A large metal–metal distance, i.e., greater than 3 Å, supported by a bridging CO leads to a clear situation that can be described as a dimetalated ketone.[32] A CO group bonding two metal centers with a short distance can now be regarded as either a distorted dimetalated ketone or a two-electron-donor bridging group between two bonded metal centers.

Braterman[33] has already argued against the idea of ketonic carbonyl groups in favor of a delocalized molecule orbital description. Colton and McCormick[34] have suggested that it makes no difference whether spin pairing occurs via bridging carbonyl groups or via π interactions between the metals. Finally a general description for the M–C(O)–M moiety can be, to our opinion, formulated in any case as a three-center, four-electron bond.

Registry No. 1, 63312-27-6; **2**, 63292-79-5; **3**, 81219-06-9; **5**, 81219-07-0; **6**, 81219-08-1.

Supplementary Material Available: Tables of observed and calculated structure factors for **5** and **6** (Tables III and VII) and root-mean-square components of thermal displacement along principal axis for **5** and **6** (Table IV and VIII) (24 pages). Ordering information is given on any current masthead page.

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(33) Braterman, P. S. *Struct. Bonding (Berlin)* **1972**, *10*, 57.
(34) Colton, R.; Mc Cormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1–52.

Preparation of Organoimido and μ-Dinitrogen Complexes of Tantalum and Niobium from Neopentylidene Complexes

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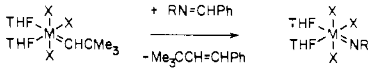
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received October 13, 1981*

Abstract: $M(CHCMe_3)(THF)_2X_3$ reacts with RN=CHPh (M = Ta, Nb; X = Cl, Br; R = Ph, CMe_3, Me) to give organoimido complexes $M(NR)(THF)_2Cl_3$ and Me_3CCH=CHPh quantitatively. The THF ligands can be displaced by phosphines to give complexes such as *cis,mer*-$Ta(NR)(PMe_3)_2Cl_3$. The $Ta(NR)L_2Cl_3$ complexes (L = PMe_3, 0.5dmpe) can be reduced in the presence of L to give the Ta(III) complexes $Ta(NR)L_4Cl$ in high yield, and these, in turn, react with ethylene or styrene to give olefin complexes $Ta(NPh)(olefin)L_3Cl$. Several ^{15}N-labeled phenylimido compounds have been prepared and examined by ^{15}N NMR and IR ($\delta(^{15}NR)$ = 300–350 vs. NH_3, $\nu_{TaNR} \approx 1350$ cm^{-1}). The products of the reaction between $M(CHCMe_3)(THF)_2Cl_3$ and PhCH=NN=CHPh are $[MCl_3(THF)_2]_2(\mu\text{-}N_2)$ and 2 equiv of Me_3CCH=CHPh. Phosphine complexes such as $[TaCl_3(PEt_3)_2]_2(\mu\text{-}N_2)$ can be prepared straightforwardly from the THF complexes. The organoimido complexes react with benzaldehyde to give RN=CHPh in high yield. The μ-N_2 complexes react with acetone to give Me_2C=NN=CMe_2 and with HCl to give $N_2H_4 \cdot 2HCl$ in high yield.

Niobium and tantalum alkylidene complexes have been studied in our group for several years.[1] We have recently found that one of the simplest, $M(CHCMe_3)(THF)_2Cl_3$,[2] reacts with internal olefins to give several turnovers of metathesis products.[3] Therefore we became interested in the possibility of developing a metathesis-like reaction of imines with these alkylidene complexes to prepare simple alkylimido analogues, $M(NR)(THF)_2Cl_3$. After this initial success,[4] it became apparent that a metathesis-like reaction between $M(CHCMe_3)(THF)_2Cl_3$ and PhCH=NN=CHPh could lead to molecules having an M=NN=M linkage; i.e., μ-dinitrogen complexes. In this paper we discuss the synthesis, characterization, and a few reactions of alkylimido and μ-dinitrogen complexes prepared by metathesis-like reactions. Simplicity and high yields made these unique routes attractive as entries into alkylimido[4] and μ-dinitrogen[5] chemistry of niobium and tantalum.

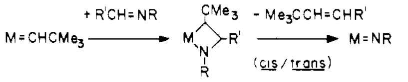
Results

When RN=CHPh is added to $M(CHCMe_3)(THF)_2X_3$ in ether, cis- and trans-Me_3CCH=CHPh and the yellow (R = Ph) or white (R = Me or CMe_3) imido complexes form quantitatively (eq 1). When PhN=CHPh is added to $M(CHCMe_3)(THF)_2X_3$, the reaction is complete in 1 h. However, when PhN=$CHCMe_3$ is used, the reaction takes 18–20 h, and when Me_3CN=$CHCMe_3$ is used, no reaction is observed after 24 h at 25 °C. These results can all be explained by steric considerations in an intermediate containing an MC_2N ring (eq 2). The cis,mer configuration for $M(NR)(THF)_2X_3$ is proposed on the basis of the presence of two types of THF ligands in the ^1H NMR spectra. When THF is added to the sample, the signals for coordinated THF are broadened due to exchange of the free THF with the coordinated THF.



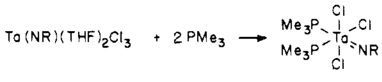
(1)

M = Nb, Ta, X = Cl, Br, R = Ph, CMe_3, Me



(2)

The reaction between $Ta(NR)(THF)_2X_3$ and PMe_3 gives light yellow $Ta(NR)(PMe_3)_2Cl_3$ (eq 3). The cis,mer configuration



(3)

is proposed since the PMe_3 ligands are inequivalent (−11.65 and −40.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum at −30 °C) and one of them (we propose the PMe_3 ligand trans to the imido ligand at

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(1) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.
(2) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236–6244.
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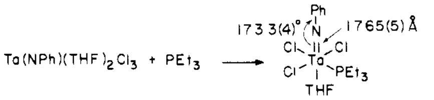
Table I. ^{15}N and ^{13}C Chemical Shift Data (ppm) for Some Phenylimido and Neopentylidene Complexes of Tantalum[a]

compd	solvent	^{15}N	compd	C_α
$Ta(NPh)(THF)_2Cl_3$	THF	369	$Ta(CHCMe_3)(THF)_2Cl_3$[2]	254
$Ta(NPh)(PEt_3)_2Cl_3$	THF	353	$Ta(CHCMe_3)(PEt_3)_2Cl_3$[2]	254
$Ta(NPh)(dmpe)_2Cl$	C_6H_5Cl	303	$Ta(CHCMe_3)(dmpe)_2Cl$[8]	217
$Ta(NPh)(PMe_3)_4Cl$	THF	304	$Ta(CHCMe_3)(PMe_3)_4Cl$[9]	208

[a] [^{15}N]Aniline (ppm 56.5) used as external reference and shifts corrected to liquid $^{15}NH_3$. For $Ph^{15}N{=}CHPh$ in $CHCl_3$ in ^{15}N chemical shift is 326 ppm.

−40.0 ppm) exchanges faster with added PMe_3 at temperatures above ca. −30 °C. When 1 equiv of PEt_3 is added to $Ta(NR)(THF)_2Cl_3$, one THF is displaced to give $Ta(NPh)(THF)(PEt_3)Cl_3$ (eq 4). A single-crystal X-ray study by



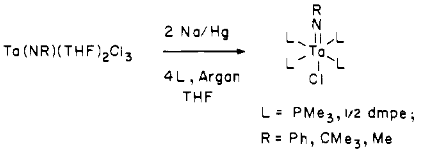
(4)

Churchill[6] shows the Ta═N bond length and the large Ta═N—Ph angle to be typical of imido complexes with a tantalum–nitrogen bond order between 2 and 3.[7]

Addition of $MgNp_2(dioxane)$ ($Np = CH_2CMe_3$) to $Ta(NPh)(THF)_2Cl_3$ yields white $Ta(NPh)Np_3(THF)$. By ^1H NMR it appears that $Ta(NPh)Np_3(THF)$ is a trigonal bipyramid with the three neopentyl groups in equatorial positions. $Ta(NPh)(CH_2CMe_3)_3(THF)$ is thermally stable and does not decompose readily to an alkylidene complex,[1] even in the presence of PMe_3.

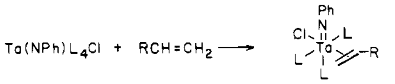
$Ta(NPh)(THF)_2Cl_3$ reacts cleanly with 1 equiv of benzaldehyde to give diphenylimine in high yield. The initial metal-containing product is probably the oxo analogue of the imido complex, but no product could be readily identified.

Preparation and Reactions of $Ta(NR)L_4Cl$ ($R = Ph, CMe_3, CH_3$; $L = PMe_3$ or 0.5dmpe). $Ta(NR)(THF)_2Cl_3$ can be reduced with 2 equiv of sodium amalgam in THF to give $Ta(NR)L_4Cl$ complexes in high yield (eq 5). The phosphine ligands in $Ta(NR)(PMe_3)_4Cl$ are labile, probably for steric reasons. Therefore $Ta(NR)(PMe_3)_4Cl$ did not analyze well. $Ta(NR)(dmpe)_2Cl$ did, however. The structure shown in eq 5 is based on the facts that down to −80 °C the phosphorus nuclei are all equivalent by $^{31}P\{^1H\}$ NMR, and the methyl group ($R = CH_3$) is a quintet in the ^1H NMR spectrum ($J_{HP} = 3.5$ Hz).



(5)

$Ta(NPh)(PMe_3)_4Cl$ reacts readily with ethylene or styrene to give olefin complexes (eq 6). As expected, $Ta(NPh)(dmpe)_2Cl$ does not react with ethylene or styrene. We proposed the structure for $Ta(NPh)L_3(olefin)$ shown in eq 6 based on the following information: a triplet and doublet are found in a 1:2 ratio ($J_{PP} = 14.6$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum, only one ethylene carbon is observed in the $^{13}C\{^1H\}$ NMR spectrum, and the unique phosphine exchanges readily with free phosphine on the NMR time scale. We believe the unique phosphine would be more labile if it were trans to the imido group as shown rather than trans to the olefin.



(6)

Table II. ^{13}C Chemical Shift Data (ppm) for some *tert*-Butylimido Complexes[a]

complex	C_α	C_β	Δ
$Ta(NCMe_3)(THF)_2Br_3$	67.0	32.0	35
$Ta(NCMe_3)(THF)_2Cl_3$	66.3	32.0	34
$Ta(NCMe_3)(PMe_3)_2Cl_3$	66.2	32.2	34
$Ta(NCMe_3)(PMe_3)_4Cl$	63.4	35.6	28
$Ta(NCMe_3)(dmpe)_2Cl$	62.6	35.6	27[b]

[a] Solvent = toluene-d_8 and $T = 238$ K unless otherwise noted. [b] $T = 305$ K.

Table III. IR Data for Phenylimido Complexes

complex	$\nu_{Ta^{14}NR}$, cm^{-1}	$\nu_{Ta^{15}NR}$, cm^{-1}	Δ
$Ta(NPh)(THF)_2Cl_3$	1360	1335	25
$Ta(NPh)(PMe_3)_2Cl_3$	1345	1325	20
$Ta(NPh)(PMe_3)_4Cl$	1340	1318	22
$Ta(NPh)(dmpe)_2Cl$	1350	1328	22
$Ta(NPh)(C_2H_4)(PMe_3)_3Cl$	1355	1332	25

NMR and IR Studies of Tantalum Imido Complexes. No ^{15}N NMR studies on imido complexes have been reported.[7] We decided to make ^{15}N-labeled imido complexes since our high-yield method could be employed in a small scale reaction and since ^{15}N-labeled aniline is readily available. The ^{15}N chemical shifts for four compounds, referenced to liquid NH_3, are listed in Table I. It is interesting to compare these data with the chemical shifts for the α-carbon atoms in the analogous neopentylidene complexes. In each case the chemical shift of the nitrogen or carbon atom bound to the more reduced metal is found at higher field.

The difference in chemical shift between the α- and β-carbon resonances of the *tert*-butyl group can be considered a qualitative measure of the electron density on the imido nitrogen atom.[7] For example, $OsO_3(N\text{-}t\text{-}Bu)$, an electrophilic imido species,[10] has a Δ value of 55, while the nucleophilic main-group phosphinimine, $Ph_3PN\text{-}t\text{-}Bu$, displays a Δ value of 16. Tantalum and niobium complexes, $M(Me_2N)_3(N\text{-}t\text{-}Bu)$, have Δ values of 32 and 35, respectively.[7] The Δ values for a series of *tert*-butylimido complexes we have prepared are listed in Table II. Although we know that the reactions of analogous alkylidene complexes depend markedly on what halides and other ligands (THF or PR_3) are present,[3] the difference of only 1 ppm between the Δ values for $Ta(NCMe_3)(THF)_2Br_3$, $Ta(NCMe_3)(THF)_2Cl_3$, and $Ta(NCMe_3)(PMe_3)_2Cl_3$ suggests that Δ values are not a sensitive measure of the influence of ligands upon the reactivity of the metal–nitrogen bond. However, the Δ values do respond in the direction they should to a lowering of the oxidation state.

Few careful ^{15}N infrared studies on organoimido complexes have been reported.[7] Locating the "M═N" vibrational modes can be troublesome since they are prone to couple with other metal–ligand modes and especially with modes of the organic substituent on the imido nitrogen atom. The IR spectra of several ^{15}N-labeled phenylimido complexes are identical with those of the ^{14}N phenylimido complexes, except a peak at ~1350 cm^{-1} in the spectra of the ^{14}N complexes is shifted 20–25 cm^{-1} to lower energy in the spectra of the ^{15}N complexes (Table III). The fairly high-energy absorptions support the contention that these bands probably represent some combination of the Ta═N stretching mode coupled to the N—C stretching mode.[7]

Preparation of μ-Dinitrogen Complexes. When PhCH═N—N═CHPh is added to an ether solution containing 1 equiv of $M(CHCMe_3)(THF)_2Cl_3$, *cis*- and *trans*-$Me_3CCH{=}CHPh$ and the orange (M = Ta) or light plum-colored (M = Nb) dinitrogen complexes are formed in high yield (eq 7). The relatively insoluble complexes precipitate from ether as they form. They are only

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[6] Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 223.

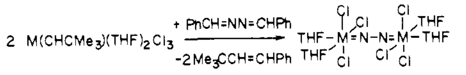
[7] Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–173.

[8] $Ta(CHCMe_3)(dmpe)_2Cl$ was prepared in a manner analogous to that used to prepare $Ta(CHCMe_3)(PMe_3)_4Cl$.[9] Turner, H. W., unpublished results.

[9] Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6609–6611.

[10] Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628.

[11] Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 218.



(7)

M = Ta or Nb

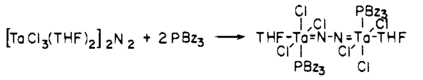
sparingly soluble in dichloromethane. We propose the structure shown in eq 7 by analogy with the alkylimido analogue shown in eq 1.

The THF ligands are displaced from $[TaCl_3(THF)_2]N_2$ by several phosphines to give bis(phosphine) complexes (eq 8). Since the bis(phosphine) complexes all display only one type of phosphorus atom in the $^{31}P\{^1H\}$ NMR spectra, they are formulated as shown in eq 8.

(8)

L = PMe_2Ph, PEt_2Ph, PEt_3, PPr_3

When PBz_3 (Bz = CH_2Ph) is added to $[TaCl_3(THF)_2]_2N_2$, however, a mono(phosphine) adduct, $[TaCl_3(THF)(PBz_3)]_2N_2$, is obtained (eq 9). A single-crystal X-ray structural study of



(9)

$[TaCl_3(THF)(PBz_3)]_2N_2$ by Churchill[11] shows it to have a geometry analogous to that of $Ta(NPh)Cl_3(THF)(PEt_3)$ (eq 4). The Ta=N distance (1.796 (5) Å) compares favorably with that in $Ta(NPh)Cl_3(THF)(PEt_3)$. The rather long N—N distance (1.282 (6) Å) and essentially linear Ta=N—N arrangement (178.9 (4)°) suggest that the valence bond description, Ta=N—N=Ta, has some validity.

The chloride ligands in $[MCl_3(THF)_2]_2N_2$ can be replaced by neopentyl ligands to give the yellow (M = Ta) or orange (M = Nb) dinitrogen complexes shown in eq 10. The neopentyl groups

$$[MCl_3(THF)_2]_2N_2 + 3MgNp_3(diox) \longrightarrow [MNp_3(THF)]_2N_2 \qquad (10)$$

M = Ta or Nb

are equivalent by NMR so we propose that they occupy the equatorial positions of a trigonal-bipyramidal arrangement of ligands about each metal (cf. $Ta(NPh)Np_3(THF)$, vide supra). An analogous reaction employing $KOCMe_3$ gives light yellow $[Ta(OCMe_3)_3(THF)]_2N_2$ in good yield.

We have not labeled any of the μ-N_2 complexes with ^{15}N for IR and ^{15}N NMR studies. We will show in a subsequent paper[12] that μ-N_2 complexes can be prepared directly from N_2 and by ^{15}N labeling that a characteristic IR mode for Ta=N—N=Ta complexes is found at ~845 cm^{-1}. In the IR spectrum of $[TaCl_3(PEt_3)_2]_2N_2$ there is a medium strength peak at 855 cm^{-1} which we assign to the Ta_2N_2 stretching mode. In other complexes we report here the 850-cm^{-1} region is obscured by peaks due to other ligands.

Reactions of μ-N_2 Complexes with Acetone or HCl. We mentioned earlier that M=NR complexes react with benzaldehyde to give RN=CHPh in high yield. One measure of how valid the Ta=N—N=Ta description is is whether our μ-N_2 complexes also will react with carbonyl compounds. Several of the μ-N_2 complexes were treated with 10 equiv of acetone. In all cases dimethylketazine is formed in fair to good yield (Table IV). A side product, 4-methyl-3-penten-2-one, must be formed by a Lewis acid-catalyzed condensation of acetone. $[TaCl_3(THF)_2]_2N_2$ is too insoluble to react readily with acetone, but some dimethylketazine is still observed. These results lend some credence to the proposal that the μ-N_2 is behaving as an imido ligand.

Several μ-N_2 complexes also react readily with excess HCl in ether to give hydrazine (as $N_2H_4 \cdot 2HCl$) only; no ammonia is observed (Table IV). These results are at least consistent with the point of view that the μ-N_2 ligand is best regarded as an N_2^{4-} ligand.

Discussion

The number of known organoimido complexes of niobium and tantalum is not large. The three types are $M(NR)(NR'R'')_3$,[13] $[Cl_3M{=}N(Me)C]_2$ and related species,[14,15] and $M(CH_2CMe_3)_3[N(Me)C{=}CHCMe_3]$.[16] The approach we have used is potentially the most general method of preparing niobium and tantalum imido complexes, since it should be successful for a number of different organic groups on the imido ligand, and once $M(NR)(THF)_2Cl_3$ is prepared, the chlorides may be replaced by the desired anionic ligand. Since the starting complexes $M(CHCMe_3)(THF)_2Cl_2$ can be prepared in high yield from MCl_5 and $Zn(CH_2CMe_3)_2$, the overall yield of an imido complex is high.

It is not surprising that the organoimido complexes should react with the carbonyl function to give imines and metal oxides since a more electronegative element should be able to form a stronger bond to an electropositive metal than the element immediately to the left of it. Nugent found that $M(NCMe_3)(NR_2)_3$ complexes also reacted with the carbonyl function.[13b]

It was interesting to find that our method can be used to prepare μ-dinitrogen complexes, the first characterizable ones of niobium or tantalum to be reported in the literature.[17] Even more interesting is the fact that they appear to be structurally unique among the hundreds of μ-dinitrogen complexes which are known.[18] The N-N bond in $[TaCl_3(THF)(PBz_3)]_2N_2$ is the longest by approximately 0.08 Å in any simple μ-N_2 complex[19] whose structure has been determined accurately.[21] As to whether the N-N bond is a "true" single bond or not is moot since there is no equivalent metal-free system with which to compare it. For example, the closest organic system is benzalamine,[22] where the sp^2-hybridized N-N bond is 1.38 Å long. But in the imidolike dinitrogen complex each nitrogen should be viewed as being sp hybridized because the Ta=N—N=Ta system is nearly linear. The N-N bond would be shorter than 1.38 Å either because of the rehybridization (and π-electron donation from N to Ta[7]) or because of conjugation throughout the Ta=N—N=Ta system.

The reaction of the μ-N_2 complexes with acetone to give dimethylketazine tends to confirm the implications of the structural results—the Ta=N bond reacts as it does in an organoimido complex. Not surprisingly, then, is the fact that these μ-N_2 complexes react with HCl to give hydrazine. These μ-N_2 complexes appear to contain the most "activated" dinitrogen to date (in a simple M_2N_2 system[19]) in the sense that the dinitrogen most closely approaches a μ-N_2^{4-} ligand.

It is interesting to compare our tantalum and niobium μ-dinitrogen complexes with $[Cp''_2Zr(N_2)]_2(\mu\text{-}N_2)$[23] (Cp'' = η^5-

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(12) Rocklage, S. M.; Turner, H. W.; Fellmann, J. D.; Schrock, R. R., in press.

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(14) Finn, P. A.; Schaefer King, M.; Kilty, P. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 220–221.

(15) (a) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525–3528. (b) *J. Am. Chem. Soc.* **1979**, *101*, 5094–5095.

(16) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370.

(17) "$[Nb(dmpe)_2Cl]_2N_2$" was first reported in a table in a review article[18a] and later in a full paper on niobium and tantalum carbonyl complexes.[18b] Although it does contain some nitrogen (by analysis) and does hydrolyze to give ca. 20% $N_2H_4 \cdot 2HCl$ in addition to some molecular nitrogen, it appears to be an intractable material. Some μ-N_2 complexes related to those we report here have been reported in a preliminary communication.[5]

(18) (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625. (b) Burt, R. J.; Leigh, G. J.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 793–799.

(19) Longer N-N bonds (ca. 1.35 Å) have been reported in complexes such as $[(PhLi)_6Ni_2N_2(ether)_2]_2$ and related species[20] in which the dinitrogen does not simply bridge two metals.

(20) Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 998.

(21) (a) An example of a compound in which the reported N-N bond length is fairly long (1.28 Å) is $[ReCl(PMe_2Ph)_4(N_2)]_2MoCl_4$.[21b] Unfortunately the error (±0.05 Å) is too large to conclude that the N-N bond is significantly longer than that in other simple μ-N_2 complexes.[18a] (b) Cradwick, P. D.; Chatt, J.; Crabtree, R. H.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 351–352.

(22) Structure reports for 1970, Pearson, W. B.; Trotter, J.; Eds.; Oosthoek, Scheltema, and Holkema: Utrecht, 1974; Vol. 35B.

Table IV. Reactions of μ-N_2 Complexes with Acetone or HCl[a]

complex	$N_2H_4 \cdot 2HCl$[b]	$(Me_2C{=}N{-})_2$	$Me_2C{=}CHCOMe$
$[TaCl_3(THF)_2]_2N_2$	80	<20	>100
$[TaCl_3(PR_3)_2]_2N_2$	85	50	34
$[Ta(O\text{-}t\text{-}Bu)_3(THF)]_2N_2$	90	52	66
$[TaNp_3(THF)]_2N_2$	86	60	31

[a] Expressed as mole percent vs. metal. [b] ±10% accuracy.

C_5Me_5) and $[Cp''_2Ti(N_2)]_2)(\mu\text{-}N_2)$.[24] The μ-N_2 ligands do not have exceptionally long N–N bonds (1.182 (5) and 1.155 (14)–1.165 (14) Å, respectively), yet they do react with HCl to give high yields of hydrazine. What is unknown at this stage is whether the titanium and zirconium complexes also react with acetone to give dimethylketazine. Irrespective of whether they do or not, it is still puzzling why the μ-N_2 ligands in the Ti and Zr species are not more like μ-N_2^{4-} ligands structurally. Perhaps they are not because terminal imido[7] (or oxo[25]) complexes of the group 4 metals may not be as favorable as those containing bridging imido or oxo ligands, for electronic reasons rather than simply because the coordination number of a group 4 metal complex is often low. In contrast, niobium and tantalum are known to form strong π bonds to O, NR, or CHR.

Experimental Section

General Procedures. All experiments were performed under an inert atmosphere by either standard Schlenk techniques or in a Vacuum atmospheres HE43-2 drybox. Solvents were rigorously purified and dried under N_2 by standard techniques and transferred into the drybox without exposure to air. $Ta(CHCMe_3)(THF)_2X_3$ (X = Cl, Br)[2], $Nb(CHCMe_3)(THF)_2Cl_3$,[2] $Ta(CHCMe_3)(PMe_3)_4Cl$,[9] PMe_3,[26] PEt_3,[26] $P(n\text{-}Pr)_3$,[26] and dmpe[27] were prepared by published methods. PMe_2Ph, PEt_2Ph, and PBz_3 were purchased and used as received. Imines were prepared by condensation of the appropriate aldehyde and amine and purified by standard methods. Deuterated solvents were passed through a short column of alumina immediately prior to use.

NMR spectra were run at ca. 35 °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 are referenced as downfield shifts from liquid NH_3. Infrared spectra were obtained on a Perkin-Elmer 283B instrument in Nujol mulls using KBr plates. Compounds were analyzed by Schwartzkopf Microanalytical Laboratories using drybox techniques. We believe the extreme lability of PMe_3 in $Ta(NR)(PMe_3)_4Cl$ prevented acceptable C and H analyses.

Preparations. $Ta(NPh)(THF)_2Cl_3$. $Ta(CHCMe_3)(THF)_2Cl_3$ (10.0 g, 20.0 mmol) was dissolved in ether (40 mL), and the solution was cooled to −30 °C. PhNCHPh (3.62 g, 20 mmol) was added, and the reaction was allowed to warm to room temperature. After 30 min yellow crystals began forming and after 90 min 8.4 g (81% yield) of product was isolated by filtration. Cis- and trans-$Me_3CCH{=}CHPh$ were identified by GC and NMR (^1H and ^{13}C): ^1H NMR (C_6D_6) δ (7.30–6.64 (m, 5, NC_6H_5), 4.19 (br m, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 3.95 (br m, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 1.35 (br m, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$), 1.11 (br m, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$). Anal. Calcd for $TaC_{14}H_{21}NO_2Cl_3$: C, 32.17; H, 4.05. Found: C, 31.91; H, 3.99.

$Ta(^{15}NPh)(THF)_2Cl_3$ was prepared by using $Ph^{15}N{=}CHPh$ (^{15}N NMR data given in text).

$Ta(NMe)(THF)_2Cl_3$. $Ta(NMe)(THF)_2Cl_3$ was prepared as in the first preparation using $MeN{=}CHPh$: ^1H NMR (C_6D_6) δ 4.62 (s, 3, NCH_3), 4.04 (br m, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 3.87 (br m, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2CH_2}}$), 1.34 (br m, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$), 1.17 (br m, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$). Anal. Calcd for $TaC_9H_{19}NO_2Cl_3$: C, 23.47; H, 4.16. Found: C, 23.09, H, 4.18.

$Ta(NCMe_3)(THF)_2Cl_3$. $Ta(NCMe_3)(THF)_2Cl_3$ was prepared by using $Me_3CN{=}CHPh$ except after 2 h the ether was removed in vacuo, leaving a sticky yellow solid. The product was taken up in a minimal amount of ether, and the solution was filtered and cooled to −30 °C. After 24 h beige crystals (80% yield) were isolated by filtration: ^1H NMR ($CDCl_3$) δ 4.30 (br m, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 4.18 (br m, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 2.00 (br m, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$), 1.88 (br m, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$), 1.23 (s, 9, $\mathrm{NC}Me_3$); $^{13}C\{^1H\}$ NMR (toluene-d_8, −35 °C) δ 78.04 (t, J_{CH} = 154 Hz, $\overline{\mathrm{O}C\mathrm{H_2CH_2CH_2}C\mathrm{H_2}}$), 72.02 (t, J_{CH} = 151 Hz, $\overline{\mathrm{O}C\mathrm{H_2CH_2CH_2}C\mathrm{H_2}}$), 66.30 (s, $\mathrm{N}C\mathrm{Me_3}$), 31.97 (q, J_{CH} = 124 Hz, $\mathrm{NC}Me_3$), 25.60 (t, J_{CH} = 133 Hz, $\overline{\mathrm{OCH_2}C\mathrm{H_2}C\mathrm{H_2CH_2}}$). Anal. Calcd for $TaC_{12}H_{25}NO_2Cl_3$: C, 28.67; H, 5.01. Found: C, 28.81; H, 5.26.

$Ta(NCMe_3)(THF)_2Br_3$. $Ta(NCMe_3)(THF)_2Br_3$ was prepared in the manner analogous to that for $Ta(NCMe_3)(THF)_2Cl_3$: ^1H NMR ($CDCl_3$) δ 4.42 (br, m, 8, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 2.02 (br, m, 8, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$), 1.44 (s, 9, $NCMe_3$); $^{13}C\{^1H\}$ NMR (toluene-d_8, −35 °C) δ 78.73 ($\overline{\mathrm{O}C\mathrm{H_2CH_2CH_2}C\mathrm{H_2}}$), 73.53 ($\overline{\mathrm{O}C\mathrm{H_2CH_2CH_2}C\mathrm{H_2}}$), 67.03 ($\mathrm{N}C\mathrm{Me_3}$), 31.80 ($\mathrm{NC}Me_3$), 25.60 ($\overline{\mathrm{OCH_2}C\mathrm{H_2}C\mathrm{H_2CH_2}}$).

$Nb(NPh)(THF)_2Cl_3$. $Nb(CHCMe_3)(THF)_2Cl_3$ (1.0 g, 2.42 mmol) was dissolved in a 1:1 mixture of ether and THF (5 mL). Diphenylimine (0.44 g, 2.42 mmol) was added to the deep purple solution. After 2 h the solvent was removed in vacuo. The remaining red-brown oil was dissolved in THF. Pentane was added, and the solution was cooled to −40 °C to give 0.4 g (40% yield) of red crystals: ^1H NMR (toluene-d_8, −30 °C) δ 7.48 (d, 2, J_{HH} = 7.3 Hz, *o*-phenyl), 6.98 (t, 2, J_{HH} = 7.7 Hz, *m*-phenyl), 6.77 (t, 1, J_{HH} = 7.3 Hz, *p*-phenyl), 3.81 (br, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 3.25 (br, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 1.35 (br, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$), 0.89 (br, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$).

$Ta(NPh)(PEt_3)(THF)Cl_3$. $Ta(NPh)(THF)_2Cl_3$ (1.0 g, 1.91 mmol) was dissolved in THF (30 mL), and PEt_3 (0.23 g, 1.91 mmol) was added. After 1 h the light orange solution was concentrated in vacuo and cooled to −30 °C to give 500 mg of yellow crystals. These were dissolved in toluene (~7 mL). Cooling to −30 °C produced 150 mg of fluffy yellow crystals which were removed by filtration. The filtrate was cooled slowly to −30 °C and left 3 days at this temperature to give crystals suitable for X-ray diffraction: ^1H NMR ($CDCl_3$) δ 7.37–6.87 (m, 5, NC_6H_5), 4.41 (br, m, 4, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 2.02 (br, m, 4, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$), 1.94 (m, 6, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.13 (m, 9, $\mathrm{PCH_2C}H_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 19.1 (s).

$Ta(NPh)(PMe_3)_2Cl_3$. $Ta(NPh)(THF)_2Cl_3$ (0.52 g, 1.0 mmol) in ether (10 mL) was treated with 2 equiv of PMe_3. The yellow slurry immediately became a homogeneous orange solution. After 30 min the ether was removed in vacuo, leaving a yellow crystalline solid: ^1H NMR (toluene-d_8, −30 °C) δ 7.17–6.64 (m, 5, NC_6H_5), 1.08 (d, 9, $^2J_{HP}$ = 6.7 Hz, PMe_3), 0.97 (d, 9, $^2J_{HP}$ = 9.2 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ −12.8 (br s), −40.8 (br s).

$Ta(^{15}NPh)(PMe_3)_2Cl_3$ was prepared from $Ta(^{15}NPh)(THF)_2Cl_3$ in a similar manner.

$Ta(NPh)(PEt_3)_2Cl_3$ was prepared in a manner analogous to that for $Ta(NPh)(PMe_3)_2Cl_3$: ^1H NMR (toluene-d_8, −30 °C) δ 7.40–6.69 (m, 5, NC_6H_5), 1.63 (m, 12, $\mathrm{PC}H_2\mathrm{CH_3}$), 0.87 (m, 18, $\mathrm{PCH_2C}H_3$); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 14.9 (s), 15.5 (s) at −30 °C.

$Ta(NCMe_3)(PMe_3)_2Cl_3$. $Ta(NCMe_3)(PMe_3)_2Cl_3$ was prepared in a manner analogous to that for $Ta(NPh)(PMe_3)_2Cl_3$. It is a light yellow, pentane-soluble oil: $^{31}P\{^1H\}$ NMR (toluene-d_8) δ −12.2 (s), −44.4 (br s), −12.5 (s), −43.2 (s) at −30 °C; $^{13}C\{^1H\}$ NMR (toluene-d_8, −35 °C) δ 66.20 ($\mathrm{N}C\mathrm{Me_3}$), 32.23 ($\mathrm{NC}Me_3$), 15.28 (br s, PMe_3), 12.78 (d, J_{CP} = 11.7 Hz, PMe_3).

$Ta(NPh)(PMe)_4Cl$. $Ta(NPh)(THF)_2Cl_3$ (3.4 g, 6.4 mmol) was dissolved in THF (75 mL) and 5 equiv of PMe_3 were added. Na/Hg amalgam (0.41% wt, 72 g, 12.8 mmol) was added under Ar. The reaction immediately turned green. The mixture was stirred vigorously for 60 min. The solution was decanted, and the THF was removed in vacuo. Ether (100 mL) was added to the residue, and the NaCl was removed by filtration. Concentrating the ether solution in vacuo and cooling to −30 °C induced crystallization (90% yield). $Ta(^{15}NPh)(PMe_3)_4Cl$ was prepared in a similar manner from $Ta(^{15}NPh)(THF)_2Cl_3$: ^1H NMR (C_6D_6) δ 7.16–6.65 (m, 5, NC_6H_5), 1.48 (t, 36, J_{HP} = 2.4 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (toluene, −50 °C) δ −13.3 (s).

$Ta(NCH_3)(PMe_3)_4Cl$. $Ta(NCH_3)(THF)_2Cl_3$ (1.0 g, 2.1 mmol) was dissolved in THF (20 mL), and 5 equiv of PMe_3 was added. The yellow solution turned bright red when sodium amalgam (0.41% wt, 24 g, 4.3

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mmol) was added under argon. The slurry was stirred vigorously for 60 min. The solution was decanted and the THF removed in vacuo. Ether (30 mL) was added, and after filtration the volume of the filtrate was reduced to 10 mL. Cooling to −30 °C produced beautiful red crystals in 90% yield: ^{1}H NMR (C_6D_6) δ 2.96 (quin, 3, $^4J_{HP}$ = 3.5 Hz, NCH_3), 1.45 (t, 36, J_{HP} = 2.4 Hz), PMe_3); $^{31}P\{^1H\}$ NMR (toluene-d_8, −50 °C) δ −13.2 (br s); $^{13}C\{^1H\}$ (toluene-d_8, −20 °C) δ 48.0 (NCH_3), 22.2 (PMe_3); IR (Nujol, cm^{-1}) 1340 ($Ta{=}NCH_3$).

Ta(NCMe$_3$)(PMe$_3$)$_4$Cl. $Ta(NCMe_3)(PMe_3)_4Cl$ was prepared in a manner analogous to that used to prepare $Ta(NCH_3)(PMe_3)_4Cl$: ^{1}H NMR (C_6D_6) δ 1.50 (br m, 36, PMe_3), 1.11 (s, 9, $NCMe_3$); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ −16.4 (br s), −15.6 (s) at −35 °C; $^{13}C\{^1H\}$ NMR (toluene-d_8, −35 °C) δ 63.35 ($N\mathit{C}Me_3$), 35.57 ($NC\mathit{Me}_3$), 24.34 (PMe_3).

Ta(NCMe$_3$)(dmpe)$_2$Cl. Dmpe (0.18 g) and sodium amalgam (0.41% wt, 6.8 g, 1.2 mmol) were added to $Ta(NCMe_3)(THF)_2Cl_3$ (0.3 g, 0.6 mmol) in ether (25 mL). After 12 h the reaction mixture was filtered through a Celite pad. The solvent was removed in vacuo from the orange filtrate to give 320 mg (90% yield) of pure product: ^{1}H NMR (C_6D_6) δ 1.53 (s, 24, $\mathit{Me}_2PCH_2CH_2P\mathit{Me}_2$), 1.21 (m, 8, $Me_2PC\mathit{H}_2C\mathit{H}_2PMe_2$), 0.97 (s, 9, $NC\mathit{Me}_3$); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 29.4 (s); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 62.60 (s, $N\mathit{C}Me_3$), 35.60 (q, J_{CH} = 124 Hz, $NC\mathit{Me}_3$), 34.04 (t, J_{CP} = 8.1, J_{CH} = 132 Hz, $Me_2P\mathit{CH}_2\mathit{CH}_2PMe_2$), 20.78 (q, J_{CP} = 4.4, J_{CH} = 128 Hz, $\mathit{Me}_2PCH_2CH_2P\mathit{Me}_2$), 19.31 (q, J_{CP} = 5.6, J_{CH} = 128 Hz, $\mathit{Me}_2PCH_2CH_2P\mathit{Me}_2$). Anal. Calcd for $TaC_{16}H_{41}NP_4Cl$: C, 32.69; H, 7.03. Found: C, 32.28; C, 7.10.

Ta(NPh)(dmpe)$_2$Cl. $Ta(NPh)(THF)_2Cl_3$ (1.05 g, 2.0 mmol) was dissolved in THF (40 mL) and dmpe (0.60 g) added. Much precipitate forms which is believed to be polymeric $Ta(NPh)(dmpe)Cl_3$. Sodium amalgam (0.41% wt, 23 g, 4.1 mmol) was added, and the slurry slowly turned green. After being stirred for 18 h, the reaction mixture was filtered through a Celite pad to give a green-red filtrate that yielded light green crystals upon concentrating it in vacuo and cooling to −30 °C; yield 0.95 g (79%): $^{31}P\{^1H\}$ NMR (C_6D_6) δ 28.6 (s). The ^{15}N-labeled species was prepared analogously.

Ta(NPh)(C$_2$H$_4$)(PMe$_3$)$_3$Cl$_2$. An ether solution (5 mL) of $Ta(NPh)(PMe_3)_4Cl$ (0.5 g, 0.82 mmol) was stirred under 40 psi of ethylene. After 1 h the yellow product was filtered off and recrystallized from a mixture of toluene and ether: ^{1}H NMR (toluene-d_8) δ 6.94–6.49 (m, 5, NC_6H_5), 1.77 (m, 2, C_2H_4), 1.58 (m, 2, C_2H_4), 1.31 (t, 18, J_{HP} = 3.1 Hz, PMe_3), 1.19 (d, 9, J_{HP} = 4.8 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (toluene-d_8, −40 °C) δ −16.2 (d, J_{PP} = 14.6 Hz, −27.2 (t, J_{PP} = 14.6 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 128.4–119.7 (m, NC_6H_5), 39.0 (s, C_2H_4), 17.7 (t, J_{CP} = 10.4 Hz, PMe_3); IR (cm^{-1}, Nujol) 1355 ($Ta{=}NC_6H_5$).

$Ta(^{15}NPh)(C_2H_4)(PMe_3)_3Cl$ was prepared analogously from $Ta(^{15}NPh)(PMe_3)_4Cl$.

Ta(NPh)(CH$_2$CMe$_3$)$_3$(THF). $Ta(NPh)(THF)_2Cl_3$ (2.09 g, 4.0 mmol) was dissolved in THF (20 mL), and 3.06 g (12.0 mmol) $Mg(CH_2CMe_3)_2$(dioxane) was added. After 24 h the THF was removed in vacuo. The resulting yellowish solid was extracted into toluene. The mixture was filtered, and the toluene was removed from the filtrate in vacuo to give a crystalline white solid. The crude product was recrystallized from ether to give 1.78 g (80%) of pure compound: ^{1}H NMR (C_6D_6) δ 7.65–6.87 (m, 5, $NC_6\mathit{H}_5$), 3.66 (br, 4, $\overline{OC\mathit{H}_2CH_2CH_2C\mathit{H}_2}$), 1.22 (s, 27, $CH_2C\mathit{Me}_3$), 1.10 (br, 4, $\overline{OCH_2C\mathit{H}_2C\mathit{H}_2CH_2}$), 0.74 (s, 6, $C\mathit{H}_2CMe_3$). Anal. Calcd for $TaC_{25}H_{46}NO$: C, 53.85; H, 8.32. Found: C, 53.68; H, 8.45.

[TaCl$_3$(THF)$_2$]$_2$N$_2$. $Ta(CHCMe_3)(THF)_2Cl_3$ (1.0 g, 2.0 mmol) was dissolved in ether (10 mL) and the purple solution cooled to −30 °C. *n*-Nonane (300 μL, 1.68 mmol) was added as an internal standard. $PhCH{=}NN{=}CHPh$ (0.21 g, 1.0 mmol) was added with stirring. The solution turned orange, and the orange product began depositing from solution. GC analysis after 2 h showed >90 mol % of the expected *cis*- and *trans*-$Me_3CCH{=}CHC_6H_5$ present; yield 0.85 g (95%). The orange product is insoluble in ether and hydrocarbons, very slightly soluble in chloroform, tetrahydrofuran, and chlorobenzene, and slightly soluble in dichloromethane: ^{1}H NMR (CD_2Cl_2) δ 4.48 (br m, 8, $\overline{OC\mathit{H}_2CH_2CH_2C\mathit{H}_2}$), 2.03 (br m, 8, $\overline{OCH_2C\mathit{H}_2C\mathit{H}_2CH_2}$).

[TaCl$_3$(PR$_3$)$_2$]$_2$N$_2$. Four equivalents of phosphine (PMe_2Ph, PEt_2Ph, PEt_3, $P(n\text{-}Pr)_3$ was added to $[TaCl_3(THF)_2]_2N_2$ (0.5 g, 0.56 mmol) in dichloromethane to give red-purple (PMe_2Ph or PEt_2Ph) or green (PEt_3, $P(n\text{-}Pr)_3$) solutions. After 1 h the solvent was removed in vacuo to yield red-purple or green microcrystals. Attempts at crystallization to produce X-ray quality crystals failed. Attempted analyses gave low C and H and high N values, probably due to loss of phosphine during combustion: $^{31}P\{^1H\}$ NMR of PEt_2Ph complex ($CDCl_3$) δ 21.1 (s); $^{31}P\{^1H\}$ NMR of PMe_2Ph complex (CH_2Cl_2) δ −0.5 (br s), −21.5 (br s); $^{31}P\{^1H\}$ NMR of $P(n\text{-}Pr)_3$ complex (toluene) δ 8.3 (s); $^{31}P\{^1H\}$ NMR of PEt_3 complex (CH_2Cl_2) δ 14.8 (s); IR of PEt_3 complex (cm^{-1}, Nujol) 855 (Ta_2N_2).

[TaCl$_3$(THF)(PBz$_3$)]$_2$N$_2$. Tribenzylphosphine (0.70 g, 2.25 mmol) was added to $[TaCl_3(THF)_2]_2N_2$ (1.0 g, 1.12 mmol) in 40 mL of dichloromethane, and the mixture was stirred for 2 h. The dichloromethane was removed in vacuo and the resulting red solid extracted with a minimal amount of CH_2Cl_2/toluene. The mixture was filtered and the filtrate was cooled to −30 °C to give crystals suitable for X-ray analysis: $^{31}P\{^1H\}$ NMR (CH_2Cl_2) 9.3 (br s).

[Ta(CH$_2$CMe$_3$)$_3$(THF)]$_2$N$_2$. $Mg(CH_2CMe_3)_2$(dioxane) (0.80 g, 3.13 mmol) was added to $[TaCl_3(THF)_2]_2N_2$ (0.93 g, 1.04 mmol) in ether (5 mL) at −30 °C. The reaction mixture was warmed to 25 °C and filtered after 3 h. The ether was removed from the filtrate in vacuo, and the resulting yellow solid was extracted with pentane. The filtrate was cooled to −30 °C to give 0.69 g (70% yield) of bright yellow crystals: ^{1}H NMR (C_6D_6) δ 3.70 (m, 4, $\overline{OC\mathit{H}_2CH_2CH_2C\mathit{H}_2}$), 1.35 (s, 27, $CH_2C\mathit{Me}_3$), 1.30 (m, 4, $\overline{OCH_2C\mathit{H}_2C\mathit{H}_2CH_2}$), 0.89 (s, 6, $C\mathit{H}_2CMe_3$). Anal. Calcd for $TaC_{19}H_{41}NO$: C, 47.50; H, 8.60; N, 2.92. Found: C, 46.89; H, 8.54; N, 3.32.

[Ta(OCMe$_3$)$_3$(THF)]$_2$N$_2$. $[TaCl_3(THF)_2]_2N_2$ (2.0 g, 2.24 mmol) was slurried in the THF (40 mL) and $KOCMe_3$ (1.51 g, 13.47 mmol) added while the mixture was stirred. The slurry immediately began lightening as KCl deposited from solution. After the mixture was stirred 18 h, the THF was removed in vacuo, yielding an oily yellow solid which was extracted with pentane. The filtrate was concentrated in vacuo until crystals began forming. The deep yellow solution was then cooled to −30 °C. The extreme solubility of the compound prevented a high yield crystallization, but 0.14 g of pure product for elemental analysis and NMR studies was obtained. The pentane was removed from the mother liquor to give 1.47 g of essentially pure product: total yield 1.61 g (80%); ^{1}H NMR (C_6D_6) δ 3.51 (m, 4, $\overline{OC\mathit{H}_2CH_2CH_2C\mathit{H}_2}$), 1.52 (s, 27, $OC\mathit{Me}_3$), 1.39 (m, 4, $\overline{OCH_2C\mathit{H}_2C\mathit{H}_2CH_2}$). Anal. Calcd for $TaC_{16}H_{35}NO_4$: C, 39.51; H, 7.27; N, 2.88. Found: C, 39.83; H, 7.32; N, 2.48.

[NbCl$_3$(THF)$_2$]$_2$N$_2$. $Nb(CHCMe_3)(THF)_2Cl_3$ (1.0 g, 2.42 mmol) was dissolved in ether (7 mL), and benzalazine (0.25 g, 1.21 mmol) was added. After 3 h 0.60 g (70% yield) of the pink-violet product was isolated by filtration. GLC analysis of the filtrate showed that 95 mol % of *cis*- and *trans*-$Me_3CCH{=}CHPh$ was produced.

[Nb(CH$_2$CMe$_3$)$_3$(THF)]$_2$N$_2$. $[NbCl_3(THF)_2]_2N_2$ (0.71 g, 1.0 mmol) was slurried in ether (35 mL), and $Mg(CH_2CMe_3)_2$(dioxane) (0.76 g, 3.0 mmol) was added slowly with stirring. The reaction mixture turned orange. After 18 h the mixture was filtered and the ether removed in vacuo to yield orange crystals. The product was extracted into pentane, from which it crystallized at −30 °C: yield 0.50 g (60%); ^{1}H NMR (C_6D_6) δ 3.67 (m, 4, $\overline{OC\mathit{H}_2CH_2CH_2C\mathit{H}_2}$), 1.39 (s, 27, $CH_2C\mathit{Me}_3$), 1.34 (m, 4, $\overline{OCH_2C\mathit{H}_2C\mathit{H}_2CH_2}$, and s, 6, $C\mathit{H}_2CMe_3$).

Hydrazine Determinations.[29] The dinitrogen complex (0.10–0.15 mmol) was dissolved in ether/THF, and 25 equiv of HCl in ether was added. The reaction was stirred overnight and the solvent removed in vacuo, leaving a beige-white residue which was extracted with H_2O, filtered through Celite (removes organometallic product), and diluted with water to 1 L in a volumetric flask. Aliquots of the above solution were treated with an H_2O/HCl solution of *p*-(dimethylamino)benzaldehyde, and the absorbance was measured at 458 nm in 1-mm path length cells after 15 min.

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Registry No. $Ta(NPh)(THF)_2Cl_3$, 75730-60-8; $Ta(NPh)(PEt_3)_2Cl_3$, 81391-16-4; $Ta(NPh)(dmpe)_2Cl$, 81391-17-5; $Ta(NPh)(PMe_3)_4Cl$, 75730-64-2; $Ta(NCMe_3)(THF)_2Br_3$, 81391-18-6; $Ta(NCMe_3)(THF)_2Cl_3$, 75730-62-0; $Ta(NCMe_3)(PMe_3)_2Cl_3$, 81372-02-3; $Ta(NCH_3)(PMe_3)_4Cl$, 81372-03-4; $Ta(NCMe_3)(dmpe)_2Cl$, 81372-04-5; $Ta(NPh)(PMe_3)_2Cl_3$, 81372-05-6; $Ta(NPh)(C_2H_4)(PMe_3)_3Cl_2$, 75730-66-4; $[TaCl_3(THF)_2]_2N_2$, 75730-57-3; $[TaCl_3(PMe_2Ph)_2]_2N_2$, 81372-06-7; $[TaCl_3(PEt_2Ph)_2]_2N_2$, 81372-07-8; $[TaCl_3(PEt_3)_2]_2N_2$, 75737-71-2; $[TaCl_3(P(n\text{-}Pr)_3)_2]_2N_2$, 81372-08-9; $[Ta(OCMe_3)_3(THF)]_2N_2$, 81372-09-0; $[Ta(CH_2CMe_3)_3(THF)]_2N_2$, 81372-10-3; $Ta(CHCMe_3)(THF)_2Cl_3$, 75331-92-9; $Ta(CHCMe_3)(THF)_2Br_3$, 75331-93-0; $Ta(NMe)(THF)_2Cl_3$, 75730-61-9; $Nb(NPh)(THF)_2Cl_3$, 81372-11-4; $Nb(CHCMe_3)(THF)_2Cl_3$, 75363-44-9; $Ta(NPh)(PEt_3)(THF)Cl_3$, 79482-72-7; $Ta(NCMe_3)(PMe_3)_4Cl$, 81372-98-4; $Ta(NPh)(CH_2CMe_3)_3(THF)$, 81372-99-5; $[TaCl_3(THF)(PBz_3)]_2N_2$, 79499-29-9; $[NbCl_3(THF)_2]_2N_2$, 81372-00-1; $[Nb(CH_2CMe_3)_3(THF)]_2N_2$, 81372-01-2; PhNCHPh, 538-51-2; MeNCHPh, 622-29-7; $Me_3CNCHPh$, 6852-58-0; $PhCH{=}NN{=}CHPh$, 588-68-1; acetone, 67-64-1; $N_2H_4{\cdot}2HCl$, 5341-61-7; $(Me_2C{=}N)_2$, 627-70-3; $Me_2C{=}CHCOMe$, 141-79-7.

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