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α-Hydride vs. β-Hydride Elimination. An Example of an Equilibrium between Two Tautomers

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The reaction between $TaNp_2(Et)Cl_2$ and L (L = PMe_3) gives a mixture of $Ta(C_2H_4)(Np)Cl_2L_2$ and $Ta(CHCMe_3)(Et)Cl_2L_2$. These tautomers are shown to be in equilibrium with each other by magnetization transfer experiments. In $Ta(C_2H_4)(Np)Cl_2L_2$ the low field chemical shift for the neopentyl α-carbon atom (139 ppm) and the low value for J_{CH} (98 Hz) suggest that at least one α-hydrogen atom is interacting with the metal, thereby making the neopentyl complex look like a neopentylidene hydride complex. The neopentylidene ligand in $Ta(CHCMe_3)(Et)Cl_2L_2$ is one of the distorted variety (close to being a neopentylidyne hydride), and there is some evidence that a β-hydrogen of the ethyl group may also be "activated" by interaction with the metal. The mixture of $Ta(C_2H_4)(Np)Cl_2L_2$ and $Ta(CHCMe_3)(Et)Cl_2L_2$ reacts with ethylene to give $Ta(C_2H_4)(Et)Cl_2L_2$ in high yield and the organic products expected from reaction of the neopentylidene ligand in $Ta(CHCMe_3)(Et)Cl_2L_2$ with ethylene.

Introduction

It is generally assumed that β-hydride elimination is more facile than α-hydride elimination.[2] When the β-position is blocked by methyl groups γ elimination appears to be the next most favorable process for relatively electron-rich, later transition metals (e.g., Pt(II))[3] and α elimination the next most favorable for relatively electron-poor, earlier transition metals (e.g., Ta(III)).[4] Since some recent results in rhenium chemistry demonstrate that an α-hydride can be removed selectively (by an *external reagent*) from an alkyl ligand which possesses β-hydrogens,[5] it is conceivable that circumstances might arise where an α-elimination process is more rapid than a β-elimination process, either respectively in two different alkyl ligands bound to the same metal or more spectacularly in the single alkyl ligand which possesses both α- and β-protons. Since the alkylidene complex must be an energetically accessible species, we might expect to encounter one of these two versions of competition between an α- and a β-hydride elimination process in complexes of Ta, W, or Re. We have now discovered an example of the first of these two versions, an equilibrium between a tantalum neopentyl ethylene complex and a tantalum neopentylidene ethyl complex.

Results

Preparation of the $Ta(C_2H_4)(Np)Cl_2L_2$/$Ta(CHCMe_3)(Et)Cl_2L_2$ Mixture. $TaNp_2Cl_3$ reacts with 0.5 equiv of $ZnEt_2$ in pentane to give a yellow oil which slowly decomposes at 25 °C but which is indefinitely stable as a solid at −30 °C. This product was shown by ^1H and ^{13}C NMR to be $TaNp_2EtCl_2$ (1). It is probably a trigonal-bipyramidal species with axial chloride ligands. It is unusual to the extent that it is relatively stable even though β-hydrogen atoms are present. ($TaNp_2Et_3$ has also been isolated but appears to be less stable than $TaNp_2EtCl_2$.[6])

Table I. ^{13}C NMR Data for Some Tantalum Neopentyl Complexes in C_6D_6

	$\delta(C\alpha)$	$J_{CH\alpha}$, Hz
$TaNp_2Cl_3(PMe_3)$	96	121[7]
$TaNp_2EtCl_2$	112	117
$TaNp_3Cl_2$	115	119
$TaNp_2Cl_3$	123	116
$TaNpCl_4$	132	110
$Ta(CHCMe_3)Np_3$	114	107[8]
$Ta(C_2H_4)(Np)Cl_2L_2$	139	98

Addition of PMe_3 to $TaNp_2EtCl_2$ gave a brown crystalline product in good yield. The brown product decomposes slowly at 25 °C in the solid state or in solution and therefore could be characterized by NMR studies only. The ^1H NMR spectrum was complex, and some assignments were therefore suspect (see Experimental Section). The ^{13}C NMR spectrum, however, was considerably more informative (Figure 1). The product is actually a mixture of two species. One is $Ta(CHCMe_3)(Et)Cl_2L_2$ (**2a**). The other is its tautomer, $Ta(C_2H_4)(Np)Cl_2L_2$ (**2b**). We have found no samples in which the ratio of **2a** to **2b** deviates from ca. 1:1. Attempts to make $Ta(CHCMe_3)(Et)Cl_2L_2$ by alkylating *trans,mer*-$Ta(CHCMe_3)Cl_3L_2$[7] with EtMgBr did not succeed. The only product was $Ta(CHCMe_3)(C_2H_4)(Et)L_2$, a trigonal-bipyramidal molecule containing apical phosphine ligands.[6]

The neopentyl ligand in **2b** is one of the more unusual ones we have seen for the following reasons. The chemical shift of its α-carbon atom is much larger than one would predict based on the fact that only two chlorides are present (cf. $TaNpCl_4$, Table I). It is, in fact, the lowest field neopentyl α-carbon atom resonance we have ever observed (Table I). In addition, J_{CH_α} (98 Hz) is the lowest we have ever observed. Note that a low value for J_{CH_α} in alkylidene ligands has been shown to be characteristic of H_α (and/or the CH_α electrons) interacting with the metal and thereby activating H_α toward abstraction to give alkylidyne complexes.[4a] For this reason we believe a low J_{CH_α} value in **2b** suggests that the α-hydrogen atom is beginning to transfer to the metal; i.e., the neopentyl complex can

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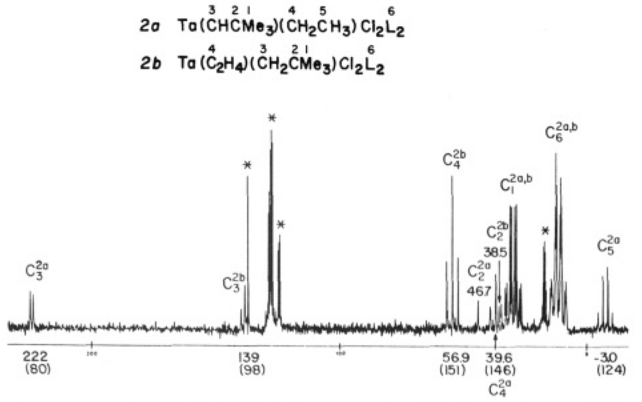
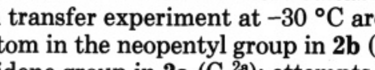


Figure 1. The 67.89-MHz ^{1}H-gated ^{13}C NMR spectrum of Ta$(CHCMe_3)(C_2H_5)Cl_2(PMe_3)_2$ (**2a**) and Ta$(CH_2CMe_3)(C_2H_4)Cl_2(PMe_3)_2$ (**2b**) in toluene-d_8 (asterisk).

be regarded as an "incipient neopentylidene hydride complex". Neopentylidene hydride complexes have been prepared by reducing tantalum(V) neopentyl complexes by two electrons.[4b]

The neopentylidene ligand in **2a** is one of the distorted variety (J_{CH} = 80 Hz) such as that found in *trans,mer*-Ta$(CHCMe_3)Cl_3(PMe_3)_2$.[7] Therefore, the Ta$=C_\alpha-C_\beta$ angle must be about 170° and the Ta$=C_\alpha-H_\alpha$ angle about 75° (cf. Ta$(\eta^5$-$C_5Me_5)(CHCMe_3)(C_2H_4)(PMe_3)$[9]). **2a** may be regarded as an "incipient neopentylidyne hydride" complex. While the ethyl ligand does not appear to be entirely normal in **2a** (J_{CH_α} (146 Hz) is not much less than the olefin CH coupling constant in the ethylene ligand in **2b** (151 Hz) and other ethylene complexes of tantalum[6]), we want to forego considering possible explanations at this time since the phenomenon may be of only incidental importance.

The most important question is whether **2a** and **2b** actually interconvert at a relatively rapid rate. In simplified form and without regard to structure, we can view the interconversion as shown in eq 1. Unfortunately, these



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complexes are not thermally stable. Above ca. 50 °C they decompose rapidly. At that temperature also the NMR spectra are broad and featureless due to what appears to be loss of PMe_3 from both **2a** and **2b**. In order to demonstrate that they do interconvert, we had to turn to magnetization transfer experiments.[10]

Magnetization Transfer Experiments. The carbon atoms whose relaxation times are most suitable for the magnetization transfer experiment at −30 °C are the tertiary carbon atom in the neopentyl group in **2b** (C_2^{2b}) and the neopentylidene group in **2a** (C_2^{2a}); attempts to utilize other carbon atoms failed. This region of the $^{13}C\{^1H\}$ NMR spectrum of the **2a**/**2b** mixture is shown in Figure 2a. Irradiating C_2^{2b} caused the intensity of the signal for C_2^{2a} to decrease significantly (Figure 2b); no other signal decreased in intensity except that ascribed to the α-carbon atom of the ethyl group in **2a** (C_4^{2a}) nearby. The reverse experiment (Figure 2c) was equally successful. In this case the intensity of the signal due to C_4^{2a} did not decrease since the irradiation frequency was further away. This confirms

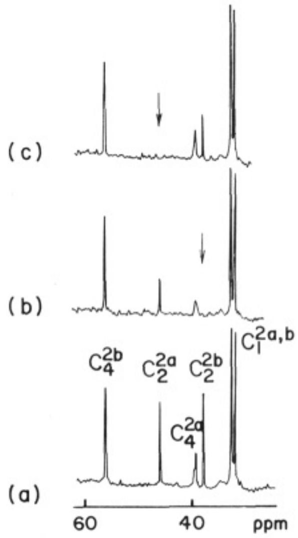

Figure 2. The 67.89-MHz ^{13}C NMR magnetization transfer experiment on the mixture of Ta$(CHCMe_3)(Et)Cl_3(PMe_3)_2$ and Ta$(C_2H_4)(Np)Cl_2(PMe_3)_2$ in toluene-d_8 at −30 °C: (a) the partial $^{13}C\{^1H\}$ NMR spectrum; (b) the partial $^{13}C\{^1H\}$ NMR spectrum irradiating C_2^{2b}; (c) the partial $^{13}C\{^1H\}$ NMR spectrum irradiating C_2^{2a}. See Figure 1 for numbering scheme.

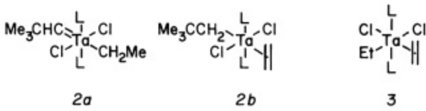

Figure 3. Possible structures for **2a**, **2b**, and **3**.

that **2a** and **2b** are interconverting at −30 °C at a rate between that of the NMR and chemical time scales. Unfortunately, the large amount of time needed to determine this rate exactly by ^{13}C NMR experiments precluded doing so.

Structures of Ta$(C_2H_4)(Np)Cl_2L_2$ and Ta$(CHCMe_3)(Et)Cl_2L_2$ and Dynamic Behavior in Solution. It is important, if not essential, to know the structures for **2a** and **2b** in solution, for if the hydrocarbon ligands are trans to each other, one might expect loss of PMe_3 to be integral part of the interconversion process. The virtually coupled pattern for the methyl protons or carbon atoms in the ^{1}H or ^{13}C NMR spectra assure that the PMe_3 ligands in each compound are trans, or nearly trans, to each other. The major question is whether the remaining geometry is cis or trans (assuming the overall geometries of **2a** and **2b** are similar). Unfortunately, no data in hand suggest one or the other. Let us for the moment assume that the two chloride ligands in **2a** and **2b** are trans (Figure 3) but keep in mind that they could be cis (cf. Ta$(C_2H_4)(Et)Cl_2L_2$ later). The ethylene ligand in **2b** probably lies parallel to the L—Ta—L axis since it lies parallel to the L—Ta—L axis in *trans,mer*-Ta$(C_2H_4)Cl_3(PMe_3)_2$.[11] Since the plane of the neopentylidene ligand in *trans,mer*-Ta$(CHCMe_3)Cl_3(PMe_3)_2$ probably contains the Cl—Ta—Cl axis,[11] we might expect the plane of the neopentylidene ligand in **2a** also to contain the Cl—Ta—Cl axis.

The ^{31}P NMR spectrum of the **2a**/**2b** mixture is shown at 205 K in Figure 4a. Interestingly, the two phosphine ligands in **2a** are inequivalent (J_{PP} = 124 Hz) at this temperature. In **2b** the phosphine ligands are still equivalent. At 300 K the phosphine ligands in **2a** are equivalent, but they still are not exchanging with those in **2b** (Figure 4b).

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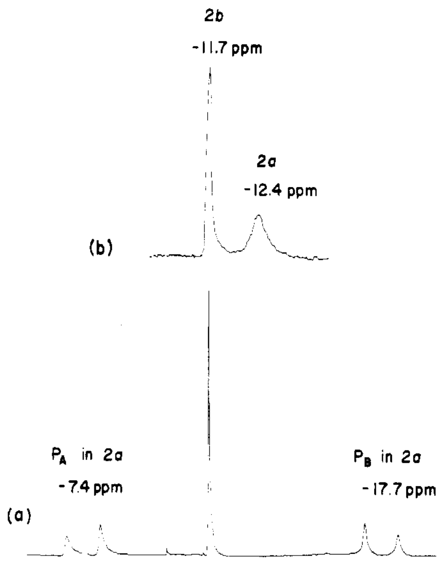


Figure 4. The 109.3-MHz ^{31}P NMR spectrum of the **2a**/**2b** mixture in toluene-d_8: (a) at 205 K; (b) at 300 K (different scale).

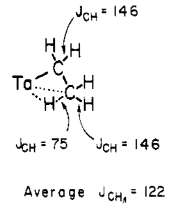


Figure 5. A possible interaction of a β-hydrogen with the metal in **2b**.

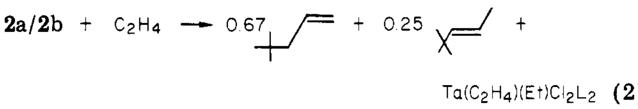
Irrespective of whether the overall geometry of **2a** is that shown in Figure 3 or the alternative with cis hydrocarbon ligands, either the neopentylidene or the ethyl ligand must be locked at low temperatures in a position so as to make the phosphines inequivalent. The possibility that the neopentylidene ligand is responsible seems the most likely to us. Either the plane of the neopentylidene ligand contains the L—Ta—L axis (not the Cl—Ta—Cl axis, as proposed earlier) or H_α is located on a face of the octahedron. There are now two examples of compounds in which H_a is located on the face of an octahedron, $[W(CH_2)(PMe_3)_4]^+$[12] and $W(CHCMe_3)(PMe_3)_2(CO)Cl_2$,[13] although in each case the metal is in a formal oxidation state two electrons below that of tantalum in $Ta(CHCMe_3)(C_2H_5)(PMe_3)_2Cl_2$.

The alternative is to propose that a β-hydrogen atom in the ethyl ligand is interacting with the metal, either along the L—Ta—L edge or on one of the faces of the octahedron. The only good reason for considering this possibility is the high value for J_{CH_2}. J_{CH_2} could be high because the ethyl ligand is being turned into an ethylene hydride; i.e., the "normal" value for J_{CH_3} is actually the average of two other "abnormal" values (Figure 5). There is some important literature precedent for interactions of methyl groups with metals in the form of a neutron diffraction structure of $[Fe(\eta^3\text{-}C_8H_{13})[P(OMe)_3]_3]^+$[14] and ^{13}C NMR parameters for this and similar compounds.[15] We consider this alternative less likely than the former since there is no structural precedent for this precise situation. Also, even though it is a perfectly reasonable and often proposed state in a β-elimination process, we do not think it necessary to establish in this case whether the β-proton interaction is or is not present in this six-coordinate complex.

We proposed that one or both α-hydrogen atom(s) is (are) interacting with the metal in **2b**. Such an interaction (along an edge or on a face) should also make the PMe_3 ligands inequivalent. We propose that freezing out this configuration on the NMR time scale is simple more difficult than in the case of **2a**.

If the structures of **2a** and **2b** are those shown in Figure 3, then PMe_3 probably is lost prior to interconversion of the two. There is still a possibility that the hydrocarbon ligands are actually *cis* to each other, in which case **2a** and **2b** could interconvert simply by migration of a proton across the face of the octahedron.

Reaction of the 2a/2b Mixture with Ethylene. The **2a**/**2b** mixture reacts with ethylene at 25 °C to give nearly black, crystalline $Ta(C_2H_4)(Et)Cl_2L_2$ (**3**). The organic products are 4,4-dimethyl-1-pentene (0.67 equiv) and 4,4-dimethyl-*trans*-2-pentene (0.25 equiv), the products expected from the reaction of the neopentylidene ligand in **2a** with ethylene (eq 2).[4a] This result could be taken



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as additional evidence that **2a** and **2b** interconvert readily. But in addition, it suggests that formation and rearrangement of a tantalacyclobutane ring formed from the neopentylidene ligand and ethylene is faster than formation and rearrangement of a tantalacyclopentane ring formed from two ethylenes. 1-Butene and eventually C_6 and C_8 olefins form but only after long reaction times.

The NMR spectra of $Ta(C_2H_4)(Et)Cl_2L_2$ suggest that it contains trans PMe_3 ligands. Since two sets of ethylene protons are observed in the ^1H NMR spectrum, **3** must contain cis chloride ligands (Figure 3). Note that the CH_2 coupling constant in the ethyl ligand is only 133 Hz, far more normal than the 146 Hz found in $Ta(CHCMe_3)(Et)Cl_2L_2$.

Discussion

The neopentyl ligand is the most susceptible ligand toward abstraction of an α-hydrogen atom to give an alkylidene complex[4a] which we have found so far. It is reasonable to suspect that it is also the most susceptible to α elimination to give an alkylidene/hydride complex.[4b] Nevertheless, we were surprised to find that α elimination from a neopentyl ligand competes with β elimination from an ethyl ligand.

We had found some evidence for a related phenomenon in the study of the reaction of ethylene with trigonal-bipyramidal neopentylidene complexes.[6] $Ta(CHCMe_3)_2(CH_2CMe_3)L_2$ (L = PMe_3) reacts with ethylene to give 3 equiv of 4,4-dimethyl-1-pentene and 4,4-dimethyl-*trans*-2-pentene (cf. eq 2) and $Ta(C_2H_4)_2(Bu)L_2$. In contrast, $Nb(CHCMe_3)_2(CH_2CMe_3)L_2$ reacts with ethylene to give 3 equiv of a mixture of 4,4-dimethyl-1-pentene and 4,4-dimethyl-*trans*-2-pentene and $Nb(C_2H_4)_2(Et)L_2$. It was proposed (inter alia) that (i) ethylene reacted more rapidly with neopentylidene ligands than with ethylene ligands, (ii) a neopentyl ligand is turned into a neopentylidene ligand by donating an α-hydrogen atom to an α-carbon atom of an intermediate α-*tert*-butyltantalacyclobutane

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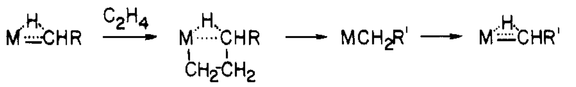
complex, and (iii) the ethyl ligand in $Nb(C_2H_4)_2(Et)L_2$ is formed by isomerization of a neoheptylniobium ethylene to an ethylniobium neoheptene complex. $Ta(C_2H_4)_2(Bu)L_2$ is a catalyst for the rapid dimerization of ethylene to 1-butene, probably via a tantalacyclopentane intermediate. $Nb(C_2H_4)_2(Et)L_2$ is not, probably because formation and rearrangement of an analogous niobacyclopentane complex is not as facile.

The selective reaction of the **2a**/**2b** mixture with ethylene to give the products shown in eq 2 (and only very slowly 1-butene and other oligomers), along with the results mentioned immediately above, could be used as evidence in support of the "alkylidene mechanism" of polymerizing ethylene.[16] A variation of the original proposal is that the alkylidene hydride need not be fully formed, only incipient, as found in **2b**.[17] Therefore a polymerization can be viewed as shown in eq 3. However, another plausible way



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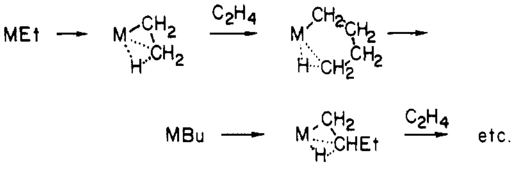
of viewing insertion of ethylene into a metal–alkyl bond involves the reaction of a related incipient olefin hydride complex with ethylene to give an incipient metallacyclopentane hydride complex (eq 4). From what we have



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observed in tantalum chemistry, the alternative in eq 3 seems more plausible than that in eq 4, at least for earlier transition metals where alkylidene complexes are now fairly common.[4a]

One puzzling fact is that **2a** is stable at all. One might have predicted on the basis of the reaction of cyclopentadienyltantalum alkylalkylidene complexes with phosphines to give alkylidyne complexes[18] and the isolation of tungsten complexes such as $W(CCMe_3)Cl_3(PMe_3)_3$[19] that **2a** would decompose to $Ta(CCMe_3)Cl_2(PMe_3)_2$ in high yield or to $Ta(CCMe_3)Cl_2(PMe_3)_3$ in lower yield. However, so far all our efforts to characterize the product of the decomposition of the **2a**/**2b** mixture in the presence of PMe_3 have been unsuccessful.

Experimental Section

General experimental procedures can be found elsewhere.[7,8] NMR data are listed in parts per million relative to Me_4Si (^1H and ^{13}C NMR) or external 85% H_3PO_4 (^{31}P NMR).

The magnetization transfer experiments were performed by using a presaturation pulse sequence. A presaturating frequency of 0.5 W was used to irradiate the desired line for 4 s. At the end of that period the irradiating frequency was gated off and then followed 0.001 s later by the short RF pulse required to obtain the FID.

Preparation of $TaNp_2EtCl_2$ (1). $TaNp_2Cl_3$ (1.41 g, 3.28 mmol) was dissolved in pentane (20 mL), and the solution was cooled to −30 °C. $ZnEt_2$ (0.21 g, 1.64 mmol) was added rapidly and the solution was warmed to 25 °C and stirred for 10 min. $ZnCl_2$ (0.24 g, 0.22 g theory) was filtered off and the solvent removed from the yellow filtrate. The yellow oil (1.36 g, 98%) slowly darkened at 25 °C. ^1H NMR ($C_6D_5CD_3$, 60 MHz, −20 °C) δ 2.52 (s, 4, CH_2CMe_3), 2.20 (m, 5, ethyl resonances), 1.22 (s, 18, CH_2CMe_3); ^{13}C NMR ($C_6D_5CD_3$, 15 MHz, −20 °C) δ 112.0 (t, $^1J_{CH}$ = 117 Hz, CH_2CMe_3), 90.8 (t, $^1J_{CH}$ = 125 Hz, CH_2CH_3), 35.3 (q, $^1J_{CH}$ = 125 Hz, CH_2CMe_3), 34.7 (s, CH_2CMe_3) , 14.4 (q, $^1J_{CH}$ = 129 Hz, CH_2CH_3).

Preparation of $Ta(CHCMe_3)(Et)Cl_2(PMe_3)_2$ (2a) and $Ta(C_2H_4)(Np)Cl_2(PMe_3)_2$ (2b). $TaNp_2EtCl_2$ (0.93 g, 2.20 mmol) was dissolved in ether (10 mL), and PMe_3 (0.35 g, 4.60 mmol, excess) in ether (5 mL) was added rapidly at −30 °C. The color changed from yellow to red. The solution was warmed to 25 °C and stirred for 10 min. The solvent was removed in vacuo. The brown oil was extracted with pentane (10 mL), and the solution was filtered and cooled to −30 °C. After 12 h 0.84 g of brown urchin-like needles were collected (76%). The crystalline product is indefinitely stable at −30 °C but decomposes in 1 h at 25 °C to give an intractable brown tar. Similar results were obtained by using pentane as a reaction solvent: ^1H NMR ($C_6D_5CD_3$, 270 MHz, −40 °C) for $Ta(CHCMe_3)(Et)Cl_2(PMe_3)_2$ δ 1.372 (br m, $^2J_{HP}$ = 7.4 Hz, PMe_3), 0.742 (s, $CHCMe_3$), −0.087 (br m, CH_2CH_3); for $Ta(C_2H_4)(Np)Cl_2(PMe_3)_2$ δ 2.431 (br m, C_2H_4), 1.459 (br t, $^2J_{HP}$ = 3.6 Hz, PMe_3), 0.556 (s, CH_2CMe_3), −1.952 (s, CH_2CMe_3); ^{13}C NMR ($C_6D_5CD_3$, 67.89 MHz, −20 °C) for $Ta(CHCMe_3)(Et)Cl_2(PMe_3)_2$ δ 222.3 (dt, $^2J_{CP}$ = 8.1 Hz, $^1J_{CH}$ = 80 Hz, $CHCMe_3$), 46.7 (s, $CHCMe_3$), 39.6 (tt, $^2J_{CP}$ = 9.5 Hz, $^1J_{CH}$ = 146 Hz, CH_2CH_3), 33.2 (q, $^1J_{CH}$ = 126 Hz, $CHCMe_3$), 15.4 (qt, $^1J_{CP}$ = 12 Hz, $^1J_{CH}$ ≈ 130 Hz, PMe_3), −3.0 (qt, $^3J_{CP}$ ≈ 3 Hz, $^1J_{CH}$ = 124 Hz, CH_2CH_3); for $Ta(C_2H_4)(Np)Cl_2(PMe_3)_2$ δ 138.9 (t, $^1J_{CH}$ = 98 Hz, CH_2CMe_3), 56.9 (tt, $^2J_{CP}$ ≈ 3 Hz, $^1J_{CH}$ = 151 Hz, C_2H_4), 38.5 (s, CH_2CMe_3), 32.7 (q, $^1J_{CH}$ = 127 Hz, CH_2CMe_3), 14.9 (qt, $^1J_{CP}$ = 12.5 Hz, $^1J_{CH}$ ≈ 130 Hz, PMe_3); ^{31}P NMR ($C_6D_5CD_3$, 109.29 MHz, +27 to −67 °C) for $Ta(CHCMe_3)EtCl_2(PMe_3)_2$ at 27 °C δ −12.4 (br s), −37 °C, coalescence of P_A and P_B resonances, −67 °C δ −7.4 (d, $^2J_{P_AP_B}$ = 124 Hz, PMe_3(A)), −17.7 (d, $^2J_{P_BP_A}$ = 126 Hz, PMe_3(B)); for $Ta(C_2H_4)(Np)Cl_2(PMe_3)_2$ δ −11.7 (a sharp singlet to −67 °C).

Preparation of $Ta(C_2H_4)(Et)Cl_2(PMe_3)_2$ (3). A sample of **2** (3.38 g, 6.72 mmol) in ether (20 mL) reacted with C_2H_4 (30 psi) in 2.5 h at 25 °C. The reaction mixture was filtered and solvent removed from the filtrate to give nearly black crystals. The crude product was dissolved in a minimal amount of ether (~15 mL). After 12 h at −30 °C, 1.95 g of irregularly shaped blue-black crystals were isolated by filtration. The volume of the mother liquor was reduced in vacuo to ~7 mL, and pentane (~3 mL) was added. After this solution was left standing at −30 °C for 16 h, an additional 0.35 g of pure compound was isolated: 75% total yield; ^1H NMR ($C_6D_5CD_3$, 250 MHz, −30 °C) δ 1.729 (m, 2, olefinic H), 1.299 (t, 18, $^2J_{HP}$ = 3.7 Hz, PMe_3), 1.081 (m, 2, CH_2CH_3), −0.104 (m, 3, CH_2CH_3), −1.031 (m, 2, olefinic H); ^{13}C NMR (C_6D_6, 15 MHz, 25 °C) 61.65 (tt, $^1J_{CP}$ = 8 Hz, $^1J_{CH}$ = 133 Hz, CH_2CH_3), 54.30 (tt, $^1J_{CP}$ ≈ 4 Hz, $^1J_{CH}$ = 151 Hz, C_2H_4), 14.20 (qt, $^1J_{CP}$ = 11.7 Hz, $^1J_{CH}$ = 129 Hz, PMe_3), 1.8 (br q, $^1J_{CP}$ ≈ 4 Hz, $^1J_{CH}$ = 125 Hz, CH_2CH_3); ^{31}P ($C_6H_5CH_3$, 36 MHz, 30 °C) δ −13 (s).

Anal. Calcd for $TaC_{10}H_{27}Cl_2P_2$: C, 25.82; H, 5.85. Found: C, 25.30, H, 5.91.

A sample of **3** (0.15 g, 0.298 mmol) in ether (~1.5 mL) which contained heptane (50 μL, 0.340 mmol) was treated with ethylene (30 psi) at 0 °C. Samples were withdrawn periodically and quenched with air. GLC analysis showed 0.67 equiv of 4,4-dimethyl-1-pentene and 0.25 equiv of 4,4-dimethyl-*trans*-2-pentene. Longer reaction times gave >1 equiv of butenes, 0.58 equiv of 3-ethyl-1-butene (identified by coinjection with an authentic sample), and ~0.3 equiv of unidentified C_8 olefins. The production of butenes was suppressed in the presence of excess PMe_3.

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Registry No. 1, 79828-19-6; **2a**, 79839-93-3; **2b**, 79839-94-4; 3, 79855-21-3; $TaNp_2Cl_3$, 61645-40-7.

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