹J_{CP} = 11.7 Hz, ¹J_{CH} ≈ 125 Hz, PMe₃). ³¹P NMR (toluene- d_8 , 36.4 MHz, 30 °C): δ 2.8 (s). IR (Nujol): 2670 cm⁻¹ (w, ν_{CH}).

(3) Ta(CHCMe₃)₂(Me)(PMe₃)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(CHCMe₃)₂(Cl)-(PMe₃)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 μ m (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.)

¹H NMR (toluene- d_8 , 60 MHz, 143 °C): δ 4.42 (br, CHCMe₃), 1.17 (br, PMe₃), 1.06 (br, CHCMe₃), -0.3 (br t, ³J_{HP} \approx 30 Hz, Me). ¹H NMR (72 °C): neopentylidene H_a resonances coalesce [$T_c = 345 \pm 10$ K, $\Delta \nu = 279 \pm 5$ Hz, $\Delta G^* = 16.0 \pm 0.5$ kcal mol⁻¹]. ¹³C NMR (toluene- d_8 , 15 MHz, 25 °C): 273.3 (br d, ¹J_{CH} = 92 Hz, CHCMe₃), 246.4 (br d, ¹J_{CH} = 90 Hz, CHCMe₃), 47.3 (s, CHCMe₃), 44.6 (s, CHCMe₃), 35.5 (q, ¹J_{CH} = 126 Hz, CHCMe₃), 18.7 ppm (qt, ¹J_{CP} = 11.7 Hz, ¹J_{CH} = 127 Hz, PMe₃). The Ta-Me group was not located.

(4) Ta(CHCMe₃)₂(Et)(PMe₃)₂. Ethyl lithium in benzene (0.58 mL of 1.08 M solution, 0.63 mmol) was added slowly to Ta(CHCMe₃)₂-(Cl)(PMe₃)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).

¹H NMR (benzene- d_6 , 270 MHz, 25 °C): δ 6.92 (br s, 1, CHCMe₃), 3.32 (br s, 1, CHCMe₃'), 1.30 (s, 9, CHCMe₃), 1.27 (s, 9, CHCMe₃'), 1.18 (t, 18, ²J_{HP} = 6.6 Hz, PMe₃), 0.915 (t, 3, J_{HH} = 8 Hz, CH₂CH₃), 0.538 (qt, 2, J_{HH} = 8 Hz, ²J_{HP} = 20 Hz, CH₂CH₃). ¹³C NMR (benzene- d_6 , 15 MHz, 25 °C): 271.4 (dt, ²J_{CP} = 6 Hz, ¹J_{CH} = 97 Hz, CHCMe₃), 244.4 (dt, ²J_{CP} = 8 Hz, ¹J_{CH} = 92 Hz, CHCMe₃'), 46.2 (s, CHCMe₃'), 44.1 (s, CHCMe₃), 39.1 (qt, ²J_{CP} ≈ 4 Hz, ¹J_{CH} ≈ 125 Hz, CH2CH₃), 35.0 (q, ¹J_{CH} = 123 Hz, CH2CMe₃), 34.5 (q, ¹J_{CH} = 123 Hz, CHCMe₃'), 18.8 (qt, ¹J_{CP} = 11 Hz, ¹J_{CH} = 130 Hz, PMe₃), 5.6 ppm (q, ¹J_{CH} ≈ 125 Hz, CH₂CH₃). ³¹P NMR (toluene- d_8 , 36.4 MHz, 30 °C): δ -2.4 (s). IR (Nujol/NaCl): 2660 cm⁻¹ (w, v_{CH}).

(5) Ta(CHCMe₃)₂(Bu)(PMe₃)₂. A solution of Ta(CHCMe₃)₂(Cl)-(PMe₃)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).

¹H NMR (benzene- d_6 , 270 MHz, 30 °C): $\delta 6.858$ (br s, CHCMe₃), 2.822 (br s, CHCMe₃'), 1.593 (br m, $J_{HH} = 6.9$ Hz), 1.292 (s, CHCMe₃), 1.265 (s, CHCMe₃'), 1.116 (br m, $J_{HH} = 6.4$ Hz), 0.588 (br m). ¹³C NMR (benzene- d_6 , 67.89 MHz, 30 °C): 272.7 (br d, ¹ $J_{CH} =$ 92 Hz, CHCMe₃), 245.6 (br d, ¹ $J_{CH} = 89$ Hz, CHCMe₃'), 51.2 (t, ¹ $J_{CH} =$ 91 Hz, CH2CMe₃), 245.6 (br d, ¹ $J_{CH} = 89$ Hz, CHCMe₃'), 51.2 (t, ¹ $J_{CH} =$ 92 Hz, CHCMe₃), 245.6 (br d, ¹ $J_{CH} = 89$ Hz, CHCMe₃'), 51.2 (t, ¹ $J_{CH} =$ 93 Hz, CH2CMe₃), 245.6 (br d, ¹ $J_{CH} = 89$ Hz, CHCMe₃'), 51.2 (t, ¹ $J_{CH} =$ 93 Hz, CH2CMe₃), 245.6 (br d, ¹ $J_{CH} = 89$ Hz, CHCMe₃'), 51.2 (t, ¹ $J_{CH} =$ 93 Hz, CH2CH2CH2CH2CH₃), 46.4 (s, CHCMe₃'), 44.0 (s, CHCMe₃), 95.1 (q, ¹ $J_{CH} = 124$ Hz, CH2CH2CH₂CH₂OH₃), 77.7 (t, ¹ $J_{CH} = 123$ Hz, CH2CH₂CH₂CH₃), 19.0 (br q, ¹ $J_{CH} = 129$ Hz, PMe₃), 14.4 ppm (q, ¹ $J_{CH} =$ 124 Hz, CH₂CH₂CH₃CH₃). ³¹P NMR (toluene- d_8 , 36.4 MHz, 30 °C): $\delta - 1.9$ (s).

(6) Ta(CHCMe₃)₂(Mes)(PMe₃)₂. Mesityllithium (0.20 g, 1.6 mmol, 7% excess) was added to Ta(CHCMe₃)₂(Cl)(PMe₃)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.

¹H NMR (benzene- d_6 , 60 MHz, 30 °C): δ 6.72 (br s, 1, CHCMe₃), 2.74 (br s, 3, para-Me), 2.26 (br s, 6, ortho-Me), 2.0 (s, 1, CHCMe₃'), 1.42 (s, 9, CHCMe₃), 1.39 (s, 9, CHCMe₃'), 1.15 (t, 18, ²J_{HP} = 3.2 Hz, PMe₃). ¹³C NMR (benzene- d_6 , 15.0 MHz, 25 °C): 275 (dt, ²J_{CP} = 6.6 Hz, ¹J_{CH} = 104 Hz, CHCMe₃), 243 (dt, ²J_{CP} = 9.9 Hz, ¹J_{CH} = 91 Hz, CHCMe₃'), 196 (s, C_{ipso}), 141 (br d, ³J_{CP} = 34 Hz, C_{ortho}), 133 (s, C_{para}), 128 (d, ¹J_{CH} = 157 Hz, C_{meta}), 48.2 (s, CHCMe₃'), 45.0 (s, CHCMe₃), 35.0 (q, ¹J_{CH} = 124 Hz, CHCMe₃) 30.0 (q, ¹J_{CH} ≈ 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, PMe₃). ${}^{31}P$ NMR (toluene- d_{8} , 36.4 MHz, 30 °C): δ 0.9 (s), -1.0 (s).

(7) Ta(CHCMe₃)₂(CD₂CMe₃)(PMe₃)₂. Ta(CHCMe₃)₂(Cl)(PMe₃)₂ (2.21 g, 4.34 mmol) was dissolved in 15 mL of pentane, and LiCD₂CMe₃ (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(CHCMe₃)₂(CD₂CMe₃)(PMe₃)₂ reacted with acetone to give 1.94 equiv of diisobutylene-D₀. No d_1 could be detected. The ¹H NMR spectrum showed no neopentyl α -proton signal.

(8) Ta(CHCMe₃)₂(Np)(PMe₃)₂. A solution of Ta(CHCMe₃)Np₃ (5.00 g, 10.8 mmol) and PMe₃ (1.80 g, 23.8 mmol, 10% excess) in 4 mL of benzene deposited orange crystals of Ta(CHCMe₃)₂(Np)(PMe₃)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%).

¹H NMR (C₆D₆, 270 MHz, 35 °C): δ 6.93 (t, 1, ³J_{HP} = 3.0 Hz, CHCMe₃), 2.08 (br s, 1, CHCMe₃'), 1.32 (t, 18, ²J_{HP} = 2.4 Hz, PMe₃), 1.21 (s, 9, CMe₃), 1.20 (s, 9, CMe₃), 1.16 (s, 9, CMe₃), 0.61 (t, 2, ³J_{HP} = 19 Hz, CH₂CMe₃). The triplets at 1.32 and 0.61 collapse to singlets on decoupling phosphorus. ¹³C NMR (toluene-d₈, 67.89 MHz, 35 °C): 274.1 (d, J_{CH} = 95 Hz, CHCMe₃), 245.6 (d, J_{CH} = 85 Hz, CHCMe₃'), 72.0 (t, J_{CH} = 108 Hz, CH₂CMe₃), 37.4 (q, J_{CH} = 122 Hz, CMe₃), 34.5 (q, J_{CH} = 122 Hz, CMe₃), 34.5 (q, J_{CH} = 122 Hz, CMe₃), 34.5 (q, J_{CH} = 125 Hz, CMe₃), 20.2 ppm (q, J_{CH} = 128 Hz, PMe₃). Molecular weight (cyclohexane): calcd 544. Found: 540.

(9) Ta(CHCMe₃)(C₂H₄)(Np)(PMe₃)₂. Ta(C₂H₄)Cl₃(PMe₃)₂ (1.5 g, 3.22 mmol) in ether (60 mL) at -30 °C was treated with solid MgNp₂(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(CHCMe₃)(C₂H₄)(Np)(PMe₃)₂ is indefinitely stable at -30 °C.

¹H NMR (toluene- d_8 , 250 MHz, -30 °C): δ 1.431 (t, 18, ² J_{HP} = 2.8 Hz, PMe₃), 1.268 (m, 2, HHC=CHH), 1.051 (s, 9, CH₂CMe₃), 0.872 (s, 9, CHCMe₃), 0.816 (br s, 1, CHCMe₃), 0.399 (t, 2, ³ J_{HP} = 21 Hz, CH₂CMe₃), -0.152 (m, 2, HHC=CHH). ¹³C NMR (toluene- d_8 , 67.89 MHz, -20 °C): 247.1 (dt, ² J_{CP} = 11.3 Hz, ¹ J_{CH} = 93 Hz, CHCMe₃), 36.2 (pt, ² J_{CP} ≈ 3 Hz, ¹ J_{CH} = 108 Hz, CH₂CMe₃), 47.0 (s, CHCMe₃), 36.2 (q, ¹ J_{CH} = 125 Hz, CH₂CMe₃), 35.8 (s, CH₂CMe₃), 34.6 (q, ¹ J_{CH} = 125 Hz, CHCMe₃), 35.8 (s, CH₂CMe₃), 34.6 (q, ¹ J_{CH} = 125 Hz, CHCMe₃), 18.5 ppm (qt, ¹ J_{CP} = 9.5 Hz, ¹ J_{CH} = 126 Hz, PMe₃). ³¹P 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-(CHCMe₃)Cl₃(PMe₃)₂ (2.04 g, 4.00 mmol) in Et₂O (50 mL) at -30 °C was mixed with an ether solution of MgEt₂(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-(CHCMe₃)(C₂H₄)(Et)(PMe₃)₂ and Ta(C₂H₄)₂(Et)(PMe₃)₂ slowly formed in the oil which could thereby be enriched in Ta(CHCMe₃)(C₂H₄)-(Et)(PMe₃)₂.

¹H NMR (benzene, 60 MHz, 25 °C): $\delta 1.35$ (t, ² $J_{HP} \approx 3$ Hz, PMe₃), 1.10 (s, CHCMe₃), 0.0 (br q, $J_{HH} \approx 9$ Hz, CH_2CH_3), -0.90 (t, $J_{HH} \approx 9$ Hz, CH_2CH_3). ¹³C 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, CHCMe₃), 47.1 (s, CHCMe₃), 40.3 (br t, ¹ J_{CH} = 123 Hz, CH_2CH_3), 34.5 (q, ¹ J_{CH} = 127 Hz, CHCMe₃), 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, PMe₃), -2.41 ppm (br q, ¹ J_{CH} = 124 Hz, CH2CH₃), third isomer, 260.2 (dt, ² J_{CP} = 10.2 Hz, ¹ J_{CH} = 80 Hz, CHCMe₃), 46.5 (s, CHCMe₃), 30.3 (br t, ¹ $J_{CH} \approx 147$ Hz, C_2H_4), 16.6 (qt, ¹ $J_{CP} \approx 127$ Hz, CHCMe₃), 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, PMe₃), 1.34 ppm (br q, ¹ J_{CH} = 126 Hz, CH₂CH₃). ¹³C NMR (5 °C): neopentylidene C_a signals coalesce [$\Delta \nu = 330 \pm 20$ Hz; $\Delta G^* \approx 13$ kcal mol⁻¹]. ³¹P NMR (toluene-d₈, 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 MgEt₂(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 MgEt₂(diox).

(b) From TaCl₅. PMe_3 (0.4 mL, excess) was added to TaCl₅ (0.72 g, 2.0 mmol) in 30 mL of ether at -30 °C to give an orange precipitate of TaCl₅(PMe_3)₂. The reaction mixture was cooled to -78 °C, and MgEt₂(diox) (0.85 g, 5.0 mmol) in 20 mL of Et₂O 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 TaNp₂Et₃. TaNp₂Et₃ (1 mmol) in 5 mL of ether or pentane reacts with PMe₃ (2 mmol) in 3 h to give 0.2 g (48%) of Ta(C₂H₄)₂-(Et)(PMe₃)₂. The complex was isolated by stripping the solvent and recrystallizing the residue from ether/pentane mixtures (see above). By ¹³C{¹H} NMR, the reaction mixture consisted of ~20% TaNp₂Et₃, ~ 20% Ta(CHCMe₃)(C₂H₄)(Et)(PMe₃)₂, and ~60% Ta(C₂H₄)₂(Et)-(PMe₃)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. ¹H NMR (benzene- d_6 , 270 MHz, 25 °C): δ 1.150 (t, 18, ² J_{HP} = 2.4 Hz, PMe₃), 0.870 (qt, 2, ² J_{HP} = 23.8 Hz, J_{HH} = 8.1 Hz, CH₂CH₃), 0.530 (m, 2, HHC=CHH), -0.294 (m, 2, HHC=CHH), -0.999 (t, 3, J_{HH} = 7.9 Hz, CH₂CH₃). ¹H³¹P} NMR (90 MHz, f_1 = 36.350 65 MHz): δ 1.15 (s, PMe₃), 0.87 (q, $J_{HH} \approx 8$ Hz, CH₂CH₃), 0.53, -0.29 (br, olefinic H), -1.00 (t, $J_{HH} \approx 8$ Hz, CH₂CH₃). ¹³C NMR (benzene- d_6 , 67.89 MHz, -20 °C): 36.89 (t, ¹ J_{CH} = 128 Hz, PMe₃), 36.41 (tt, ² J_{CP} = 7.3 Hz, ¹ J_{CH} = 150 Hz, C₂H₄), 14.04 (qt, ¹ $J_{CP} = 9.5$ Hz, ¹ J_{CH} = 128 Hz), -2.28 ppm (q, ¹ J_{CH} = 123 Hz, CH₂CH₃). ³¹P 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 ¹³C[¹H] 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.

¹³C NMR (toluene-d₈, 67.89 MHz, -20 °C): Ta(C₂H₄)₂(Bu)(PMe₃)₂, 52.6 (tt, ${}^{2}J_{CP} = 4.4$ Hz, ${}^{1}J_{CH} = 118$ Hz, CH₂CH₂CH₂CH₃), 39.4 (tt, ${}^{2}J_{CP} = 7.3$ Hz, ${}^{1}J_{CH} = 145$ Hz, $C_{2}H_{4}$), 33.5 (t, ${}^{1}J_{CH} = 124$ Hz, CH₂CH₂CH₂CH₃(CH₃), 28.2 (t, ${}^{1}J_{CH} = 124$ Hz, CH₂CH₂CH₂CH₂CH₃), 14.7 (qt, ${}^{1}J_{CP} \approx 11$ Hz, ${}^{1}J_{CH} = 128$ Hz, PMe₃), 12.7 ppm (q, ${}^{1}J_{CH} = 124$ Hz, CH₂CH₂CH₂CH₃); "Ta(C₂H₄)(1-butene)(Bu)(PMe₃)₂", 56.3 (br d, ${}^{1}J_{CH} = 146$ Hz, CH₂=CHCH₂CH₃), 54.3 (br t, ${}^{1}J_{CH} = 147$ Hz, CH₂= CHCH₂CH₃), 51.0 (br t, ${}^{1}J_{CH} = 117$ Hz, CH₂CH₂CH₂CH₂CH₃), 36.0 (br t, ${}^{1}J_{CH} \approx 133$ Hz, ${}^{-}CH_{2}$ -), 22.2 (q, ${}^{1}J_{CH} \approx 120$ Hz, ${}^{-}CH_{2}$ -), 28.8 (t, ${}^{1}J_{CH} \approx 120$ Hz, ${}^{-}CH_{2}$ -), 15.9 (qt, ${}^{1}J_{CH} \approx 114$ Hz, ${}^{1}J_{CH} \approx 128$ Hz, PMe₃), 8.8 ppm (q, ${}^{1}J_{CH} = 124$ Hz, ${}^{-}CH_{3}$). ³¹P NMR (toluene-d₈, 36.4 MHz, ${}^{-}20$ °C): Ta(C₂H₄)₂Bu(PMe₃)₂, 6.2 (s); "Ta(C₂H₄)(1-butene)Bu(PMe₃)₂", δ 7.5 (s).

(13) Ta(1,3-butadiene)(C₂H₄)(Cl)(PMe₃)₂. (a) From Ta(C₂H₄)Cl₃-(PMe₃)₂. Ta(C₂H₄)Cl₃(PMe₃)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 C₂H₄. A solution of ether/THF (1:1, 30 mL) containing PMe₃ (0.6 mL, 6.3 mmol, excess) was added by syringe. The reaction mixture was pressurized with C₂H₄ (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(CHCMe₃)₂(Cl)(PMe₃)₂. Ta(CHCMe₃)₂(Cl)(PMe₃)₂ (4.28 g, 8.41 mmol) was dissolved in pentane (\sim 40 mL), and the solution was pressurized with C₂H₄ (35 psi) for 24 h at 40 °C. The yellow solution became deep red (\sim 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 ¹H 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. ¹H NMR (toluene- d_8 , 270 MHz, -30 °C): δ 4.826 (m, 1,

CH₂=CH--CH=CH₂), 4.600 (m, 1, CH₂=CH--CH=CH₂), 1.380 (d, 9, ²J_{HP} = 7.3 Hz, PMe₃), 0.957 (d, 9, ²J_{HP} = 6.7 Hz, PMe₃'), 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 [$\Delta \nu = 62 \pm$ 5 Hz, ΔG^{\bullet} = 17 ± 1 kcal mol⁻¹]. ¹³C NMR (toluene-d₈, 67.89 MHz, -30 °C): 94.87 (d, ¹J_{CH} = 160 Hz, CH₂=CH--CH=CH₂), 92.57 (d, ¹J_{CH} = 163 Hz, CH₂=CH--CH=CH₂), 51.79 (tt, ²J_{CP} = 5.6 Hz, ¹J_{CH} = 147 Hz, CH₂=CH₂), 43.40 (ddd, ²J_{CP} = 5.7 Hz, ¹J_{CH} = 155 and 148 Hz, CH₂=CH₂), 34.75 (ddd, ²J_{CP} = 7.8 Hz, ¹J_{CH} = 141 and 149 Hz, CH₂=CH--CH=CH₂), 30.19 (tt, ²J_{CP} = 8.2 Hz, ¹J_{CH} = 150 Hz, CH₂=CH--CH=CH₂), 14.92 (qd, ¹J_{CP} = 21.6 Hz, ¹J_{CH} = 130 Hz, PMe₃), 13.54 (qd, ¹J_{CP} = 23.3 Hz, ¹J_{CH} = 130 Hz, PMe₃'). ¹³C NMR (15.0 Hz, 60 °C): ethylene carbon atom resonances coalesce [$T_c = 60 \pm$ ± 10 °C, $\Delta \nu = 129 \pm 5$ Hz, $\Delta G^{*} = 16 \pm 1$ kcal mol⁻¹]. ¹³C NMR (t5.0 MHz, 100 °C): 93.95 (s, CH₂=CH--CH=-CH₂), 47.8 (br s, CH₂= CH₂), 33.1 (s, CH₂=CH--CH=-CH₂), 14.9 ppm (d, ¹J_{CP} ≈ 12 Hz, PMe₃). ³¹P NMR (CDCl₃, 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)(C₂H₄)(Et)(PMe₃)₂. Ta(C_4H_6)(C₂H₄)(Cl)-(PMe₃)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 LiC₂H₅ (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 TaC₁₄H₃₃P₂: C, 37.84; H, 7.48. Found: C, 37.23; H, 7.32. ¹H NMR (toluene- d_8 , 270 MHz, -40 °C): δ 4.92 (m, CH₂=

CH—CH=CH₂), 3.46 (m, CH₂=CH—CH=CH₂), 1.30 (d, ²J_{HP} ≈ 6 Hz, PMe₃), 0.87 (d, ²J_{HP} ≈ 6 Hz, PMe₃'), 1.55, 1.16, 0.76, -0.16, and -0.37 (m, olefinic and CH₂ resonances), -0.05 (t, ³J_{HH} = 7.7 Hz, CH₂CH₃). ¹³C NMR (toluene-d₈, 67.89 MHz, -40 °C): major isomer, 102.3 (d, ¹J_{CH} = 157 Hz, CH₂=CH—CH=CH₂), 89.0 (d, ¹J_{CH} = 163 Hz, CH₂=CH—CH=CH₂), 48.6 ppm (tt, ²J_{CP} = 5.7 Hz, ¹J_{CH} = 146 Hz, CH₂=CH₂), 42.1 (td, ²J_{CP} = 4.8 Hz, ¹J_{CH} = 149 Hz, CH₂=CH₂), 33.9 (td, ²J_{CP} = 5.8 Hz, ¹J_{CH} = 150 Hz, CH₂=CH—CH=CH₂), 33.6 (t, ¹J_{CH} = 116 Hz, CH₂CH₃), 25.1 (td, ²J_{CP} = 9.0 Hz, ¹J_{CH} = 149 Hz, CH₂=CH—CH=CH₂), 15.0 (qd, ¹J_{CP} = 17.7 Hz, ¹J_{CH} = 130 Hz, PMe₃), 13.5 (qd, ¹J_{CP} = 19.4 Hz, ¹J_{CH} ≈ 130 Hz, PMe₃'), 5.8 ppm (q, ¹J_{CH} = 123 Hz, CH₂CH=CH=CH₂), 51.7 (CH₂=CH₂), 43.2 (CH₂=CH₂), 15.5 ppm (CH₂CH₃). (Other signals could not be found in this sample). ³¹P NMR (toluene-d₈, 109.3 MHz, -47 °C): δ -6.4 (s) and -11.4 (s) (major isomer) was 3:1 at -47 °C and 1:1 at 30 °C.

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Thioether Ligation in Iron-Porphyrin Complexes: Models for Cytochrome c

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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, $\beta = 90.29 (2)^{\circ}$, monoclinic, space group P_1/c , Z = 4; 5, a = 13.225 (3) Å, b = 17.967 (5) Å, c = 10.283 (2) Å, $\alpha = 91.07 (2)^{\circ}$, $\beta = 99.22 (2)^{\circ}$, $\gamma = 76.59 (2)^{\circ}$, triclinic, space group P_1 , Z = 2; 7, a = 17.830 (3) Å, b = 18.781 (3) Å, c = 18.187 (3) Å, orthorhombic, space group P_{21}/c_{1} , Z = 4; 6, a = 13.007 (7) Å, b = 19.188 (9) Å,

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

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