the other atoms, and ΔE_R is the change in relaxation energy. The E_R values were calculated from the relation $E_R = 0.25[\Phi_{val}(C) - \Phi_{val}(N^+)$, where $\Phi_{val}(C)$ is the valence potential in the ground-state molecule and $\Phi_{val}(N^+)$ is the valence potential in the ion, approximated by replacing the C nucleus by the N nucleus.[12,13] CNDO/2 wave functions were used.[40] We assumed that the relative valence-electron populations of the atoms in the $Co(CO)_3$ groups were the same as calculated for $HCo(CO)_4$,[41] that Q_C = −0.2 in acetylene,[42] and that $(\Delta Q_H/\Delta Q_C) = 0.2$.[43] The experimental geometry of C_2H_2[44] was used, and symmetric idealized geometries for $HC[Co(CO)_3]_3$[45] and $(HC)_2[Co(CO)_3]_2$[46] were assumed. In the cobalt complexes, we assumed Co–CO and C–O bond distances of 1.8 and 1.1 Å, and a C–H bond distance equal to that in benzene. The calculated relaxation energies for C_2H_2, $HC[Co(CO)_3]_3$, and $(HC)_2[Co(CO)_3]_2$ are 7.68, 10.35, and 10.18 eV, respectively.

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Registry No. $Et_3SiC[Co(CO)_3]_3$, 64115-67-9; $HC[Co(CO)_3]_3$, 15664-75-2; $CH_3C[Co(CO)_3]_3$, 13682-04-7; $BrC[Co(CO)_3]_3$, 19439-14-6; $ClC[Co(CO)_3]_3$, 13682-02-5; $(CH_3)_2NC[Co(CO)_3]_3$, 41751-69-3; $CH_3OC[Co(CO)_3]_3$, 41751-68-2; $[Co(CO)_3]_4$, 17786-31-1; $(HC)_2[Co(CO)_3]_2$, 12264-05-0; $(Me_3SiC)_2[Co(CO_3)]_2$, 14767-82-9; $(Me_3CC)(Me_3SiC)[Co(CO)_3]_2$, 80926-03-0; $(CO)_3Fe(Co_3(CO)_9H$, 21750-96-9.

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Preparation of Tantalum μ-Dinitrogen Complexes from Molecular Nitrogen and Reduced Tantalum Complexes

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Tantalum pentachloride is reduced under argon by sodium amalgam in the presence of PMe_3 to give red paramagnetic $TaCl_3(PMe_3)_3$ in 80% yield. It decomposes readily in solution to give $[TaCl_3(PMe_3)_2]_2$. It reacts with hydrogen to give $[TaCl_3(PMe_3)_2]_2H_2$ and with ethylene to give *trans*-$Ta(C_2H_4)(PMe_3)_2Cl_3$, but it does not react with molecular nitrogen to give known $[TaCl_3(PMe_3)_2]_2(\mu\text{-}N_2)$. $Ta(C_2H_4)(PMe_3)_2Cl_3$ is reduced by sodium amalgam in the presence of PMe_3 under argon to give $Ta(C_2H_4)(PMe_3)_4Cl$ in high yield. $Ta(C_2H_4)(PMe_3)_4Cl$, like $Ta(CHCMe_3)(PMe_3)_4Cl$, reacts readily with molecular nitrogen to give μ-dinitrogen complexes. The dinitrogen complexes react with HCl to give hydrazine dihydrochloride in high yield and with acetone to give dimethylketazine. The dinitrogen complexes have been labeled with $^{15}N_2$ and studied by ^{15}N NMR and IR spectroscopy.

Introduction

We recently reported some simple μ-dinitrogen complexes of tantalum and niobium which were prepared by reacting neopentylidene complexes with azines.[1] These appear to be best regarded as complexes of N_2^{4-} according to structural investigations[2] and reactions with HCl and acetone which are analogous to those of tantalum and niobium imido complexes.[1] The natural question is whether these or some related μ-N_2 complexes can be prepared by reacting a reduced tantalum or niobium complex with molecular nitrogen. In this paper we show that μ-dinitrogen complexes containing neopentylidene or ethylene ligands can be prepared in this manner but that at least one member of the class of compounds which was prepared via the azine route cannot. Details of the preparation and properties of two new reduced tantalum complexes, $TaCl_3(PMe_3)_3$ and $Ta(C_2H_4)(PMe_3)_4Cl$, are included. Some of these results have appeared in a preliminary communication.[3]

Results

Preparation of Reduced Tantalum Complexes. Tantalum pentachloride is reduced smoothly by sodium amalgam under argon in the presence of excess PMe_3 to give bright red $TaCl_3(PMe_3)_3$ in 80% yield. A cryoscopic molecular weight study shows it to be a monomer. Since two types of PMe_3 resonances are observed in the high-field ^1H NMR spectrum (at δ −6.21 (area 2) and 9.57 (area 1)), $TaCl_3(PMe_3)_3$ is best formulated as an octahedron containing meridional PMe_3 ligands. $TaCl_3(PMe_3)_3$ can also be prepared by heating Ta_2Cl_6(tetrahydrothiophene)$_3$[4] with excess PMe_3 in benzene at 60 °C for 12 h in a sealed tube. To our knowledge $TaCl_3(PMe_3)_3$ is the only simple monomeric adduct of MCl_3 (M = Nb[5] or Ta).

The peculiar chemical shifts of the PMe_3 protons in the ^1H NMR spectrum and the fact that no $^{31}P\{^1H\}$ NMR

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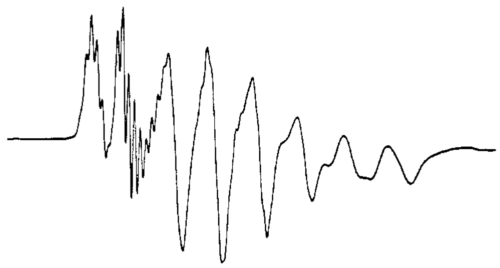

Figure 1. The EPR spectrum of $TaCl_3(PMe_3)_3$ in toluene at 77 K (peak separation ≈ 240 G at 9.162 GHz).

spectrum could be observed at 25 °C suggests that this d^2 complex is paramagnetic. Although no EPR spectrum is observed at room temperature, at 77 K an eighth-line pattern (g_{av} = 1.92) with a peak separation of ~240 G (at 9.162 GHz) is observed (Figure 1).

$TaCl_3(PMe_3)_3$ decomposes readily in solution to give a dimer, $[TaCl_3(PMe_3)_2]_2$. The ^{31}P NMR spectrum (two singlets, −32 and −54 ppm) suggests that $[TaCl_3(PMe_3)_2]_2$ is a bioctahedron containing two phosphine ligands in axial positions on one metal and two in equatorial positions on the other metal. A recent single-crystal X-ray structural study has shown this to be the case.[6] $TaCl_3(PMe_3)_3$, like $[TaCl_3(PMe_3)_2]_2$, reacts readily with molecular hydrogen to give $[TaCl_3(PMe_3)_2]_2H_2$[6] and with ethylene to give *trans*-$Ta(C_2H_4)(PMe_3)_2Cl_3$.[7] All these results suggest that one PMe_3 ligand is lost to give incipient $TaCl_3(PMe_3)_2$. Although an associative reaction between $TaCl_3(PMe_3)_3$ and H_2 or C_2H_4 would be difficult to rule out, it seems considerably less likely.

When $Ta(C_2H_4)(PMe_3)_2Cl_3$ is reduced by sodium amalgam in the presence of PMe_3 under argon, $Ta(C_2H_4)(PMe_3)_4Cl$ can be isolated in high yield. $Ta(C_2H_4)(PMe_3)_4Cl$ is extremely sensitive to oxygen and dinitrogen and difficult to isolate and handle. The signal for the ethylene protons is a quintet at 2.25 ppm (J_{HP} = 3.7 Hz) in the ^1H NMR spectrum, as is the signal for the ethylene carbon atoms at 33.2 ppm (J_{CH} = 146 ppm) in the ^{13}C NMR spectrum. The quintet pattern for the signals suggests that no PMe_3 is being lost on the NMR time scale and that the ethylene ligand is probably rotating about the Ta–ethylene bond axis in an octahedral molecule containing four PMe_3 ligands in a plane. The absence of a $^{31}P\{^1H\}$ NMR spectrum at temperatures down to −60 °C suggests that this formally d^4 metal complex is slightly paramagnetic (cf. $ReCl_3(PMe_3)_3$[8]).

Because we believed $Ta(C_2H_4)(PMe_3)_4Cl$ did not analyze due to loss of PMe_3 in the solid state, we prepared a $Ta(C_2H_4)(dmpe)_2Cl$ complex. $Ta(C_2H_4)(dmpe)_2Cl$ appears to be analogous to $Ta(C_2H_4)(PMe_3)_4Cl$ and does analyze correctly. It can be prepared and handled under dinitrogen.

$Ta(CHCMe_3)(PMe_3)_4Cl$ has been reported in a preliminary communication.[9] A discussion of the preparation and properties of it and several analogues will be presented elsewhere.

Formation of $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$. When $Ta(CHCMe_3)(PMe_3)_4Cl$ is dissolved in a mixture of ether and tetrahydrofuran and the solution is exposed to dinitrogen (1 atm), the dinitrogen complex, $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$, precipitates as a yellow powder in 50–60% yield. IR and NMR studies suggest that this molecule contains an imido-like dinitrogen ligand bridging two tantalum centers.

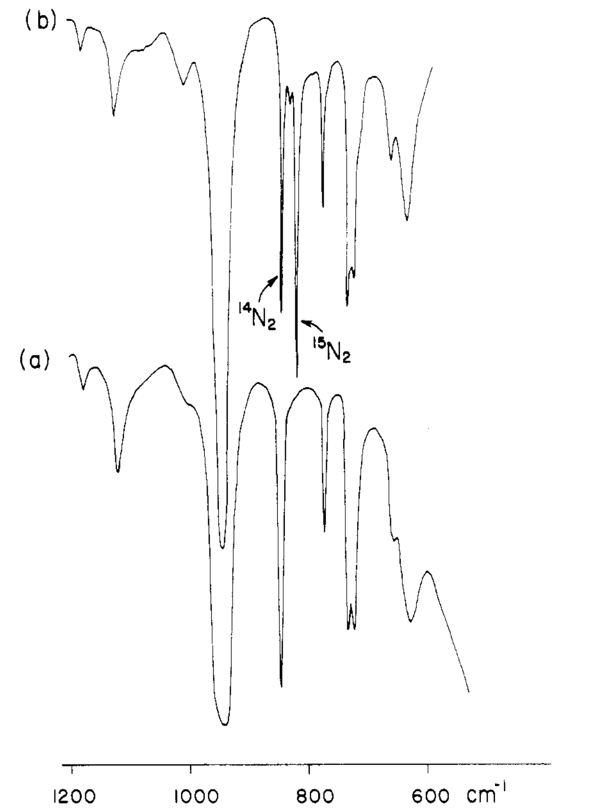

Figure 2. (a) The IR spectrum of $[Ta(CHCMe_3)L_2Cl]_2(\mu\text{-}^{14}N_2)$. (b) The IR spectrum of a mixture of $[Ta(CHCMe_3)L_2Cl]_2(\mu\text{-}^{14}N_2)$ and $[Ta(CHCMe_3)L_2Cl]_2(\mu\text{-}^{15}N_2)$ (L = PMe_3).

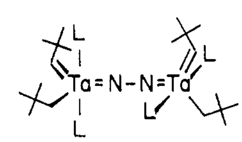

Figure 3. A drawing of the structure of $[Ta(CHCMe_3)L_2(CH_2CMe_3)]_2(\mu\text{-}N_2)$[2a] (L = PMe_3).

The ^{15}N-labeled complex can be prepared straightforwardly by stirring a solution of $Ta(CHCMe_3)(PMe_3)_4Cl$ under $^{15}N_2$. The IR spectrum of the $^{15}N_2$ derivative differs from that of the $^{14}N_2$ derivative in only one respect. A medium strength peak at 847 cm^{-1} is shifted to 820 cm^{-1} in the IR spectrum of the $^{15}N_2$ derivative (Figure 2). Since this molecule is not centrosymmetric (see later), we do not know if this band is due to an N–N stretching mode, Ta–N stretching mode, or, most likely, a mode characteristic of the entire Ta_2N_2 linkage. The ^{15}N NMR spectrum of $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$ consists of a sharp singlet at 414 ppm (relative to liquid NH_3).

The presence of a $\mu\text{-}N_2$ ligand is further confirmed by the reaction of $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$ with HCl to give $N_2H_4\cdot 2HCl$ quantitatively and with acetone to give $Me_2C{=}N{-}N{=}CMe_2$ (dimethylketazine). This type of reactivity is characteristic of imido complexes such as $Ta(NR)(THF)_2Cl_3$[1] and suggests further that the $\mu\text{-}N_2$ ligand is imido-like, i.e., that the $Ta_2(\mu\text{-}N_2)$ linkage is best described as $Ta{=}N{-}N{=}Ta$. Since attempts to prepare X-ray quality crystals of $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$ were unsuccessful, we prepared methyl and neopentyl derivatives, $[Ta(CHCMe_3)(PMe_3)_2R]_2(\mu\text{-}N_2)$. A crystal structure of the neopentyl derivative has been reported[2a]

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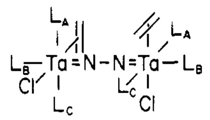

Figure 4. A drawing of the proposed structure of $[Ta(C_2H_4)L_3Cl]_2(\mu\text{-}N_2)$ ($L = PMe_3$).

and is shown schematically in Figure 3. The tantalum–nitrogen bond length of 1.84 Å is close to that found in tantalum(V) imido complexes (e.g., 1.765 Å in $Ta(NPh)(THF)(PEt_3)Cl_3$[10]). The N(1)–N(2) distance of 1.298 Å is the longest yet observed in a simple bridging dinitrogen complex and represents a substantial reduction in bond order from that observed in free N_2 (N:N = 1.0976 Å). One could argue convincingly that the μ-N_2 ligand is structurally more like an imido ligand (i.e., Ta=N—N=Ta) than in any other simple μ-N_2 complex which has been structurally characterized.[1]

Formation of $[Ta(C_2H_4)(PMe_3)_3X]_2(\mu\text{-}N_2)$. Reduction of $Ta(C_2H_4)(PMe_3)_2X_3$ under dinitrogen in the presence of excess PMe_3 gives orange microcrystals of $[Ta(C_2H_4)(PMe_3)_3X]_2(\mu\text{-}N_2)$ (X = Cl or Br). These complexes also can be prepared by exposing $Ta(C_2H_4)(PMe_3)_4X$ to dinitrogen; in this way the analogous $^{15}N_2$ complexes can be prepared. The presence of dinitrogen is suggested by the shift of a peak at 825 cm^{-1} in the IR spectrum of the $^{14}N_2$ derivative to 793 cm^{-1} in the $^{15}N_2$ derivative (X = Cl) and by a resonance at 374 ppm (downfield of liquid NH_3) in the $^{15}N_2$ spectrum (X = Cl). The presence of dinitrogen can be demonstrated chemically by the reaction of the chloro derivative with HCl to give $N_2H_4{\cdot}2HCl$ quantitatively and with acetone to give dimethylketazine (85%).

The structure of $[Ta(C_2H_4)(PMe_3)_3X]_2(\mu\text{-}N_2)$ is believed to be that shown in Figure 4. At 213 K *three* PMe_3 ligands are observed by NMR. We believe that rotation of the two ends of the molecule is restricted by the two interlocking L–Ta–L units analogous to the situation observed for $[Ta(CHCMe_3)(PMe_3)_2(CH_2CMe_3)]_2(\mu\text{-}N_2)$.[2a] At higher temperatures one of the three phosphines dissociates from Ta and will exchange with any PMe_3 which is added. The remaining two PMe_3 ligands become equivalent but do not exchange with added PMe_3. We propose that the PMe_3 ligand trans to the μ-N_2 ligand is the labile one and that once it dissociates the configuration about each metal can become tetragonal pyramidal. The two ends can then rotate relative to one another and thereby equilibrate the two trans PMe_3 ligands. Consistent with this proposal is the fact that two signals for ethylene carbon atoms are found at low temperature. These two signals coalesce to one at temperatures where the PMe_3 ligand trans to the μ-N_2 ligand is lost.

$[Ta(C_2H_4)(PMe_3)_3X]_2(\mu\text{-}N_2)$ should be structurally analogous to $Ta(NR)(C_2H_4)(PMe_3)_3X$.[1] In the imido complex, however, only two types of PMe_3 ligands are found at low temperatures, even though the same type of temperature-dependent NMR behavior (exchange of the unique PMe_3 ligand with added PMe_3) is observed.

Since a PMe_3 ligand must be lost to form the μ-N_2 complexes we have described so far, and since dmpe is comparatively tightly bound, we would expect $Ta(C_2H_4)(dmpe)_2Cl$ to be stable in the presence of dinitrogen. This is the case. We previously noted that $Ta(CHCMe_3)(dmpe)_2Cl$ can be prepared in a dinitrogen atmosphere.[14] Is also shows no tendency to lose dmpe and form a dinitrogen complex.

Attempts To Prepare $[TaCl_3(PMe_2]_2(\mu\text{-}N_2)$. Since we have prepared $[TaCl_3(PMe_3)_2]_2(\mu\text{-}N_2)$ via the "azine route"[1] and since one PMe_3 ligand could be replaced by a μ-N_2 ligand in the two previous cases we have discussed here, we expected to be able to prepare $[TaCl_3(PMe_3)_2]_2(\mu\text{-}N_2)$ by exposing $TaCl_3(PMe_3)_3$ to dinitrogen. Unfortunately we have seen no evidence for $[TaCl_3(PMe_3)_2]_2(\mu\text{-}N_2)$ in the ^{31}P NMR and IR spectra of the crude, solid product of these reactions obtained by removing all volatiles in vacuo. Under 1 atm of dinitrogen the predominant result is largely formation of $[TaCl_3(PMe_3)_2]_2$; a solution of $[TaCl_3(PMe_3)_2]_2$ is stable in a dinitrogen atmosphere indefinitely. In theory we should be able to prepare the μ-N_2 complex by removing the labile PMe_3 ligand and/or adding dinitrogen at high pressure. We have tried the latter (1000 psi N_2) but still see no evidence for formation of $[TaCl_3(PMe_3)_2]_2(\mu\text{-}N_2)$. By ^{31}P NMR many products are formed, some of them possibly through reaction with water or oxygen, which at high pressures are difficult to eliminate entirely from a small scale reaction. We have obtained samples prepared under these conditions which analyze for some nitrogen (up to 1%). However, we can confidently say that according to IR and NMR studies this nitrogen is not present as the dinitrogen product we sought. We have no explanation at this time.

Discussion

The main features of this type of tantalum μ-N_2 complex have been discussed elsewhere.[1,2] What we want to do here is try to understand why μ-N_2 complexes can be prepared by adding dinitrogen to reduced ethylene or neopentylidene complexes, but not by adding dinitrogen to $TaCl_3L_3$.

The main problem with forming $[TaCl_3L_2]_2(\mu\text{-}N_2)$ from $TaCl_3L_3$ and dinitrogen is probably a kinetic one; $[TaCl_3L_2]_2$ forms too rapidly when $TaCl_3L_3$ loses L, and $[TaCl_3L_2]_2$ does not react readily with dinitrogen. $[TaCl_3L_2]_2$ does not react readily even with PMe_3 or C_2H_4. The structure of $[TaCl_3L_2]_2$[6] shows that the Ta–Ta bond is only 2.721 (1) Å long, the tantalum to bridging chloride bond lengths are approximately the same as the tantalum to terminal chloride bond lengths, and there is only 0.05-Å difference between a bridging chloride to Ta(1) distance (2.477 Å) and a bridging chloride to Ta(2) distance (2.427 Å). Although steric interaction between the "axial" set of PMe_3 ligands on one tantalum and the "axial" set of chlorides on the other tantalum is severe, it is apparently not great enough to cause the dimer to break into monomeric units readily.

The structure of $[TaCl_3L_2]_2$ should be compared with that for $[Ta(CHCMe_3)Cl_3L]_2$.[15] In $[Ta(CHCMe_3)Cl_3L]_2$, in which the neopentylidene and PMe_3 ligands occupy "equatorial" sites, the $TaCl_2Ta$ bridge is markedly unsymmetric. The Ta–Cl distance to the bridging chloride which is trans to PMe_3 is 2.448 Å while the Ta–Cl distance to the bridging chloride which is trans to the neopentylidene ligand is 2.815 Å. The resulting Ta···Ta distance (4.061 Å) is much too long to be called a significant bonding interaction. It is probably for these reasons that

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$[Ta(CHCMe_3)Cl_3L]_2$ can be cleaved readily with L to give $Ta(CHCMe_3)Cl_3L_2$.[16] While a structural study of $[Ta(C_2H_4)Cl_3L]_x$[7] (x probably equals 2) has not been done, we do know that $[Ta(C_2H_4)Cl_3L]_2$ is also cleaved readily by L to give *trans,mer*-$Ta(C_2H_4)Cl_3L_2$. Therefore $[Ta(C_2H_4)Cl_3L]_2$ also is likely to contain an unsymmetric bridge and long Ta···Ta distance. The common feature of these two dimers is the "trans effect" of the neopentylidene and ethylene ligands.

The hypothetical dimers formed by loss of L from $Ta(CHCMe_3)L_4Cl$ or $Ta(C_2H_4)L_4Cl$ would contain more reduced metals than the dimers mentioned immediately above, but a lower metal oxidation state and *potentially* greater tendency to form stronger Ta–Ta bonds cannot compensate for several significant problems associated with formation of hypothetical $[Ta(CHCMe_3)L_3Cl]_2$ and $[Ta(C_2H_4)L_3Cl]_2$. We can safely assume that at least one tantalum to bridging chloride distance would tend to be long and the Ta···Ta interaction therefore weak. What is perhaps even more important is the presence of *three* PMe_3 ligands. These would be found in a *mer* arrangement if the neopentylidene or ethylene occupies an equatorial site. Therefore, each axial site would be occupied by a PMe_3 ligand, sterically a totally implausible situation. Such a dimer would not form. A more crowded (on one tantalum) *fac* arrangement of the three PMe_3 ligands, and location of the ethylene or neopentylidene ligand at an axial site, could result in a dimer having only PMe_3/neopentylidene (or ethylene) as the only axial/axial interactions. In the balance, however, this situation is not necessarily much more favorable sterically than that in which the PMe_3 ligands are arranged in a *mer* fashion. The conclusion is that the five-coordinate fragments, $Ta(CHCMe_3)L_3Cl$ and $Ta(C_2H_4)L_3Cl$, will not be able to dimerize and that dinitrogen therefore can coordinate readily to form μ-dinitrogen complexes.

One final point which may help explain why alkylidene or olefin μ-N_2 complexes form is that tantalum complexes having two π-bonding ligands are common. Examples are $Ta(CHCMe_3)_2RL_2$,[12a,b] $Ta(CHCMe_3)(C_2H_4)(CH_2CMe_3)L_2$,[12c] $Ta(C_2H_4)_2ClL_2$,[12c] and $Ta(NSiMe_3)(CHCMe_3)ClL_2$.[12d] That an imido-like μ-N_2 complex analogous to the latter, or a six-coordinate species containing a cis ethylene and imido-like μ-N_2 ligand, should form readily therefore makes chemical sense.

Experimental Section

All experiments were performed either in standard Schlenk apparatus or in a Vacuum Atmospheres HE43-2 drybox. Solvents were rigorously purified and dried by standard techniques and transferred into the drybox without exposure to air. $Ta(CHCMe_3)(PMe_3)_2X_3$ (X = Cl, Br),[16] $Ta(C_2H_4)(PMe_3)_2Cl_3$,[7] PMe_3,[17] and dmpe[18] were prepared by published methods. $^{15}N_2$ (>95%) was purchased from Merck and Co. and manipulated on a vacuum line by using a Toepler pump. Deuterated solvents were degassed and passed through a short column of activated alumina immediately prior to use. The preparation of $Ta(CHCMe_3)(PMe_3)_4X$ (X = Cl, Br) and $Ta(C_2H_4)(PMe_3)_4Cl$ is best accomplished by using solvents that have been subjected to successive freeze–pump–thaw cycles in vacuo. Blue $Ta(C_2H_4)(THF)_2Cl_3$ was prepared by treating $Ta(CHCMe_3)(THF)_2Cl_3$[16] in THF with ethylene (30 psi) for 1 h and removing all volatiles in vacuo.[12d]

NMR spectra were run at ca. 25 °C on a JEOL FX-90Q or at ca. 25 °C on a Bruker WM-250 spectrometer unless otherwise noted. ^1H and ^{13}C spectra are referenced to tetramethylsilane and ^{31}P spectra are referenced to H_3PO_4. Coupling constants are given in hertz. ^{15}N spectra were run at 9.04 MHz with a pulse delay of ~5 s and a tip angle of 45°. Chemial shifts were established using external [^{15}N]aniline and [^{15}N]diphenylimine standards whose chemical shifts relative to external NH_3 are known. Compounds were analyzed by Schwartzkopf Microanalytical Laboratories using drybox techniques. We believe the extreme lability of PMe_3 in $Ta(CHCMe_3)(PMe_3)_4Br$, $Ta(C_2H_4)(PMe_3)_4Cl$, and $[Ta(CHCMe_3)(R)(PMe_3)_2]_2(\mu\text{-}N_2)$ (R = Cl, Br, CH_2CMe_3, CH_3) prevented acceptable C and H analyses. Similar problems have been encountered in the past.[16]

Preparation of $TaX_3(PMe_3)_3$. A solution of PMe_3 (5 mL, 53 mmol) in 50 mL of ether containing 112 g (20 mmol) of 0.41% sodium amalgam was cooled to −30 °C. Solid $TaCl_5$ (3.6 g, 10 mmol) was added, and the reaction mixture was warmed to room temperature slowly. The color of the solution changed from green to red. The mixture was filtered through Celite and the ether removed from the filtrate in vacuo. The crude, red, crystalline product was extracted with 25 mL of ether, and the solution was filtered. Pentane (~2 mL) and PMe_3 (~0.1 mL) were added to the filtrate. Cooling the solution to −30 °C for 12 h gave 2.76 g of irregularly shaped deep red crystals. Concentrating and cooling the mother liquor to −30 °C gave an additional 1.26 g of pure product; total yield 4.0 g (78%). An analytically pure sample was obtained by repeated crystallizations from ether in the presence of PMe_3.

Anal. Calcd for $TaC_9H_{27}Cl_3P_3$: C, 20.97; H, 5.28. Found: C, 20.69; H, 5.21. ^1H NMR (C_6D_6): δ −6.21 (s, 18), 9.57 (s, 9).

$TaBr_3(PMe_3)_3$ was prepared analogously.

^1H NMR (C_6D_6): δ −11.52 (s, 18), 14.79 (s, 9).

The preparation of $TaCl_3(PMe_3)_3$ from $Ta_2Cl_6(THT)_3$ was trivial (10 equiv of PMe_3, benzene, 60 °C, 12 h, sealed tube; ether workup as above).

Reactions of $TaCl_3(PMe_3)_3$. (a) With Ethylene. $TaCl_3(PMe_3)_3$ (0.516 g, 1.00 mmol) was dissolved in benzene (6 mL) which contained toluene (0.276 g, 3.00 mmol) as an internal NMR standard. This solution was pressurized with C_2H_4 (30 psi) and heated to 50 °C for 1.5 h. The volatiles were trapped in vacuo, leaving 0.44 g of $Ta(C_2H_4)Cl_3(PMe_3)_2$ (95%) which was identified by comparison of its NMR spectrum with that of an authentic sample. The solution in the trap contained 1 equiv of PMe_3/Ta (by ^1H NMR).

(b) With Molecular Hydrogen. $TaCl_3(PMe_3)_3$ (0.52 g, 1.0 mmol) was dissolved in ether (5 mL), and the red solution was pressurized with hydrogen (35 psi). A green solid began depositing from solution after 1 h. After 12 h the product was isolated by filtration; yield 0.44 g (85%). Crystals of $[TaCl_3(PMe_3)_2]_2H_2$ can be obtained from concentrated toluene solutions by adding ether and cooling.

^1H NMR (toluene-d_8): δ 8.41 (m, 2, TaH_2Ta), 1.70 (d, 9, J_{HP} = 9.8 Hz, P_{ax}-CH_3), 1.38 (d, 18, J_{HP} = 9.4 Hz, P_{eq}-CH_3), 1.25 (d, 9, J_{HP} = 9.0 Hz, P'_{ax}-CH_3). $^{31}P\{^1H\}$ NMR (toluene-d_8, 101 MHz): 13.3 (d, 1, $J_{PP'}$ = 7.3 Hz, P_{ax}), −4.8 (s, 2, P_{eq}), −20.2 ppm (d, 1, $J_{PP'}$ = 7.3 Hz, P'_{ax}) IR (Nujol, cm^{-1}): 1260 (Ta–H–Ta).

$[TaCl_3(PMe_3)_2]_2D_2$ was prepared analogously.

IR (Nujol, cm^{-1}): 890 (Ta–D–Ta).

Preparation of $Ta(C_2H_4)(PMe_3)_4Cl$. Since this complex is extremely sensitive to dinitrogen, all solvents were subjected to three freeze–pump–thaw cycles prior to use. $Ta(C_2H_4)(THF)_2Cl_3$ (2.29 g, 5.0 mmol) and PMe_3 (3 mL, 32 mmol) were stirred in THF (75 mL) under argon. Sodium amalgam (0.41%, 56.1 g, 10.0 mmol) was added, and the blue solution turned green. After the solution was stirred for 2 h, the THF was removed in vacuo, ether (75 mL) was added to the residue, and the green slurry was filtered through Celite. The solids and Celite were washed twice with 15 mL of ether. The ether was slowly removed from the filtrate in vacuo to give the deep violet crystalline product; yield 2.2 g (80%).

^1H NMR (toluene-d_8): δ 2.25 (quintet, 4, J_{HP} = 3.7 Hz, C_2H_4), 1.38 (t, 36, J_{HP} = 2.4 Hz, PMe_3). $^{13}C\{^1H\}$ NMR (toluene-d_8): 33.17 (q, J_{CH} = 146 Hz, J_{CP} = 2 Hz, C_2H_4), 20.42 ppm (t, J_{CH} = 128 Hz, J_{CP} = 8.6 Hz, PMe_3).

Preparation of $Ta(C_2H_4)(dmpe)_2Cl$. Dmpe (1.20 g, 8.0 mmol) was added to blue $Ta(C_2H_4)(THF)_2Cl_3$ (1.83 g, 4.0 mmol) in THF (40 mL) under dinitrogen. Sodium amalgam (45 g, 8 mmol) was added, and after 2 h the THF was removed in vacuo from the

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

(17) (a) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149–156. (b) Zingaro, R. A.; McGlothlin, R. E. *J. Chem. Eng. Data* **1963**, *8*, 226–229.

(18) Parshall, G. W. *J. Inorg. Nucl. Chem.* **1960**, *14*, 291–292.

forest green reaction mixture. Ether (50 mL) was added and the mixture filtered through Celite. The green ether solution was concentrated in vacuo, filtered (fine), and cooled to −30 °C. After 24 h large dark green crystals were filtered off; yield 1.63 g (76%).

Anal. Calcd for $TaCl_{14}H_{36}P_4Cl$: C, 30.87; H, 6.66. Found: C, 31.06; H, 6.81. ^1H NMR (C_6D_6): δ 1.77 (br m, J_{HP} = 2.9 Hz, $Me_2PCH_2CH_2PMe_2$), 1.36 and 1.17 (br s, $Me_2PCH_2CH_2PMe_2$), −0.69 (quint, J_{HP} = 2.4 Hz, C_2H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): 41.81 (t, J_{CH} = 147 Hz, C_2H_4), 41.10 (t, J_{CH} = 129 Hz, J_{CP} = 8.5 Hz, $Me_2PCH_2CH_2PMe_2$), 24.85 and 22.73 ppm (q, J_{CH} = 128 Hz, J_{CP} = 5.8 Hz, $Me_2PCH_2CH_2PMe_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): 17.5 ppm (s).

Preparation of $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$. $Ta(CH_2CMe_3)_2Cl_3$ (2.15 g, 5 mmol) was added to a 1:1 ether/THF solution containing sodium amalgam (56.1 g, 0.41%, 10 mmol) and PMe_3 (1.4 g, 17.5 mmol). The reaction mixture was stirred for 2 h, filtered through a Celite pad, and evaporated to dryness. The brown oily residue was washed with cold pentane (20 mL), leaving a yellow solid. The crude yellow product was recrystallized from ether; yield 0.93 g (45%).

^1H NMR (C_6D_6): δ 8.79 (br s, 1, CHCMe$_3$), 1.32 (t, 18, $^2J_{HP}$ = 3.5 Hz, PMe_3), 1.29 (s, 9, CHCMe$_3$). ^{13}C NMR (C_6D_6, 15 MHz): 274.5 (d, J_{CH} = 91 Hz, CHCMe$_3$), 46.6 (s, CHCMe$_3$), 35.0 (q, J_{CH} = 125 Hz, CHCMe$_3$), 15.2 ppm (q, J_{CH} = 129 Hz, J_{CP} = 12 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (toluene-d_8): −11.2 ppm (s). Spectrum unchanged to −70 °C. IR (Nujol, cm^{-1}): 2590 (m, CH_α), 847 (s, Ta_2N_2).

Preparation of $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}^{15}N_2)$. $^{15}N_2$ (1.82 mmol) was added to $Ta(CHCMe_3)(PMe_3)_4Cl$ (1.0 g, 1.70 mmol) in pentane (20 mL) by using a Toepler pump, and the solution was stirred for 12 h. The labeled dinitrogen complex was isolated by filtration and recrystallized from ether; yield 0.37 g (48%).

^{15}N NMR (THF, 9.04 MHz, ppm): 414 (s). IR (Nujol, cm^{-1}): 820 (Ta_2N_2).

Preparation of $[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$. $LiCH_2CMe_3$ (0.05 g, 0.57 mmol) was dissolved in ether (3 mL) and added dropwise to an ether solution (20 mL) of $[Ta(CHCMe_3)(PMe_3)_2Cl]_2N_2$ (0.26 g, 0.28 mmol) at −30 °C. The reaction mixture was warmed to room temperature, stirred for 1 h, filtered through a Celite pad, and evaporated to dryness. The crude orange product was recrystallized from pentane; yield 0.20 g (74%).

Anal. Calcd for $Ta_2C_{32}H_{78}P_4N_2$: C, 39.35; H, 8.05; N, 2.87. Found: C, 37.49; H, 7.53; N, 2.52. ^1H NMR (C_6D_6): δ 6.22 (br s, 1, CHCMe$_3$), 1.37 (s, 9, CH_2CMe_3), 1.35 (t, 18, $^2J_{HP}$ = 2.9 Hz, PMe_3), 1.28 (s, 9, CHCMe$_3$), 0.63 (t, 2, $^2J_{HP}$ = 16.6 Hz, CH_2CMe_3). ^{13}C NMR (C_6D_6): 270.5 (d, J_{CH} = 88 Hz, J_{CP} = 6.6 Hz, CHCMe$_3$), 71.5 (t, J_{CH} = 108 Hz, CH_2CMe_3), 47.7 (s, CHCMe$_3$), 38.2 (q, J_{CH} = 123 Hz, CH_2CMe_3), 35.9 (s, CH_2CMe_3), 35.2 (q, J_{CH} = 124 Hz, CHCMe$_3$), 16.8 ppm (q, J_{CH} = 127 Hz, J_{CP} = 11 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (toluene-d_8): −10.9 ppm (s).

Preparation of $[Ta(CHCMe_3)(CH_3)(PMe_3)_2]_2(\mu\text{-}N_2)$. $LiCH_3$ (1 mL, 1.7 M, 1.7 mmol) was added dropwise to $[Ta(CHCMe_3)(PMe_3)_2Cl]_2N_2$ (0.8 g, 0.86 mmol) in ether (30 mL) at −30 °C. The reaction mixture was warmed to room temperature, stirred for 1 h, filtered through a Celite pad, and evaporated to dryness. The crude orange product was recrystallized from pentane; yield 0.72 g (94%).

^1H NMR (C_6D_6): δ 2.21 (s, 9, CHCMe$_3$), 2.20 (t, 18, J_{HP} = 12 Hz, PMe_3), 0.79 (t, 3, J_{HP} = 13.7 Hz, CH_3). ^{13}C NMR (C_6D_6): 269.4 (d, J_{CH} = 90 Hz, CHCMe$_3$), 47.1 (s, CHCMe$_3$), 35.3 (q, J_{CH} = 123 Hz, CHCMe$_3$), 27.2 (q, J_{CH} = 113 Hz, CH_3), 15.6 ppm (q, J_{CH} = 129 Hz, J_{CP} = 11.7 Hz, PMe_3).

Preparation of $[Ta(C_2H_4)(PMe_3)_3Cl]_2(\mu\text{-}N_2)$. $Ta(C_2H_4)(PMe_3)_2Cl_3$ (2.0 g, 4.3 mmol) was added to a 1:1 ether/THF solution (50 mL) containing sodium amalgam (0.41%, 48.2 g, 8.6 mmol) and PMe_3 (0.8 mL, 8.6 mmol). After 2 h the red mixture was filtered through Celite. The solvent was removed from the filtrate in vacuo, leaving a red-brown solid which was extracted with ether (50 mL). The solution was filtered, and the filtrate was concentrated until the product began to crystallize. The solution was then cooled to −30 °C for 12 h. The orange product can be isolated as a powder. The mother liquor was concentrated in vacuo and cooled to −30 °C to give an additional crop; total yield 1.21 g (60%).

^1H NMR (toluene-d_8, 270 MHz, 60 °C): δ 1.35 (t, 18, $^2J_{HP}$ = 3.0, PMe_3(A)), 0.70 (d, 9, $^2J_{HP}$ = 3.9, PMe_3(B)), 0.43 (br, 4, C_2H_4). ^1H NMR (toluene-d_8, 270 MHz, −60 °C): δ 1.50 (br, 9, PMe_3(A)), 1.23 (br, 9, PMe_3(A′)), 0.75 (br, 4, C_2H_4), 0.52 (d, 9, $^2J_{HP}$ = 4.7 Hz, PMe_3(B)). ^{13}C NMR (toluene-d_8, 22.5 MHz, 30 °C): 30.27 (t, J_{CH} = 144 Hz, $^2J_{CP} \approx 6$ Hz, C_2H_4), 16.53 (q, J_{CH} = 126 Hz, J_{CP} = 9.8 Hz, PMe_3(A)), 14.56 ppm (q, J_{CH} = 127 Hz, J_{CP} = 10.7 Hz, PMe_3(B)). $^{13}C\{^1H\}$ NMR (−30 °C): 29.48 (m, CH_2CH_2), 29.03 (m, CH_2CH_2), 16.21 (br t, PMe_3(A)), 13.89 ppm (br s, PMe_3(B)). $^{31}P\{^1H\}$ NMR (toluene-d_8, 36.2 Hz, 60 °C): −14 (s, 2, PMe_3(A)), −46.4 ppm (br s, 1, PMe_3(B)). $^{31}P\{^1H\}$ NMR (−70 °C): −14.3 (d, $^2J_{P_AP_B}$ = 10.2 Hz, PMe_3(A)), −45 ppm (t, $^2J_{P_AP_B}$ = 10.2 Hz, PMe_3(B)). IR (Nujol, cm^{-1}): 825 (Ta_2N_2).

Reactions To Give N_2H_4·2HCl and Dimethylketazine. Details concerning these reactions can be found in an earlier paper.[1]

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Registry No. $TaBr_3(PMe_3)_3$, 80864-71-7; $TaCl_3(PMe_3)_3$, 80864-72-8; $Ta(C_2H_4)Cl_3(PMe_3)_2$, 71860-94-1; $[TaCl3(PMe_3)_2]_2H_2$, 80864-73-9; $Ta(C_2H_4)(PMe_3)_4Cl$, 80864-74-0; $Ta(C_2H_4)(dmpe)_2Cl$, 80864-75-1; $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$, 75730-55-1; $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}^{15}N_2)$, 75789-80-9; $[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$, 75737-70-1; $[Ta(CHCMe_3)(CH_3)(PMe_3)_2]_2(\mu\text{-}N_2)$, 75730-56-2; $[Ta(C_2H_4)(PMe_3)_3Cl]_2(\mu\text{-}N_2)$, 80878-12-2; $Ta(C_2H_4)(THF)_2Cl_3$, 80864-76-2.