of the donor is 0–2 kcal/mol below that of the acceptor, the rate constant is more than 2 orders of magnitude below the diffusion-controlled value. Thus, the observed rate of energy transfer from ^{3}TPP to C_{70} would be expected if the C_{70} triplet energy is 33–35 kcal/mol, in excellent agreement with the value of Wasielewski et al.[7]

C_{70}, like C_{60},[6] produces singlet oxygen in large quantities, as measured by $^1O_2$ luminescence at 1268 nm.[11] The quantum yield ($\Phi_{^1O_2}$) is 0.81 ± 0.15 when excited at both 355 and 532 nm. Since $^1O_2$ is formed by energy transfer from the highly populated C_{70} triplet state to molecular oxygen, these values also represent a lower limit for the quantum yield of triplet production (Φ_T). In excellent agreement with this conclusion, the value for Φ_T at 355 nm, as determined by comparison with benzophenone (see Experimental Section), were in the range 0.9 ± 0.15 in four separate experiments. Thus S_Δ, the efficiency of formation of $^1O_2$ from the triplet, is 1.0 within experimental error.

We were unable to detect $^1O_2$ quenching by C_{70} in C_6D_6. Marginal quenching was detected with C_{60},[6] the mechanism of which is presently unknown, but solubility limitations precluded measurements at high enough concentration to detect any quenching by C_{70}, even of the magnitude seen with C_{60}. As with C_{60}, however, no destruction of starting material or formation of new products (by UV–visible absorption spectra and HPLC) occurs under O_2, following hundreds of laser pulses at either excitation wavelength or with broad-band excitation with a powerful lamp for many hours.

Discussion

Because of the reduced symmetry of C_{70} relative to C_{60}, the $S_0 \rightarrow S_1^*$ transition is not as strongly forbidden, and the visible maxima are much stronger. This lowered forbiddenness also accounts for the fact that weak fluorescence from this transition can be observed in C_{70}, in contrast to C_{60}. Increased triplet–triplet absorption coefficients (roughly 1.5 times that of C_{60}) may be caused by the same factor.

As with C_{60}, the small S–T splitting in C_{70} ($\Delta E_{S_1-T} \approx 9$ kcal/mol) is probably a result of the large diameter of the molecule and the resulting small electron–electron repulsion energy.[21] This small splitting, the probable low value of the fluorescence rate constant (from the low extinction coefficient), and the expected large spin–orbital interaction in the spheroidal C_{70} explains why intersystem crossing (ISC) is a dominant process. Wasielewski has measured the rates of intersystem crossing ($C_{60} = 3.0 \times 10^{10}$ s^{-1} and $C_{70} = 8.7 \times 10^9$ s^{-1}). The larger diameter and resulting lower curvature of C_{70} than C_{60} would predict a smaller spin–orbit coupling and provide a rationale for the lower intersystem crossing rate constant and somewhat lower triplet production efficiency in C_{70}.

The singlet oxygen quantum yields at 532 and 355 nm, while high, are slightly lower than unity. With C_{60}, the yield is 0.74 at 355 nm, but 1.0 at 532 nm.[6] The lower yield for C_{70} at 532 nm, in comparison with C_{60}, must result from minor pathways for deactivation of $^1C_{70}$ other than intersystem crossing, for instance, internal conversion.

The very high singlet oxygen yield and inertness to destruction of C_{70} suggests potential for photodynamic damage to biological systems, as with C_{60}.[6] Experiments to test this suggestion are in progress.

Acknowledgment. This work was supported by NSF Grant No. CHE89-11916 and NIH Grant No. GM-20080. We thank F. Ettl, F. Diederich, and R. Whetten for C_{70} and C_{60} and A. Darmanyan for helpful discussion.

Note Added in Proof. A recent letter[22] suggests that C_{60} and C_{70} are unstable to light. We have exposed solutions of each in benzene to unfiltered light from a 300-W xenon lamp for many hours under O_2 without observable degradation (UV–vis and HPLC). Also, solutions of both compounds were allowed to stand in a California window exposed to full skylight for 9 days; C_{60} was unchanged, while C_{70} showed <1% formation of an unidentified new product by HPLC.[23] We concur that samples on some batches of alumina and on other adsorbents have variable stability, with C_{70} being lost more readily than C_{60}, but we do not believe that light is an important contributor to this destruction.

Registry No. C_{60}, 99685-96-8; C_{70}, 135105-58-7; rubrene, 517-51-1; oxygen, 7782-44-7.

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Synthesis and Formal [4 + 2] Cycloaddition Reactions of Vinylimido Complexes of Titanocene

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Abstract: Sources of the methylidene complex of titanocene, $Cp_2Ti{=}CH_2$, react with nitriles in the presence of donor ligands to afford vinylimido titanocene complexes. The vinylimido complexes react readily with ketones, nitriles, and imines, yielding products that retain the elements of the imido ligand. In no case are products of formal [2 + 2] metathesis obtained. Concerted or stepwise [4 + 2] cycloadditions are suggested as possible mechanisms for these coupling reactions.

Metal–ligand multiply bonded species play a myriad of diverse roles in inorganic and organometallic chemistry.[1] Reports of such complexes as intermediates and isolated species continue to grow in number at a rapid rate. As more and more data are obtained, it becomes possible to formulate generalizations about the reactivity of these species with various classes of organic substrates. Imido complexes of both early and late transition metals, for example, react with aldehydes and ketones in metathesis-type

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[†] University of Oregon.
[‡] University of California.

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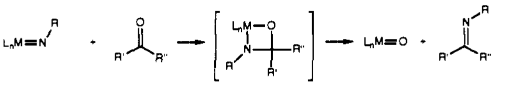
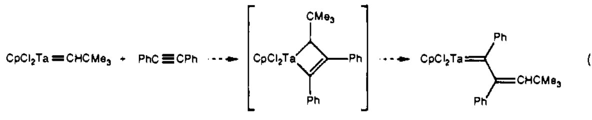
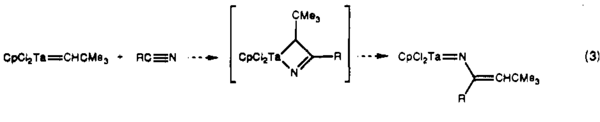
reactions, producing metal oxo complexes and organic imines (eq 1). These reactions are often presumed to proceed via [2 + 2] cycloaddition, followed by electrocyclic decomposition driven by the formation of a strong M=O bond.[2]


(1)

Transition metal carbene complexes often react similarly through formal [2 + 2] cycloadditions. For example, metallacyclobutenes are produced as either isolable species[3] or reactive intermediates[4-6] upon reaction with alkynes (eq 2), and azametallacyclobutenes are postulated as intermediates in reactions with nitriles[6] (eq 3).


(2)


(3)

Electrocyclic ring opening of metallacyclobutenes, as illustrated in eqs 2 and 3, has been suggested to play a role in transition metal catalyzed alkyne polymerization[7-14] and in the formation of carbocyclic and heterocyclic compounds through the reactions of Fischer-type carbene complexes with alkynes, nitriles, and other unsaturated functionalities.[15-19] In the latter cases, there is some question about whether the metallacyclobutene ring itself opens to give a vinylcarbene complex or whether this ring opening is preceded by a carbon monoxide insertion step (eq 4).[20] More recently, some doubt has been raised about the viability of metallacyclobutene intermediates in these reactions.[21]

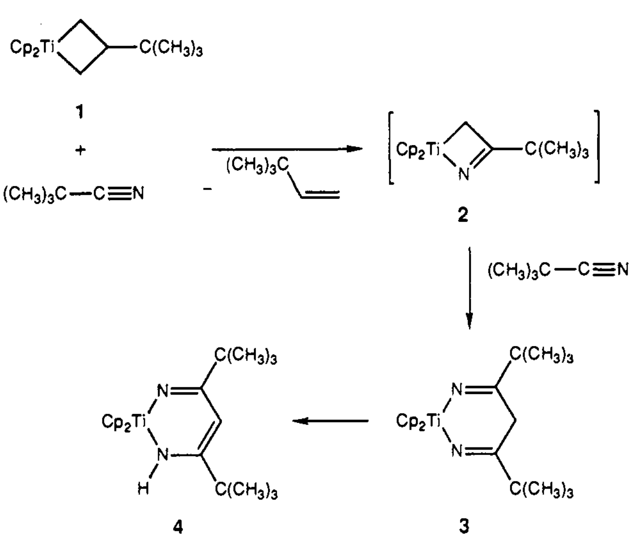


Figure 1. Formation of diazatitanacyclohexadienes.

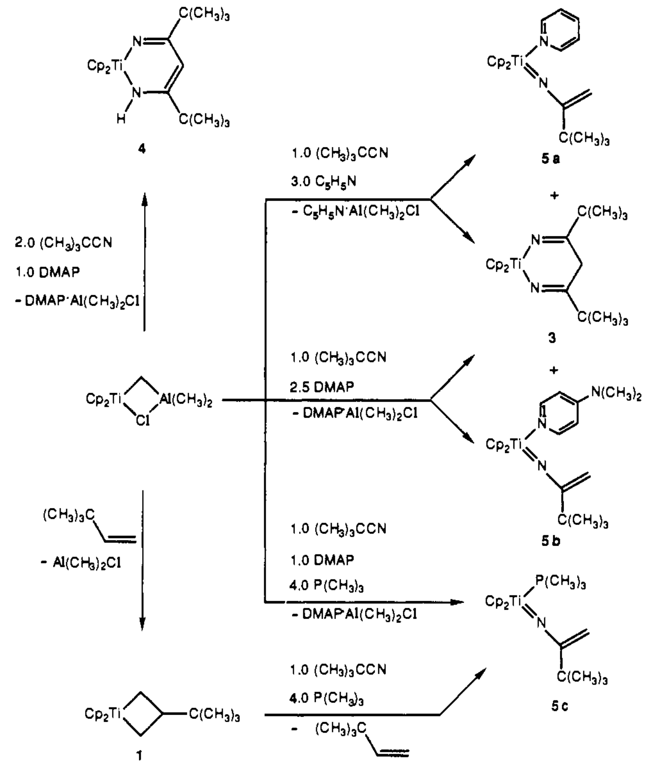
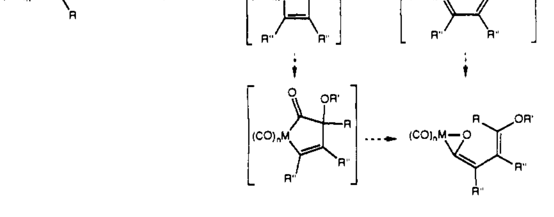


Figure 2. Formation of vinylimido complexes from $Cp_2Ti{=}CH_2$ sources.


(4)

We recently reported the formation of vinylimido complexes of titanocene through the reaction of sources of the methylidene complex of titanocene with nitriles in the presence of trapping ligands (eq 5).[22] These imido complexes, the first of titanocene

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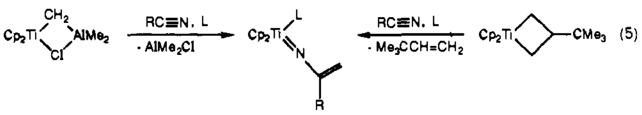
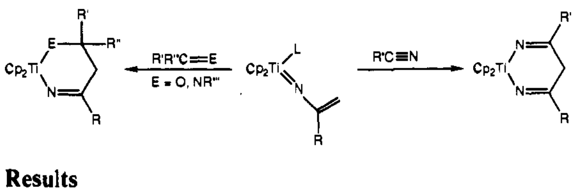


(5)

to be reported,[23] display unique reactivity toward unsaturated organic substrates. *In sharp contrast to reactions of other imido complexes, they have never been observed to undergo [2 + 2] metathesis reactions with ketones, nitriles, or imines.* Instead, as we demonstrate herein, the imido complexes react with these substrates to produce new metallacyclic complexes that retain the original imido group (eq 6).

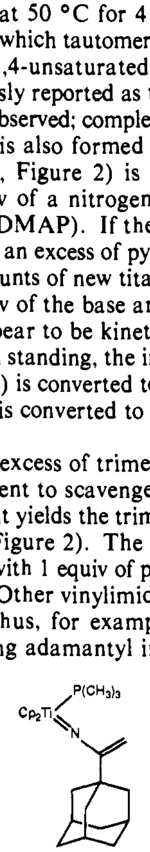


(6)

Results

Treatment of titanacyclobutane[24] **1** (Figure 1) with 2 equiv of pivalonitrile in benzene at 50 °C for 4 h affords the diazatitanacyclohexa-2,5-diene **3**, which tautomerizes at a somewhat lower rate to the conjugated 2,4-unsaturated isomer **4**. The azatitanacyclobutene **2**, previously reported as the initial product of this reaction,[25] is in fact not observed; complex **3** is the first observable product.[26] Complex **4** is also formed when Tebbe's reagent[27] ($Cp_2TiCH_2 \cdot Al(CH_3)_2Cl$, Figure 2) is treated with 2 equiv of pivalonitrile and 1 equiv of a nitrogenous base such as 4-(dimethylamino)pyridine (DMAP). If the amount of pivalonitrile is reduced to 1 equiv and an excess of pyridine or DMAP is used, however, significant amounts of new titanium complexes (**5a** and **5b**) incorporating 1 equiv of the base are also produced (Figure 2). These materials appear to be kinetically labile under these reaction conditions; upon standing, the initially observed mixture of **5a** and **3** (ca. 1:2 ratio) is converted to only **3**, while the initial 2:1 mixture of **5b** and **3** is converted to a 1:2 mixture of the two complexes.

In the presence of an excess of trimethylphosphine with only 1 equiv of DMAP (present to scavenge the dimethylaluminum chloride), Tebbe's reagent yields the trimethylphosphine complex **5c** as the sole product (Figure 2). The titanacyclobutane **1** also affords **5c** when treated with 1 equiv of pivalonitrile and an excess of trimethylphosphine. Other vinylimido complexes can also be prepared analogously; thus, for example, 1-cyanoadamantane affords the corresponding adamantyl imido complex **6**.



6

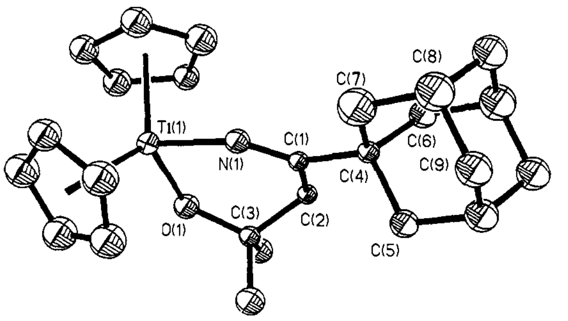


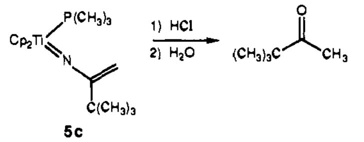
Figure 3. Molecular structure of $Cp_2TiN{=}C(1\text{-adamantyl})CH_2C(CH_3)_2O$ (**7b**).

Table I. Crystal Data for $Cp_2TiN{=}C(1\text{-adamantyl})CH_2C(CH_3)_2O$ (**7b**) and $Cp_2TiN{=}C(1\text{-adamantyl})CH_2C(1\text{-adamantyl}){=}N$ (**10**)

compd	**7b**	**10**
empirical formula	$C_{25}H_{33}NOTi$	$C_{33}H_{40}N_2Ti \cdot C_7H_8$
color, habit	red prism	red block
cryst size, mm	0.2 × 0.4 × 0.6	0.35 × 0.40 × 0.42
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.253 (8)	11.565 (8)
b, Å	13.146 (10)	16.957 (11)
c, Å	15.164 (12)	17.009 (10)
α, deg	102.80 (3)	83.00 (5)
β, deg	91.42 (4)	82.91 (5)
γ, deg	102.22 (3)	78.25 (5)
vol, Å^3	2132 (3)	3224 (3)
Z	4	4
fw	411.4	606.7
calcd density, Mg/m^3	1.282	1.250
abs coeff, mm^{-1}	0.410	0.29
F(000)	880	1304

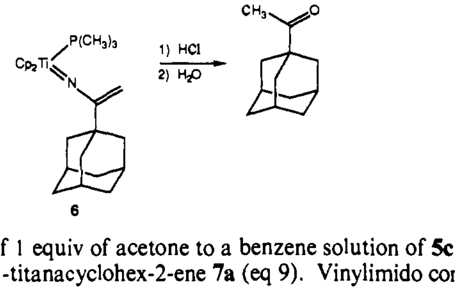
Complexes **5a–c** and **6** display characteristic pairs of signals for the two inequivalent vinylic protons, which appear as mutually coupled doublets in their ^{1}H NMR spectra. Interestingly, **5c** and **6** display long-range ^{31}P coupling to one of these hydrogens ($^5J_{PH} \approx 1.0$ Hz), as confirmed by analysis of ^{31}P-decoupled ^{1}H NMR spectra. The two cyclopentadienyl rings in each complex appear to be equivalent in both the ^{1}H and ^{13}C NMR spectra, with long-range coupling to phosphorus, $J_{PH} = 2.4$ Hz, apparent in the ^{1}H NMR spectra of **5c** and **6**.

Treatment of a dry benzene solution of **5c** with dry HCl gas results in the immediate precipitation of titanocene dichloride. Aqueous workup of the resulting mixture affords the anticipated 3,3-dimethyl-2-butanone (pinacolone, eq 7), which was isolated and characterized as its (2,4-dinitrophenyl)hydrazone derivative. Similarly, **6** affords 1-acetyladamantane (eq 8).



5c

(7)



6

(8)

Addition of 1 equiv of acetone to a benzene solution of **5c** gives 2-aza-6-oxa-1-titanacyclohex-2-ene **7a** (eq 9). Vinylimido complex **6** also reacts readily with acetone, affording **7b** (eq 10). Protonolysis of **7a** with dry HCl in benzene followed by aqueous workup

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Table II. Solution and Refinement Data for $Cp_2\overline{TiN{=}C(1\text{-adamantyl})CH_2C(CH_3)_2O}$ (**7b**)

system used	Siemens SHELXTL PLUS (VMS)
solution	Patterson/direct methods (PATT)
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
Cp rings	rigid pentagons, C-C 1.420 Å
other constraints	chemically equivalent distances (not Ti-Cp) constrained to be nearly equal
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.004F^2$
no. of params refined	209
final R indices (obsd data)	R = 10.20%, R_w = 10.73%
goodness-of-fit	2.04
largest Δ/σ	0.003
data-to-param ratio	10.3:1
largest diff peak	1.26 e Å^{-3}
largest diff hole	-0.73 e Å^{-3}

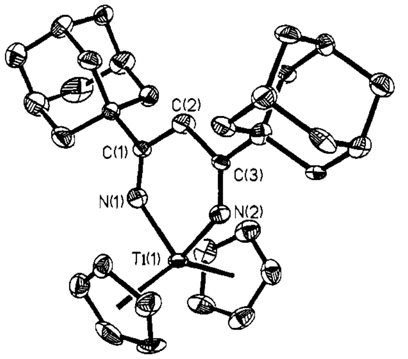
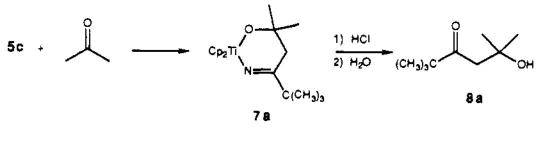


Figure 4. Molecular structure of $Cp_2\overline{TiN{=}C(1\text{-adamantyl})CH_2C(1\text{-adamantyl}){=}N}$ (**10**).

affords β-hydroxy ketone **8a**; analogous treatment of **7b** affords **8b**.



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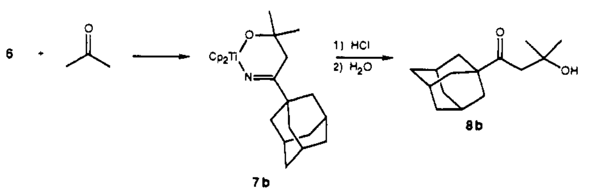
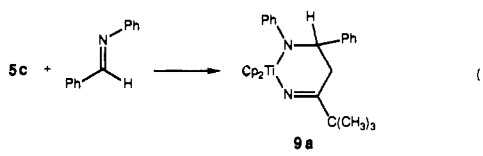


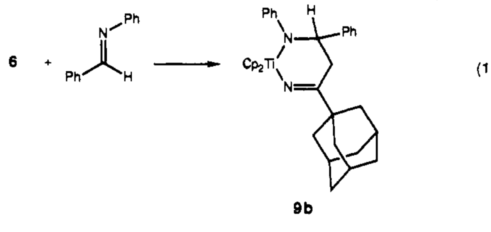
(10)

The structure of **7b** was unambiguously determined by X-ray crystallography (Figure 3); crystal and structure solution data are presented in Tables I and II. Atomic positional coordinates and representative bond lengths and angles for each of the two molecules in the asymmetric unit are presented in Tables III–V. (Average values of bond distances and angles are used in the following discussion.) The 2-aza-6-oxa-1-titanacyclohexene ring is nearly planar, with only the methylene group twisted appreciably out of planarity. The O–Ti–N angle at 89.6° is only slightly closed down from that seen in simple acyclic titanocene derivatives[28] (e.g., the Cl–Ti–Cl angle in Cp_2TiCl_2 is 95.2°), although it is appreciably larger than that reported for smaller ring titanacyclic complexes (e.g., the C–Ti–C angle in titanacyclobutenes[3a,29] is ca. 69°). The C(1)–C(2)–C(3) angle at 118.1° is considerably distorted from idealized tetrahedral geometry, perhaps in response to ring strain; the other bond angles at carbon in **7b** all appear to be normal. The Ti—O—C and Ti—N=C angles are both quite wide (132.5° and 133.4°, respectively), most probably also reflecting ring strain, although the relatively short Ti—O bond (1.878 Å) suggests a possible contribution of Ti—O multiple bonding to the bonding scheme. The other bond lengths and angles in **7b** are unremarkable, supporting the presence of a localized C=N double bond (1.244 Å) and C—C single bonds (1.520 Å and 1.549 Å) within the titanacyclic ring.

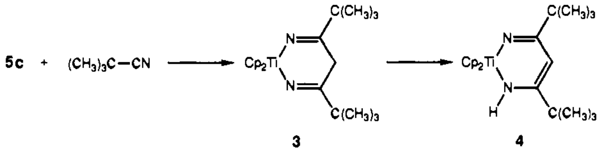
Vinylimido complex **5c** reacts with benzylideneaniline to afford diazatitanacyclohexene **9a** (eq 11), while **6** similarly affords **9b** (eq 12). These reactions are quite sluggish, requiring approximately 2 weeks at 60 °C to proceed to completion. Treatment of **5c** with pivalonitrile affords the diazatitanacyclohexadienes **3** and **4** (eq 13), previously obtained directly from reactions of Tebbe's reagent or titanacyclobutane **1** with pivalonitrile in the absence of trimethylphosphine.[25]



(11)

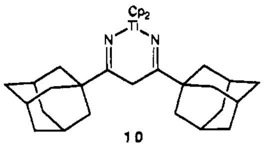


(12)



(13)

Complex **10**, the adamantyl analogue of **3**, has been crystallographically characterized (Figure 4); crystal and structure solution data are presented in Tables I and VI. Atomic positional coordinates and representative bond lengths and angles for each of the two molecules in the asymmetric unit are presented in Tables VII–IX. (Average values of bond distances and angles are used in the following discussion.)



10

The six atoms within the metallacyclic ring of **10** are very nearly coplanar, with the methylene group lifted only slightly out of the best plane containing these atoms. Addition of a second multiple bond to the metallacyclic ring apparently precludes the significant out-of-plane movement seen for this methylene group in the monounsaturated complex, **7b**. The N–Ti–N bond angle at 88.6° is not appreciably different from that seen in **7b** (89.6°), and again differs only slightly from that reported for acyclic titanocene derivatives. The C=N bond distances at 1.258 Å are consistent with formulation as double bonds (typical length 1.28 Å) and inconsistent with single bond character (typical length 1.47 Å). The N–C–C bond angles, all falling near 120°, are also consistent with this formulation. The C(1)–C(2)–C(3) angle (118.5°) and the two Ti–N–C angles (132.9° and 133.1°) display distortions similar to those seen for the analogous angles in **7b**, again suggesting the presence of some ring strain in **10**.

Discussion

Treatment of titanacyclobutane **1** (Figure 1) with pivalonitrile affords the diazatitanacyclohexa-2,5-diene **3**, which then tautomerizes to the conjugated 2,4-unsaturated isomer (**4**). Analogous

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[28] Tkachev, V. V.; Atovmyan, L. O. *Zh. Strukt. Khim.* **1972**, *13*, 287.

[29] Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6151–6153.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $Cp_2TiN{=}C(1\text{-adamantyl})CH_2C(CH_3)_2O$ (**7b**)[a]

atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
Ti(1)	2066 (3)	3081 (3)	10962 (2)	17 (1)	Ti(2)	7009 (3)	2382 (3)	2146 (2)	18 (1)
O(1)	3377 (8)	3097 (9)	10220 (6)	25 (3)	O(2)	8406 (8)	2655 (8)	2941 (6)	18 (3)
N(1)	946 (10)	2734 (10)	9888 (7)	21 (4)	N(2)	5995 (11)	2343 (11)	3161 (8)	23 (4)
C(1)	1054 (12)	2359 (12)	9072 (9)	13 (4)	C(31)	6207 (12)	2514 (12)	3995 (9)	16 (4)
C(2)	2291 (12)	2128 (11)	8766 (10)	15 (4)	C(32)	7542 (14)	2932 (18)	4408 (13)	70 (8)
C(3)	3423 (13)	2916 (10)	9265 (9)	18 (4)	C(33)	8583 (15)	2634 (14)	3866 (10)	39 (6)
C(4)	33 (11)	2087 (9)	8331 (8)	15 (4)	C(34)	5215 (11)	2457 (10)	4648 (9)	24 (5)
C(5)	301 (13)	2766 (13)	7632 (9)	27 (5)	C(35)	5168 (15)	1541 (13)	5123 (11)	34 (5)
C(6)	−165 (14)	922 (10)	7810 (10)	26 (5)	C(36)	5422 (16)	3491 (13)	5385 (10)	45 (6)
C(7)	−1167 (11)	2239 (16)	8730 (11)	45 (6)	C(37)	3966 (11)	2269 (14)	4151 (10)	31 (5)
C(8)	−2225 (16)	1931 (11)	8004 (10)	45 (6)	C(38)	2943 (15)	2214 (11)	4793 (10)	41 (6)
C(9)	−1927 (14)	2617 (14)	7315 (11)	38 (6)	C(39)	2948 (15)	1315 (14)	5276 (13)	51 (6)
C(10)	−739 (11)	2485 (12)	6894 (10)	35 (5)	C(40)	4182 (12)	1504 (14)	5795 (10)	47 (6)
C(11)	−904 (17)	1318 (11)	6390 (11)	38 (6)	C(41)	4410 (19)	2556 (11)	6508 (12)	44 (6)
C(12)	−1199 (12)	614 (15)	7065 (10)	47 (6)	C(42)	4403 (12)	3462 (14)	6033 (11)	49 (6)
C(13)	−2378 (14)	768 (12)	7494 (11)	37 (5)	C(43)	3174 (14)	3269 (13)	5504 (11)	42 (6)
C(14)	4557 (13)	2497 (13)	9023 (11)	28 (5)	C(44)	9835 (18)	3292 (16)	4251 (17)	103 (10)
C(15)	3574 (15)	3959 (12)	8963 (12)	33 (5)	C(45)	8597 (22)	1495 (15)	3913 (18)	109 (11)
C(16)	1903 (11)	2219 (9)	12237 (6)	34 (5)	C(46)	7281 (13)	3512 (11)	1088 (8)	58 (7)
C(17)	809	1799	11667	36 (5)	C(47)	6048	3389	1309	34 (5)
C(18)	1103	1212	10828	38 (5)	C(48)	6038	3919	2232	61 (7)
C(19)	2378	1269	10880	26 (5)	C(49)	7265	4369	2581	83 (9)
C(20)	2872	1892	11751	33 (5)	C(50)	8033	4118	1874	49 (6)
C(21)	3190 (9)	4930 (11)	11583 (9)	43 (6)	C(51)	7531 (12)	1071 (12)	921 (9)	52 (7)
C(22)	2604	4552	12305	43 (6)	C(52)	6292	1076	726	71 (8)
C(23)	1325	4354	12105	35 (5)	C(53)	5601	685	1401	60 (7)
C(24)	1120	4610	11261	40 (6)	C(54)	6413	439	2012	47 (6)
C(25)	2273	4966	10938	44 (6)	C(55)	7606	677	1715	36 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Bond Lengths (Å) for $Cp_2TiN{=}C(1\text{-adamantyl})CH_2C(CH_3)_2O$ (**7b**)[a]

Ti–O	1.878 (8)	C(O)–C(H_2)	1.520 (16)
Ti–N	1.942 (10)	C–C(H_3)	1.516 (12)
C–O	1.419 (14)	C(N)–C(adamantyl)	1.514 (15)
C–N	1.244 (13)	C–C(adamantyl)	1.525 (3)
C(N)–C(H_2)	1.549 (16)		

[a] Chemically equivalent distances (other than Ti–Cp) were constrained to be nearly equal. Individual distances are not given. The Cp rings were constrained to be regular pentagons with C–C 1.420 Å.

Table V. Bond Angles (deg) for $Cp_2TiN{=}C(1\text{-adamantyl})CH_2C(CH_3)_2O$ (**7b**)

O(1)–Ti(1)–N(1)	89.5 (5)	O(2)–Ti(2)–N(2)	89.8 (5)
Ti(1)–O(1)–C(3)	131.8 (8)	Ti(2)–O(2)–C(33)	133.2 (9)
Ti(1)–N(1)–C(1)	132.4 (11)	Ti(2)–N(2)–C(31)	134.3 (10)
N(1)–C(1)–C(4)	124.4 (13)	N(2)–C(31)–C(34)	123.2 (12)
C(1)–C(2)–C(3)	116.0 (8)	C(31)–C(32)–C(33)	120.3 (9)
O(1)–C(3)–C(2)	112.0 (11)	O(2)–C(33)–C(32)	111.9 (15)
O(1)–C(3)–C(14)	107.5 (12)	O(2)–C(33)–C(44)	109.9 (15)
C(2)–C(3)–C(14)	110.5 (11)	C(32)–C(33)–C(44)	114.5 (14)
O(1)–C(3)–C(15)	110.7 (11)	O(2)–C(33)–C(45)	108.2 (14)
C(2)–C(3)–C(15)	109.5 (13)	C(32)–C(33)–C(45)	106.4 (17)
C(14)–C(3)–C(15)	106.4 (13)	C(44)–C(33)–C(45)	105.4 (17)
C(1)–C(4)–C(5)	112.4 (10)	C(31)–C(34)–C(35)	112.3 (13)
C(1)–C(4)–C(6)	111.0 (12)	C(31)–C(34)–C(36)	110.7 (11)
C(1)–C(4)–C(7)	110.8 (11)	C(31)–C(34)–C(37)	110.7 (11)

results are obtained if Tebbe's reagent [$Cp_2TiCH_2{\cdot}Al(CH_3)_2Cl$] is used in place of titanacyclobutane **1**. However, the tautomerization is quite slow in the latter reaction mixtures—sequestration of adventitious bases by $Al(CH_3)_2Cl$ may shut down base-catalyzed tautomerization pathways. Similar results are obtained in analogous reactions using 1-cyanoadamantane in place of pivalonitrile. The latter reactions were examined in the hopes of adding crystallinity to the reaction products. This hope was realized: complex **10** crystallized from a solution of **6** (vide infra) in which it was a minor component. Crystallographic analysis (Figure 4) confirms the indicated structure for this complex.

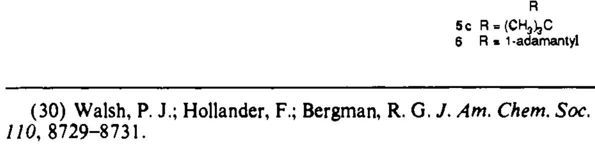
The 2-azatitanacyclobut-2-ene **2**, a possible intermediate in the formation of complex **3**, has not yet been directly observed.[22,26]

Table VI. Solution and Refinement Data for $Cp_2TiN{=}C(1\text{-adamanty})CH_2C(1\text{-adamantyl}){=}N$ (**10**)

system used	Siemens SHELXTL PLUS (VMS)
solution	Patterson/direct methods (PATT)
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic *U*
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0013F^2$
no. of params refined	650
final *R* indices (obsd data)	$R = 9.15\%$, $R_w = 11.14\%$
goodness-of-fit	2.04
largest Δ/σ	0.22
data-to-param ratio	7.0:1
largest diff peak	1.53 e $Å^{-3}$
largest diff hole	−0.65 e $Å^{-3}$

Interestingly, stable tautomeric metallacycles, 2-azazirconacyclobut-3-enes, are formed in the reaction of a zirconocene imide complex with alkynes.[30]

Addition of only 1 equiv of pivalonitrile to titanacyclobutane **1** or to Tebbe's reagent results in the formation of the diazatitanacyclohexadiene **3** in ca. 50% yield, suggesting that reaction of the putative **2** with the second equivalent of nitrile is appreciably faster than with the first. However, if Tebbe's reagent (or titanacyclobutane **1**) is treated with only 1 equiv of a nitrile in the presence of a donor ligand, such as trimethylphosphine or triethylphosphine, the initial condensation product may be trapped in its ligated ring-opened form (eq 14). Confirmation of the proposed structures for these products was obtained through both spectral analysis and study of their reaction chemistry, as discussed in the following sections.



(14)

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(30) Walsh, P. J.; Hollander, F.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729–8731.

Table VII. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Cp$_2$TiN=C(1-adamantyl)CH$_2$C(1-adamantyl)=N (**10**)[a]

atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
Ti(1)	2162 (2)	2647 (1)	115 (1)	21 (1)	C(45)	12482 (6)	7547 (6)	5196 (5)	23 (4)
N(1)	492 (4)	2863 (5)	−83 (5)	24 (3)	C(46)	12425 (6)	7094 (5)	3866 (5)	20 (4)
N(2)	2535 (7)	3470 (4)	−759 (4)	24 (3)	C(47)	12323 (7)	8553 (5)	4003 (6)	26 (4)
C(1)	−66 (7)	3295 (5)	−622 (5)	18 (4)	C(48)	13678 (7)	8433 (5)	3858 (5)	27 (4)
C(2)	488 (7)	3841 (6)	−1275 (5)	28 (4)	C(49)	14204 (9)	8214 (6)	4657 (5)	34 (5)
C(3)	1783 (6)	3893 (5)	−1254 (5)	19 (4)	C(50)	13838 (6)	7431 (5)	5056 (5)	25 (4)
C(4)	−1357 (6)	3239 (5)	−693 (4)	21 (4)	C(51)	14312 (8)	6755 (5)	4513 (5)	27 (4)
C(5)	−1932 (8)	2908 (8)	103 (5)	43 (5)	C(52)	13777 (6)	6979 (5)	3717 (5)	26 (4)
C(6)	−2157 (7)	4039 (5)	−956 (7)	33 (4)	C(53)	14152 (9)	7757 (5)	3316 (6)	31 (4)
C(7)	−1340 (8)	2642 (6)	−1302 (6)	33 (4)	C(54)	8291 (6)	6568 (4)	5650 (4)	20 (4)
C(8)	−2587 (7)	2518 (6)	−1389 (6)	42 (5)	C(55)	8587 (9)	5832 (4)	5171 (5)	23 (4)
C(9)	−3128 (11)	2190 (7)	−581 (6)	56 (6)	C(56)	8836 (8)	6345 (5)	6442 (5)	22 (4)
C(10)	−3190 (8)	2774 (6)	47 (7)	52 (6)	C(57)	6943 (6)	6776 (5)	5832 (6)	20 (4)
C(11)	−3958 (9)	3581 (7)	−235 (6)	50 (5)	C(58)	6472 (8)	6060 (4)	6303 (4)	22 (4)
C(12)	−3416 (7)	3925 (6)	−1036 (5)	31 (4)	C(59)	6789 (7)	5329 (5)	5819 (5)	25 (4)
C(13)	−3340 (9)	3333 (5)	−1658 (6)	34 (4)	C(60)	8137 (6)	5106 (5)	5639 (5)	20 (4)
C(14)	2261 (6)	4524 (5)	−1863 (4)	24 (4)	C(61)	8700 (9)	4894 (5)	6425 (5)	27 (4)
C(15)	1977 (9)	5334 (5)	−1500 (5)	26 (4)	C(62)	8369 (7)	5625 (4)	6910 (5)	21 (4)
C(16)	3613 (6)	4280 (6)	−2031 (6)	28 (4)	C(63)	7023 (7)	5848 (6)	7093 (5)	28 (4)
C(17)	1737 (9)	4653 (6)	−2663 (4)	27 (4)	C(64)	8795 (6)	7692 (4)	3046 (4)	30 (4)
C(18)	2237 (7)	5305 (5)	−3229 (5)	24 (4)	C(65)	7541	7817	3211	30 (5)
C(19)	1932 (9)	6103 (5)	−2843 (5)	30 (4)	C(66)	7067	8626	2925	31 (4)
C(20)	2477 (7)	5994 (6)	−2054 (5)	29 (4)	C(67)	8028	9001	2587	30 (4)
C(21)	3823 (7)	5729 (5)	−2197 (6)	29 (4)	C(68)	9096	8424	2658	31 (4)
C(22)	4128 (8)	4934 (5)	−2583 (5)	30 (4)	C(69)	7884 (9)	9441 (5)	5137 (5)	51 (6)
C(23)	3588 (7)	5046 (7)	−3374 (5)	33 (4)	C(70)	6751	9460	4886	50 (6)
C(24)	2475 (7)	1786 (5)	−957 (4)	37 (5)	C(71)	6696	9909	4126	49 (6)
C(25)	3609	1868	−775	35 (5)	C(72)	7795	10168	3907	49 (6)
C(26)	3767	1498	9	38 (5)	C(73)	8529	9879	4531	53 (6)
C(27)	2731	1188	313	38 (5)	C(81)	4472 (8)	1073 (6)	2691 (5)	81 (5)
C(28)	1933	1366	−284	31 (4)	C(82)	4091	432	2423	84 (5)
C(29)	1561 (6)	3784 (4)	913 (4)	27 (4)	C(83)	4742	38	1789	82 (5)
C(30)	2821	3617	806	38 (5)	C(84)	5775	286	1423	75 (5)
C(31)	3221	2835	1192	42 (5)	C(85)	6156	926	1690	56 (4)
C(32)	2207	2519	1538	44 (5)	C(86)	5505	1319	2324	59 (4)
C(33)	1182	3105	1366	33 (5)	C(87)	5893 (15)	2002 (11)	2634 (10)	94 (6)
Ti(2)	8246 (2)	8720 (1)	3973 (1)	18 (1)	C(91)	822 (10)	10353 (8)	2567 (7)	84 (5)
N(3)	9941 (4)	8458 (4)	4106 (5)	20 (3)	C(92)	999	9808	1992	146 (9)
N(4)	8019 (6)	7821 (4)	4773 (4)	22 (3)	C(93)	391	10003	1314	158 (9)
C(41)	10476 (6)	7898 (5)	4506 (5)	16 (4)	C(94)	−393	10742	1211	162 (10)
C(42)	10050 (6)	7282 (6)	5098 (6)	24 (4)	C(95)	−569	11286	1786	63 (4)
C(43)	8726 (6)	7282 (5)	5142 (5)	16 (4)	C(96)	38	11092	2464	226 (14)
C(44)	11937 (6)	7773 (4)	4403 (4)	17 (4)	C(97)	−50 (16)	11559 (11)	2994 (11)	100 (6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VIII. Refined Mean Values for Constrained Bond Lengths (Å) for Cp$_2$TiN=C(1-adamantyl)CH$_2$C(1-adamantyl)=N (**10**)

Ti-N	1.954 (4)
C-N	1.258 (6)
C(N)-C(H$_2$)	1.523 (6)
C(N)-C(adamantyl)	1.534 (6)
C-C(adamantyl)	1.530 (2)

Table IX. Bond Angles (deg) for Cp$_2$TiN=C(1-adamantyl)CH$_2$C(1-adamantyl)=N (**10**)

N(1)-Ti(1)-N(2)	88.6 (3)	N(3)-Ti(2)-N(4)	88.7 (3)
Ti(1)-N(1)-C(1)	132.5 (6)	Ti(2)-N(3)-C(41)	133.3 (6)
Ti(1)-N(2)-C(3)	133.1 (7)	Ti(2)-N(4)-C(43)	133.1 (6)
N(1)-C(1)-C(2)	124.0 (7)	N(3)-C(41)-C(42)	122.4 (6)
N(1)-C(1)-C(4)	120.3 (7)	N(3)-C(41)-C(44)	121.7 (7)
C(2)-C(1)-C(4)	115.6 (6)	C(42)-C(41)-C(44)	115.8 (6)
C(1)-C(2)-C(3)	117.9 (7)	C(41)-C(42)-C(43)	119.1 (7)
N(2)-C(3)-C(2)	123.5 (8)	N(4)-C(43)-C(42)	122.8 (7)
N(2)-C(3)-C(14)	120.5 (7)	N(4)-C(43)-C(54)	120.9 (7)
C(2)-C(3)-C(14)	116.0 (7)	C(42)-C(43)-C(54)	116.3 (6)
C(1)-C(4)-C(5)	110.5 (7)	C(41)-C(44)-C(45)	112.7 (6)
C(1)-C(4)-C(6)	115.0 (7)	C(41)-C(44)-C(46)	108.7 (7)
C(1)-C(4)-C(7)	107.8 (6)	C(41)-C(44)-C(47)	109.7 (6)
C(3)-C(14)-C(15)	107.9 (6)	C(43)-C(54)-C(55)	108.8 (6)
C(3)-C(14)-C(16)	110.1 (6)	C(43)-C(54)-C(56)	113.4 (7)
C(3)-C(14)-C(17)	114.7 (7)	C(43)-C(54)-C(57)	109.4 (6)

Spectral Analysis. The ^{1}H NMR spectra of complexes **5a–c** and **6** show, as their most characteristic feature, two mutually coupled doublets ($^2J_{HH}$ = 1.4–1.8 Hz) for the inequivalent methylene hydrogens. One of the two hydrogens is also weakly coupled to the phosphorus of the phosphine ligand in complexes **5c** and **6**; this small coupling ($^5J_{PH}$ = 1.0 Hz for **5c**, 1.1 Hz for **6**) disappears in ^{31}P-decoupled ^{1}H NMR spectra, confirming its assignment as a long-range P–H coupling. These methylene resonances appear at quite high field (e.g., δ 3.35 and 3.85 for **5c**; see the Experimental Section for other complexes), and in some cases, in fact, even higher than predicted for typical organic enamines.[31] Although the factors affecting chemical shift may be complex,[32] it appears that the vinylimido ligand in these complexes may be quite electron-rich (vide infra).

Other ^{1}H NMR spectral features are also in accord with the formulation of **5a–c** and **6** as vinylimido complexes. Single cyclopentadienyl resonances are observed for each complex (vide infra), with weak P–H coupling seen in the phosphine complexes **5c** and **6** (J_{PH} = 2.4 Hz). The *tert*-butyl group in **5a–c** appears as a sharp singlet at ca. 1.3 ppm, while the complexed PMe$_3$ of **5c** and **6** appears as a phosphorus-coupled doublet near δ 1.0. (Observation of this P–H coupling, $^2J_{PH}$ = 6.9 Hz, confirms the presence of complexed PMe$_3$; free PMe$_3$ under our experimental

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(31) Pascual, C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164.

(32) For example, see: Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, 1977; pp 283–294.

conditions appears as a broad singlet, with incompletely resolved P–H coupling.) Identifiable resonances for the complexed pyridine and DMAP ligands in **5a** and **5b**, respectively, have not been observed. Apparently, exchange of these more weakly bound ligands with excess ligand in solution is rapid, resulting in the appearance of only exchange-averaged signals.

The ^{13}C NMR spectra of **5c** and **6** are completely consistent with the proposed structures. Again, single cyclopentadienyl resonances are observed ($^{1}J_{CH}$ = 170 Hz), even in the phosphine complexes. (Nonobservable P–C coupling in CpTi–phosphine complexes is well precedented.[33]) The methylene carbon of **5c** appears as an AMNX pattern ($^{1}J_{CH1} \approx {}^{1}J_{CH2} \approx 155$ Hz, $^{4}J_{PC}$ = 4.9 Hz) at δ 84.3; both the chemical shift and the magnitude of the C–H coupling constant support its assignment as an olefinic carbon. Adamantyl complex **6** displays an analogous resonance for its methylene carbon. Other resonances, C–H coupling constants, and P–C coupling constants provide confirmatory support as well. For example, the $^{n}J_{CP}$ coupling constants follow a distance order analogous to that observed in alkylcarbene complexes of titanocene bearing phosphine ligands.[33,34] Finally, the coordinated phosphine on complexes **5c** and **6** gives rise to a single, sharp resonance in their proton-decoupled ^{31}P NMR spectra.

Alternative formulation of **5c** and **6** as PMe$_3$ complexes of the corresponding azatitanacyclobutenes (**2**) is ruled out by the magnitude of $^{2}J_{HH}$ for the methylene group (1.4–1.8 Hz observed vs ca. 12–15 Hz expected for a CH$_2$ group or ca. 2 Hz for a $=$CH$_2$ group) and by the magnitude of $^{1}J_{CH}$ for the methylene group (155 Hz), which are consistent with a $=$CH$_2$ group but not a CH$_2$. The observed pattern of long-range P–C coupling constants also appears inconsistent with the azatitanacyclobutene formulation. Finally, a nonplanar geometry for the azatitanacyclobutene would be required for it to display two distinct resonances for the methylene hydrogens. Such a geometry would also give rise to two distinct cyclopentadienyl resonances, yet only one such resonance is resolved by both ^{1}H and ^{13}C NMR spectroscopy.

The observation of chemically equivalent cyclopentadienyl rings for the vinylimido complexes suggests that the imido ligand in these complexes is linear. Analogous linear imido ligand geometry has been defined by X-ray crystallography for simple alkyl- and aryl-substituted imido complexes of zirconium,[30,35] vanadium,[36–38] and osmium.[39] We will discuss the bonding implications of this geometry further in a subsequent paper.

Reactivity. Vinylimido complexes **5c** and **6** react with acetone, benzylideneaniline, and nitriles to form new metallacyclic products that incorporate the vinylimido ligand. For example, their reactions with acetone produce 2-aza-6-oxa-1-titanacyclohex-2-enes **7a** and **7b** in high yield. Spectral analysis suggests the proposed structures for these complexes, and the structure of **7b** has been confirmed by X-ray crystallographic analysis (Figure 3). Chemical confirmation for these structures is provided by their protonolysis to afford, after hydrolysis, the anticipated β-hydroxy ketones **8a** and **8b**. The nonbasic nature of the titanium methylidene reagents and the use of readily preparable nitriles in place of ketones or aldehydes in these reaction sequences suggest that this chemistry may function as a useful, completely directed, aldol reaction equivalent. Similarly, complex **5c** reacts with benzylideneaniline to afford the diazatitanacycle **9a**, while analogous treatment of **6** affords metallacycle **9b**. Nitriles also couple with the vinylimido complexes; for example, addition of 1-cyanoadamantane to **6** affords the diazatitanacyclohexadiene **10**. Further details of the symmetrical and unsymmetrical coupling of unsaturated organic substrates, including nitriles, ketones, and imines, with the vinylimido complexes will be presented at a later time. Interestingly, the vinylimido complex **5c** does not appear to react with alkynes even after prolonged reaction times. In contrast, Bergman's zirconocene imido complex reacts readily with alkynes to afford azazirconacyclobutenes.[40]

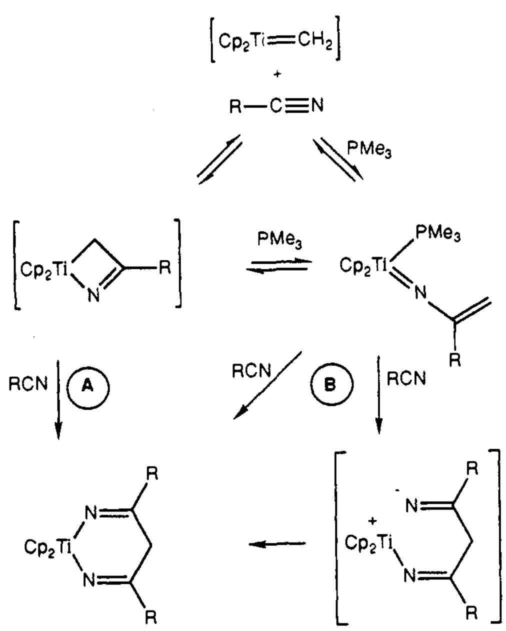

Figure 5. Possible mechanisms for the formation of diazatitanacyclohexadienes.

These reactions are especially noteworthy in that they constitute the first report of reaction chemistry of a transition metal imido complex with such substrates not proceeding through a formal [2 + 2] reaction pathway. The acetone reaction provides the most dramatic illustration of this most unusual reactivity. In all reported reactions of transition metal imido complexes with ketones, facile [2 + 2] cycloaddition followed by fragmentation to afford the corresponding metal oxo complex is observed (eq 1). In sharp contrast, the titanocene vinylimido complexes, **5c** and **6**, do not yield *any* [Cp$_2$Ti=O]$_n$ in their reactions with acetone, even though formation of this very stable, oligomeric oxide could be expected to provide a strong driving force for the [2 + 2] reaction. Rather, **5c** and **6** react to give six-membered ring products in which the imido nitrogen is still attached to titanium.

Several possible reaction paths for these coupling reactions are suggested in Figure 5. Path A, direct insertion of nitrile (or ketone or imine) into the Ti–C bond of an intermediate azatitanacyclobutene, parallels reported reaction chemistry of titanacyclobutenes.[41,42] Alternatively, the vinylimido complex could condense directly with the reacting nitrile (or ketone or imine), perhaps through either a concerted or a stepwise [4 + 2] cycloaddition reaction (path B),[43] a reaction path resembling that proposed for

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[33] Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721–724.

[34] Binger, P.; Mueller, P.; Benn, R.; Mynott, R. *Angew. Chem.* **1989**, *101*, 647–648.

[35] Related but non-cyclopentadienyl containing zirconium complexes have also been proposed as reactive intermediates: Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731–8733.

[36] Wiberg, N.; Häring, H.-W.; Schubert, U. *Z. Naturforsch. B* **1980**, *35b*, 599–603.

[37] Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *J. Organomet. Chem.* **1984**, *270*, C49–C52.

[38] Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 7945–7952.

[39] Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642–1643.

[40] Lack of reactivity of the imido ligand with alkynes is not unique, however. For example, several tantalum imido complexes have been reported to coordinate alkynes to give imido complexes bearing alkyne ligands, but these coordinated alkynes do not appear to react further with the imido ligand itself. For example, see: Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3860–3868.

[41] Doxsee, K. M.; Mouser, J. K. M. *Organometallics* **1990**, *9*, 3012–3014.

[42] Meinhart, J. D.; Grubbs, R. H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 171–180.

[43] Though no such [4 + 2] cycloaddition reaction of a "metalladiene" has been firmly documented, we note recent reports that were reasonably proposed as possibly proceeding via such cycloadditions: (a) Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. P.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 1251–1253. (b) Xu, Y. C.; Challener, C. A.; Dragisich, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 792.

the coupling of nitriles by scandium, zirconium, and chromium alkyl complexes.[44,45] In the latter reaction sequences, the key coupling of the second nitrile appears to occur via what is essentially an enamine aldol-type condensation, chemistry that is not inconsistent with the apparently electron-rich vinyl group of the titanocene vinylimido complexes.

Conclusions

Reactions of nitriles with the titanocene methylidene complex in the presence of good donor ligands readily produce vinylimido complexes. These vinylimido complexes couple efficiently with unsaturated organic substrates (ketones, nitriles, and imines) to afford new metallacycles, formal [4 + 2] cycloadducts, which retain all the elements of the vinylimido ligand. In contrast to the reactivity of other reported imido complexes, no [2 + 2] cycloaddition products or complexes derived from such products have been observed.

Experimental Section

All manipulations of air- and/or moisture-sensitive compounds were performed using glovebox or standard Schlenk line techniques.[46] Argon used in Schlenk work was purified by passage through columns of BASF Catalyst R3-11 (regenerated by passage of 90% nitrogen and 10% hydrogen-forming gas) and 4-Å molecular sieves (Linde, activated in vacuo at 250 °C). Compounds were stored in a nitrogen-filled Vacuum Atmospheres glovebox equipped with an MO-40-1 purification Dri-Train. NMR spectra were recorded in dry, deoxygenated C_6D_6 or toluene-d_8 unless otherwise indicated. Chemical shifts are reported in parts per million (δ) referenced to residual protons or carbons of solvent. ^{31}P NMR data are referenced to external 85% H_3PO_4.

Glassware was dried by heating at 140 °C for at least 1 h and cooling to room temperature under vacuum or a flow of argon. All NMR samples were prepared in the drybox and capped with rubber septa or Teflon stopcocks and then flame sealed outside the drybox under nitrogen or vacuum.

Materials. Benzene, toluene, and diethyl ether were dried and deoxygenated over either sodium/benzophenone or NaK/benzophenone ketyl. Pentane was stirred over concentrated H_2SO_4, washed with H_2O, dried over CaH_2, and then dried and deoxygenated over either sodium/benzophenone or NaK/benzophenone ketyl, with ca. 1% tetraglyme present to solubilize the ketyl. Dried degassed solvents were vacuum transferred into dry glass vessels equipped with Teflon valve closures and stored under argon or, alternatively, kept in solvent stills under nitrogen. Benzene-d_6 and toluene-d_8 were dried, deoxygenated, and vacuum transferred from sodium/benzophenone ketyl. Deuterated solvents were stored in the glovebox.

$Cp_2TiCH_2{\cdot}Al(CH_3)_2Cl$ (Tebbe's reagent) and 1,1-bis(η^5-cyclopentadienyl)-3-*tert*-butyl-1-titanacyclobutane were prepared by reported procedures.[47] 4-(*N*,*N*-Dimethylamino)pyridine (DMAP, Aldrich) was recrystallized from toluene and dried under vacuum. Trimethylphosphine was kept in the glovebox and used as received (Aldrich) with no further purification. Pivalonitrile was dried over CaH_2, deoxygenated, and vacuum transferred. 1-Cyanoadamantane (Aldrich) was recrystallized from ethanol and dried under vacuum.

Formation of $Cp_2Ti{=}NC[C(CH_3)_3]{=}CH_2{\cdot}$Pyridine (5a). $Cp_2TiCH_2{\cdot}Al(CH_3)_2Cl$ (10 mg. 0.0351 mmol) was dissolved in 0.5 g of toluene-d_8. Pivalonitrile (3.90 μL, 0.0351 mmol) and pyridine (8.50 μL, 0.105 mmol) were added to this solution simultaneously. The NMR tube was then sealed under nitrogen, and the reaction was followed by NMR spectroscopy at room temperature. After 20 min, a 1:2 mixture of the vinylimido complex **5a** and untautomerized diaza complex **3** was observed. Isolation of pure **5a** from these reaction mixtures has not yet proved possible. ^1H NMR (toluene-d_8): δ 1.27 (s, 9 H, $(CH_3)_3C$), 3.55 (d, 1 H, $^2J_{HH}$ = 1.4 Hz, $=CH$), 4.08 (d, 1 H, $^2J_{HH}$ = 1.4 Hz, $=CH$), 5.90 (s, 10 H, Cp). The coordinated pyridine apparently exchanges with free pyridine and with pyridine$\cdot Al(CH_3)_2Cl$, resulting in exchange-broadened resonances at δ 8.4, 6.8, and 6.5; the $Al(CH_3)_2$ resonance appears at δ −0.218. Complex **3** ^1H NMR: δ 1.04 (s, 18 H, $(CH_3)_3C$), 3.01 (s, 2 H, CH_2), 5.64 (s, 10 H, Cp).[22]

Formation of $Cp_2Ti{=}NC[C(CH_3)_3]{=}CH_2{\cdot}$DMAP (5b). Substitution of DMAP for pyridine in the above procedure afforded a mixture of vinylimido complex **5b** and **3**. Isolation of pure **5b** from these reaction mixtures has not yet proved possible. ^1H NMR (C_6D_6): δ 1.37 (s, 9 H, $(CH_3)_3C$), 3.80 (d, 1 H, $^2J_{HH}$ = 1.8 Hz, $=CH$), 4.22 (d, 1 H, $^2J_{HH}$ = 1.8 Hz, $=CH$), 6.1 (s, 10 H, Cp). ^{13}C NMR (C_6D_6): δ 30.2 [$(CH_3)_3C$], 37.0 [$(CH_3)_3C$], 87.8 (t, $^1J_{CH}$ = 154 Hz, $=CH_2$), 110.1 (d, $^1J_{CH}$ = 169 Hz, Cp), 175.0 (s, CN). The coordinated DMAP apparently exchanges with free DMAP and with DMAP$\cdot Al(CH_3)_2Cl$, resulting in exchange-broadened resonances.

Preparation of $Cp_2Ti{=}NC[C(CH_3)_3]{=}CH_2{\cdot}P(CH_3)_3$ (5c) from $Cp_2TiCH_2{\cdot}Al(CH_3)_2Cl$. A solution of pivalonitrile (0.146 g, 1.76 mmol), DMAP (0.2146 g, 1.756 mmol), and trimethylphosphine (0.730 mL, 7.06 mmol) in 6 mL of benzene was added to a solution of $Cp_2TiCH_2{\cdot}Al(CH_3)_2Cl$ (0.500 g, 1.76 mmol) in 4 mL of benzene. The solution was stirred at room temperature for 4 h and then frozen in an ice–salt bath. Following the removal of solvent from the frozen sample in vacuo, the remaining solid was dissolved in pentane. This dark-red solution was cooled to −35 °C, filtered to remove the pale-colored DMAP–aluminum adduct, and evaporated under reduced pressure at −35 °C to afford **5c** as a dark-red solid in essentially quantitative yield. This material is ca. 90–95% pure, with the major contaminant being diazatitanacyclohexadiene complex **3**. Full characterization of **5c** is provided below. In small-scale reactions carried out in benzene-d_6 and followed by ^1H NMR spectroscopy, analysis after ca. 15 min of reaction time showed a mixture of vinylimido complex **5c** and the trimethylphosphine complex of $Cp_2Ti{=}CH_2$.[48] After an additional 3–6 h at room temperature, conversion to **5c** was complete.

Preparation of $Cp_2Ti{=}NC[C(CH_3)_3]{=}CH_2{\cdot}P(CH_3)_3$ (5c) from 1,1-Bis(η^5-cyclopentadienyl)-3-*tert*-butyl-1-titanacyclobutane. Trimethylphosphine (75 μL, 0.72 mmol) was added to a solution of the titanacyclobutane (50.0 mg, 0.181 mmol) and pivalonitrile (15.0 mg, 0.181 mmol) in 3 mL of benzene. This mixture was heated in a closed Schlenk tube at 55 °C for ca. 12 h, occasionally venting the tube to the argon manifold to prevent any pressure buildup. The dark-red solution was then frozen in an ice–salt bath, and all volatiles were removed in vacuo, affording a microcrystalline, dark-red solid (54 mg, 85%). ^1H NMR (C_6D_6): δ 0.93 (d, 9 H, $^2J_{PH}$ = 6.9 Hz, $P(CH_3)_3$), 1.22 (s, 9 H, $(CH_3)_3C$), 3.35 ("t", 1 H, $^2J_{HH}$ = 1.6 Hz, $^5J_{PH}$ = 1.0 Hz, $=CH$), 3.85 (d, 1 H, $^2J_{HH}$ = 1.6 Hz, $=CH$), 5.66 (d, 10 H, $^3J_{PH}$ = 2.4 Hz, Cp). $^1H\{^{31}P\}$NMR (C_6D_6): resonance at δ 3.35 collapses to doublet ($^2J_{HH}$ = 1.6 Hz), resonance at δ 5.66 collapses to singlet. ^{13}C NMR (C_6D_6): δ 17.2 (d of q, $^1J_{CH}$ = 129.4 Hz, $^1J_{CP}$ = 18.3 Hz, $P(CH_3)_3$), 30.2 (q, $^1J_{CH}$ = 125.2 Hz, $(CH_3)_3C$), 37.1 (d, $^4J_{CP}$ = 3.7 Hz, $(CH_3)_3C$), 84.3 (AMNX pattern, $^4J_{CP}$ = 4.9 Hz, $^1J_{CH1} \approx {}^1J_{CH2} \approx$ 155 Hz, $=CH_2$), 106.8 (d, $^1J_{CH}$ = 169.5 Hz, Cp), 174.2 (d, $^3J_{CP}$ = 1.7 Hz, CN). ^{31}P NMR (C_6D_6): δ −0.42. EI-MS (90 eV):[49] *m/e* 276 (48, M − PMe_3 + H), 219 (13, M − PMe_3 − ^tBu + H), 178 (100, Cp_2Ti), 113 (7, CpTi), 65 (C_5H_5), fragments for PMe_3 (76, 61, 59, 57, 45).[50] Prolonged heating of the sample in the inlet probe leads to volatilization of a new species that displays a cluster of ions around *m/e* 544; this may be the dimer ($[Cp_2Ti{=}NC^tBu{=}CH_2]_2$) expected to form[51] upon loss of trimethylphosphine from **5c**. None of this higher mass material is seen in the mass spectra obtained after shorter periods of heating, and we believe it is only formed upon pyrolysis of the sample in the mass spectrometer inlet port. Anal. Calcd for $C_{19}H_{30}NPTi$: C, 64.96; H, 8.61; N, 3.99. Found: C, 65.28; H, 8.31; N, 4.27.

Preparation of $Cp_2Ti{=}NC$(1-adamantyl)$=CH_2{\cdot}P(CH_3)_3$ (6) from 1,1-Bis(η^5-cyclopentadienyl)-3-*tert*-butyl-1-titanacyclobutane. Trimethylphosphine (0.632 mL, 6.10 mmol) was added to a solution of the titanacyclobutane (0.4219 g, 1.527 mmol) and 1-cyanoadamantane

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(44) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443–450.

(45) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 5868–5870.

(46) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley & Sons: New York, 1986. Also see: Gill, G. B.; Whiting, D. A. *Aldrichimica Acta* **1986**, *19*, 31–41.

(47) (a) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223–230. (b) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491–7496. (c) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658–1661. (d) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613. (e) Ott, K. C. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1982, pp 64–65.

(48) Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583–589.

(49) Although we have successfully recorded parent ions for a number of titanocene derivatives, metallocene derivatives frequently do not display parent ions. Production of zirconocene as the major fragmentation pathway of a zirconocene derivative has been reported: James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1967**, *6*, 1979–1983. Interestingly, titanocene (*m/e* 178) is the dominant fragment observed in the mass spectrum of **5c**. See also: Litzow, M. R.; Spalding, T. R. *Mass Spectrometry of Inorganic and Organometallic Compounds*; Elsevier: New York, 1973.

(50) This fragmentation pattern is consistent with that reported for trimethylphosphine: Wada, Y.; Kiser, R. W. *J. Phys. Chem.* **1964**, *68*, 2290–2295.

(51) Compare Bergman's zirconium imido complex,[30] which is monomeric when coordinated with tetrahydrofuran but dimeric when ligand-free.

(0.2462 g, 1.527 mmol) in 20 mL of benzene. The solution was heated in a closed Schlenk tube at 40 °C for ca. 23 h, occasionally venting the tube to the argon manifold to prevent any pressure buildup. The dark-red solution was then frozen in an ice–salt bath, and all volatiles were removed in vacuo, affording a microcrystalline, dark-red solid (0.5886 g, 90%). This product, which was stored at −30 °C, is 90–95% pure, with the major contaminant being the diazatitanacyclohexadiene complex corresponding to **3**. Full characterization of **6** is provided below.

Preparation of $Cp_2Ti{=}NC(\text{1-adamantyl}){=}CH_2{\cdot}P(CH_3)_3$ (6) from $Cp_2TiCH_2{\cdot}Al(CH_3)_2Cl$. To a solution of $Cp_2TiCH_2{\cdot}Al(CH_3)_2Cl$ (0.500 g, 1.76 mmol) in 3 mL of toluene was added a solution of DMAP (0.2146 g, 1.757 mmol), 1-cyanoadamantane (0.2833 g, 1.757 mmol), and trimethylphosphine (0.700 mL, 6.76 mmol) in 2 mL of toluene. The mixture was allowed to stand at room temperature for 4 h and then cooled at −78 °C overnight, precipitating **6** as a dark-red microcrystalline solid. ^1H NMR (C_6D_6): δ 0.95 (d. 9 H. $^2J_{PH}$ = 7.1 Hz, $P(CH_3)_3$), 1.7–2.1 (m, 15 H, adamantyl), 3.37 ("t", 1 H, $^2J_{HH}$ = 1.5 Hz, $^5J_{PH}$ = 1.1 Hz. ═CH), 3.79 (d, 1 H, $^2J_{HH}$ = 1.5 Hz, ═CH), 5.70 (d, 10 H, $^3J_{PH}$ = 2.4 Hz, Cp). ^{13}C NMR (C_6D_6): δ 16.8 (d of q, $^1J_{CH}$ = 135.2 Hz, $^1J_{CP}$ = 18.3 Hz, $P(CH_3)_3$), 29.6 (d, $^1J_{CH}$ = 131.8 Hz, adamantyl CH), 37.5 (d, $^4J_{CP}$ = 3.2 Hz, adamantyl quaternary C), 37.7 (t, $^1J_{CH}$ = 124.5 Hz, adamantyl CH_2), 41.9 (t, $^1J_{CH}$ = 125.5 Hz, adamantyl CH_2), 84.2 (AMNX pattern, $^4J_{CP}$ = 4.9 Hz, $^1J_{CH1} \approx {}^1J_{CH2} \approx$ 155 Hz, ═CH_2), 106.8 (d, $^1J_{CH}$ = 169.3 Hz, Cp), 174.9 (s, CN). ^{31}P NMR (C_6D_6): δ −0.86. EI-MS (90 eV): *m/e* 354 (51, M − PMe_3 + H), 219 (10, M − PMe_3 − adamantyl + H), 178 (100, Cp_2Ti), 135 (29, adamantyl), 113 (7, CpTi), 65 (C_5H_5), fragments for PMe_3 (76, 61, 59, 57, 45). Anal. Calcd for $C_{25}H_{36}NPTi$: C, 69.92: H, 8.45; N, 3.26. Found: C, 68.63; H, 8.08; N, 3.12.

Protonolysis of Complex 5c. Vinylimido complex **5c** (0.0800 g, 0.228 mmol) was dissolved in 2 mL of ether. The solution was cooled in an ice–salt bath and treated with excess dry HCl gas. Titanocene dichloride (43 mg, 76%) immediately precipitated from the solution. The mixture was stirred for 5 min at room temperature, opened to the air, quenched with 5 mL of H_2O, and filtered through a medium sintered-glass frit. The filtrate was neutralized with 10% aqueous NaOH and then extracted with ether. The aqueous solution was saturated with NaCl and then extracted twice with ether. The combined ether extracts (total 20 mL) were dried ($MgSO_4$) and then diluted with 4 mL of absolute ethanol. To this solution was added 4 mL of a stock (2,4-dinitrophenyl)hydrazine solution (3 g of (2,4-dinitrophenyl)hydrazine in 15 mL of concentrated H_2SO_4, 20 mL of H_2O, and 70 mL of 95% ethanol). The yellow solution was condensed to ca. 10 mL and then cooled to 0 °C, precipitating the yellow 2,4-DNP derivative of pinacolone (20 mg, 31%), mp 123.5–125.0 °C (ethanol, lit.[52] mp 125.0 °C). Spectral properties are identical with those for an authentic sample prepared as described below.

Pinacolone (2,4-Dinitrophenyl)hydrazone. Pinacolone (28.0 mg, 0.280 mmol) was dissolved in a mixture of 20 mL of ether and 4 mL of absolute ethanol. To this solution was added 4 mL of (2,4-dinitrophenyl)hydrazine solution (prepared as described above). The yellow solution was condensed and cooled to 0 °C. The bright-yellow solid (50 mg, 63%) that precipitated was isolated by filtration, mp 125.5–126.0 °C (lit.[51] mp 125.0 °C). ^1H NMR (C_6D_6): δ 0.95 (s, 9 H, $(CH_3)_3C$), 1.28 (s, 3 H, CH_3), 7.4 (d, 1 H, *J* = 9.6 Hz, ArH), 7.8 (dd, 1 H, *J* = 9.6, 2.5 Hz, ArH), 8.8 (d, 1 H, *J* = 2.5 Hz, ArH), 10.5 (br s, 1 H, NH). ^{13}C NMR (C_6D_6): δ 11.3 (CH_3), 27.4 [$(CH_3)_3C$], 39.0 [$(CH_3)_3C$], 116.0 (aromatic CH), 123.3 (aromatic CH), 129.3, 129.5 (aromatic CH), 137.9, 145.2, 162.3.

Protonolysis of Complex 6. Vinylimido complex **6** (0.100 g, 0.233 mmol) was dissolved in 4 mL of ether. The solution was cooled in an ice–salt bath and treated with excess dry HCl gas. Titanocene dichloride immediately precipitated from the solution. The mixture was stirred for 5 min at room temperature, opened to the air, quenched with 5 mL of H_2O, and filtered through a medium sintered-glass frit. The filtrate was neutralized with 10% aqueous NaOH and then extracted with ether. The aqueous solution was saturated with NaCl and then extracted twice with ether. The combined ether extracts (total 40 mL) were dried ($MgSO_4$) and evaporated, affording 1-acetyladamantane 0.026 g (63%) as a colorless, crystalline solid. Spectral properties were identical with those of an authentic sample obtained commercially (Aldrich).

Preparation of $Cp_2\overline{TiN{=}C[C(CH_3)_3]CH_2C(CH_3)_2O}$ (7a). Vinylimido complex **5c** (0.100 g, 0.285 mmol) was dissolved in 2.5 mL of benzene. Acetone (27.5 μL, 0.3745 mmol) was added to this solution, and the mixture was stirred at room temperature for 20 h. Removal of volatiles in vacuo afforded 0.079 g (83%) of **7a** as a dark-red solid. ^1H NMR (C_6D_6): δ 1.03 (s, 9 H, $C(CH_3)_3$), 1.10 (s, 6 H, $(CH_3)_2C$), 1.92 (s, 2 H, CH_2), 5.85 (s, 10 H, Cp). ^{13}C NMR (C_6D_6): δ 27.6 (q, $^1J_{CH}$ = 124.3 Hz, $C(CH_3)_3$), 30.3 (q, $^1J_{CH}$ = 126.1 Hz, $(CH_3)_2C$), 40.4 (s, $C(CH_3)_3$), 48.6 (t, $^1J_{CH}$ = 124.8 Hz, CH_2), 81.5 (s, CO), 113.8 (d, $^1J_{CH}$ = 172.2 Hz, Cp), 170.3 (s, C═N). EI-MS (90 eV): *m/e* 333 (11, M^+), 276 (25, M − acetone + H), 218 (74, M − acetone − ${}^tBu$), 194 (8, Cp_2TiO), 178 (100, Cp_2Ti), 139 (8, M − Cp_2TiO), 129 (35, CpTiO), 113 (26, CpTi), 82 (62, $N{=}C(CH_2)C(CH_3)_2$), 57 (18, ${}^tBu$). High-resolution EI-MS (90 eV): calcd for $C_{19}H_{27}NOTi$ 333.1572, found 333.1577.

Preparation of $Cp_2\overline{TiN{=}C(\text{1-adamantyl})CH_2C(CH_3)_2O}$ (7b). Vinylimido complex **6** (0.100 g, 0.233 mmol) was dissolved in 2.5 mL of benzene. Acetone (22.2 μL, 0.3027 mmol) was added to this solution, and the mixture was stirred at room temperature for 13 h. Removal of volatiles in vacuo afforded 0.0847 g (88.5%) of **7b** as a dark-red solid. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a diethyl ether solution of **7b**. ^1H NMR (C_6D_6): δ 1.12 (s, 6 H, $(CH_3)_2C$), 1.93 (s, 2 H, CH_2CO), 1.65–2.2 (m, 15 H, adamantyl), 5.87 (s, 10 H, Cp). ^{13}C NMR (C_6D_6): δ 30.4 (q, $^1J_{CH}$ = 125.0 Hz, $(CH_3)_2C$), 37.4 (t, $^1J_{CH}$ = 124.6 Hz, adamantyl CH_2), 40.0 (t, $^1J_{CH}$ = 126.0 Hz, adamantyl CH_2), 42.9 (s, adamantyl quaternary C), 47.5 (t, $^1J_{CH}$ = 124.5 Hz, CH_2CO), 81.3 (s, CO), 113.8 (d, $^1J_{CH}$ = 172.1 Hz, Cp), 171.1 (s, C═N), (tertiary adamantyl resonance not resolved). EI-MS (90 eV): *m/e* 411 (13, M^+), 354 (18, M − acetone + H), 218 (34, M − acetone − adamantyl), 217 (56, M − Cp_2TiO), 194 (8, Cp_2TiO), 178 (100, Cp_2Ti), 135 (57, adamantyl), 129 (24, CpTiO), 113 (19, CpTi), 82 (32, $N{=}C(CH_2)C(CH_3)_2$). High-resolution EI-MS (90 eV): calcd for $C_{25}H_{33}NOTi$ 411.2041, found 411.2050.

X-ray Analysis of $Cp_2\overline{TiN{=}C(\text{1-adamantyl})CH_2C(CH_3)_2O}$ (7b). Crystal data are presented in Table I. Data were collected at 130 K on a Siemens R3m/V diffractometer using Mo Kα radiation (λ = 0.71073 Å) with a highly oriented graphite crystal monochromator for 2θ = 0.0–45.0°, using a constant ω scan speed of 58.6° min^{-1} and an ω scan range of 1.00° over the index ranges $0 \le h \le 12$, $-14 \le k \le 13$, $-16 \le l \le 16$, giving 5568 independent reflections [2148 reflections with $I \ge 3\sigma(I)$]. Background measurements were performed with a stationary crystal and a stationary counter at ±1.00° offsets from peak, each for 50.0% of the total scan time. Two standard reflections were measured every 198 reflections. Solution and refinement details are summarized in Table II. Two molecules of the complex make up the asymmetric unit. Final atomic coordinates and equivalent isotropic displacement coefficients are presented in Table III, and representative bond lengths and angles are presented in Tables IV and V. Anisotropic displacement coefficients for the two titanium atoms in the asymmetric unit, hydrogen atom coordinates and isotropic displacement coefficients, and observed and calculated structure factors are provided in the supplementary material.

Protonolysis of Complex 7a. Complex **7a** (0.0398 g, 0.119 mmol) was dissolved in ca. 1 mL of benzene and treated with excess dry HCl gas. The resulting mixture was chromatographed through a short column of silica. Elution with 10% methanol in pentane afforded the β-keto enamine,[25] resulting from hydrolysis of a small amount of diazatitanacyclohexadiene **4** present as an impurity in the sample of **5c**. Elution with methanol then afforded the β-hydroxy ketone, **8a**.[53] ^1H NMR (C_6D_6): δ 0.80 (s, 9 H, $(CH_3)_3$), 1.18 (s, 6 H, $(CH_3)_2C$), 2.25 (s, 2 H, CH_2). On one occasion, the product isolated was the corresponding α,β-unsaturated ketone, resulting from dehydration of **8a**.[53] ^1H NMR (C_6D_6): δ 0.93 (s, 9 H, $(CH_3)_3$), 1.45 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 5.34 (s, 1 H, ═CH).

Protonolysis of Complex 7b. Analogous treatment of complex **7b** afforded a mixture of β-hydroxy ketone **8b** and the α,β-unsaturated ketone dehydration product. **8b** ^1H NMR (C_6D_6): δ 1.24 (s, 6 H, $(CH_3)_2C$), 1.5–1.9 (m, 15 H, adamantyl), 2.77 (s, 2 H, CH_2). α,β-Unsaturated ketone ^1H NMR (C_6D_6): δ 1.56 (s, 3 H, CH_3), 1.5–1.9 (m, 15 H, adamantyl), 2.15 (s, 3 H, CH_3), 5.74 (s, 1 H, ═CH).

Preparation of $Cp_2\overline{TiN{=}C[C(CH_3)_3]CH_2CHPhN}Ph$ (9a). Vinylimido complex **5c** (prepared from 30 mg of titanacyclobutane, as described above) was dissolved in ca. 0.5 g of C_6D_6. Benzylideneaniline (19.7 mg, 0.109 mmol) was added to this solution, which was then heated at 60 °C in a sealed NMR tube. The progress of the reaction was monitored by NMR spectroscopy. The reaction was complete in 14 days. Evaporation of volatiles afforded crude **9a** in quantitative yield. This material was dissolved in a minimum of toluene, layered with pentane, and cooled, affording **9a** as a dark-red powder. ^1H NMR (C_6D_6): δ 1.03 (s, 9 H, $(CH_3)_3C$), 2.0 (dd, 1 H, $^3J_{HH}$ = 4.0 Hz, $^2J_{HH}$ = 15.9 Hz, CH_2), 2.7 (dd, 1 H, $^3J_{HH}$ = 4.8 Hz, $^2J_{HH}$ = 15.9 Hz, CH_2), 5.0 ("t", 1 H,

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${}^3J_{\mathrm{apparent}}$ = 4.0 Hz, CHN), 5.55 (s, 5 H, Cp), 5.60 (s, 5 H, Cp), 6.6–7.2 (m, 10 H, ArH). ^{13}C NMR (C_6D_6): δ 27.7 (q, ${}^1J_{\mathrm{CH}}$ = 126.5 Hz, (CH$_3$)$_3$C), 39.8 (s, (CH$_3$)$_3$$C$), 40.4 (t, ${}^1J_{\mathrm{CH}}$ = 126.0 Hz, CH$_2$), 64.7 (d, ${}^1J_{\mathrm{CH}}$ = 131.3 Hz, CHN), 111.7 (d, ${}^1J_{\mathrm{CH}}$ = 173.2 Hz, Cp), 112.0 (d, ${}^1J_{\mathrm{CH}}$ = 173.0 Hz, Cp), 119.9 (d, ${}^1J_{\mathrm{CH}}$ = 153.2 Hz, Ar), 126.1*, 127.4*, 127.9*, 128.5*, 147.0 (s, Ar), 163.6 (s, Ar), 174.2 (s, C═N). (* = Ar, multiplicity not determined because of overlap with solvent resonances.) One aromatic carbon was not resolved (presumably because of overlap with solvent resonances). EI-MS (90 eV): *m/e* 456 (7, M$^+$), 359 (5, M – NC(^{t}Bu)CH$_2$), 276 (35, M – PhNCHPh + H), 181 (65, PhNCHPh), 178 (100, Cp$_2$Ti), 113 (18, CpTi), 77 (35), 65 (15), 57 (43, ^{t}Bu), 51 (20), 39 (22). High-resolution EI-MS (90 eV): calcd for $C_{29}H_{32}N_2Ti$ 456.2045, found 456.2040. Anal. Calcd for $C_{29}H_{32}N_2Ti$: C, 76.30; H, 7.07; N, 6.14. Found: C, 76.48; H, 7.01; N, 5.96.

Preparation of $\mathbf{Cp_2\overline{TiN{=}C(1\text{-}adamantyl)CH_2CHPhN}Ph}$ (9b). Vinylimido complex **6** (prepared from 30 mg of titanacyclobutane, as described above) was dissolved in ca. 0.5 g of C_6D_6. Benzylideneaniline (19.7 mg, 0.109 mmol) was added to this solution, which was then heated at 60 °C in a sealed NMR tube. The progress of the reaction was monitored by NMR spectroscopy. The reaction was complete in 14 days. Evaporation of volatiles afforded crude **9b** in quantitative yield. This material was dissolved in a minimum of benzene and layered with pentane, affording **9b** as a dark-red powder. ^{1}H NMR (C_6D_6): δ 1.6–2.1 (m, 16 H, adamantyl + half of CH$_2$), 2.75 (dd, 1 H, ${}^3J_{\mathrm{HH}}$ = 4.5 Hz, ${}^2J_{\mathrm{HH}}$ = 15.9 Hz, CH$_2$), 5.0 ("t", 1 H, ${}^3J_{\mathrm{apparent}}$ = 4.2 Hz, CHN), 5.59 (s, 5 H, Cp), 5.61 (s, 5 H, Cp), 6.6–7.2 (m, 10 H, ArH). ^{13}C NMR (C_6D_6): δ 28.8 (d, ${}^1J_{\mathrm{CH}}$ = 133.5 Hz, adamantyl CH), 37.0 (t, ${}^1J_{\mathrm{CH}}$ = 127.0 Hz, adamantyl CH$_2$), 39.2 (s, adamantyl), 40.0 (adamantyl CH$_2$ and CH$_2$ of **9b**), 64.2 (d, ${}^1J_{\mathrm{CH}}$ = 129.9 Hz, CHN), 111.6 (d, ${}^1J_{\mathrm{CH}}$ = 172.9 Hz, Cp), 112.0 (d, ${}^1J_{\mathrm{CH}}$ = 172.9 Hz, Cp), 119.7 (d, ${}^1J_{\mathrm{CH}}$ = 152.6 Hz, Ar), 126.2*, 127.4*, 127.9*, 128.6*, 147.0 (s, Ar), 163.8 (s, Ar), 174.7 (s, C═N). (* = Ar, multiplicity not determined because of overlap with solvent resonances.) One aromatic carbon was not resolved (presumably because of overlap with solvent resonances). EI-MS (90 eV): *m/e* 515 (60, M – 19), 354 (18), 178 (19, Cp$_2$Ti), 135 (15, adamantyl), 113 (13, CpTi), 93 (28), 77 (100), 65 (22), 55 (21), 51 (55), 39 (18). Anal. Calcd for $C_{35}H_{38}N_2Ti\cdot 0.5C_6H_6$: C, 79.56; H, 7.20; N, 4.88. Found: C, 79.38; H, 7.29; N, 5.30.

Formation of Complexes 3 and 4 from 5c. Vinylimido complex **5c** was generated in solution by the reaction of titanacyclobutane **1** (10.0 mg, 0.0362 mmol), pivalonitrile (3.00 mg, 0.0361 mmol), and trimethylphosphine (15.0 μL, 0.145 mmol) in 0.5 g of C_6D_6. Pivalonitrile (4.00 μL, 0.0362 mmol) was added to this solution, and the progress of the reaction was monitored by NMR spectroscopy. In the presence of excess trimethylphosphine, the reaction is very slow and no tautomerized diazatitanacyclohexadiene, complex **4**, is observed. Even after heating the reaction mixture for 3 days at 75 °C only a mixture of the vinylimido complex **5c** and the diazatitanacyclohexadiene complex **3** is observed. If the reaction of pivalonitrile with the vinylimido complex **5c** is carried out in the absence of excess phosphine, the vinylimido complex is converted to the untautomerized complex **3** in about 24 h at room temperature. This complex was converted to the tautomerized isomer, **4**, by continuous heating at 45 °C for 15 days. Complex **3** ^{1}H NMR (C_6D_6): δ 1.05 (s, 18 H, *t*-Bu), 3.01 (s, 2 H, CH$_2$), 5.67 (s, 10 H, Cp). ^{13}C NMR (C_6D_6): δ 28.53 (q, *J* = 125 Hz, CH$_3$), 40.20 (s, C-CH$_3$), 41.30 (t, *J* = 123 Hz, CH$_2$), 112.48 (d, *J* = 173 Hz, Cp), 165.0 (s, C═N). Complex **4** (mp 133–135.5 °C) ^{1}H NMR (C_6D_6): δ 1.02 (s, 9 H, *t*-Bu), 1.21 (s, 9 H, *t*-Bu), 4.86 (d, 1 H, *J* = 1.46 Hz, CH═), 5.70 (s, 10 H, Cp), 5.9 (br, 1 H, NH). ^{13}C NMR (C_6D_6): δ 29.51 (CH$_3$), 29.89 (CH$_3$), 37.10 (CCH$_3$), 37.64 (CCH$_3$), 87.70 (CH═), 110.99 (Cp), 175.02 (C═N or ═CN), 175.73 (═CN or C═N). IR (C_6H_6): ν 3371, 3314 cm^{-1} (NH). EI-MS M$^+$ 358 (relative intensity 18), Cp$_2$Ti$^+$ 178 (100). Anal. Calcd for $C_{21}H_{30}N_2Ti$: C, 70.38; H, 8.44; N, 7.82. Found: C, 68.68; H, 8.41; N, 6.98.

Crystallization of Complex 10. Vinylimido complex **6** was generated from titanacyclobutane **1** (30.0 mg, 0.109 mmol), 1-cyanoadamantane (17.5 mg, 0.109 mmol), and trimethylphosphine (60.0 μL, 0.580 mmol) in 0.5 g of C_6D_6. Cooling a saturated diethyl ether solution of this sample, which contained ca. 15% **10**, to −35 °C afforded crystals of complex **10** suitable for X-ray crystallographic analysis. ^{1}H NMR: δ 1.6–2.1 (m, 30 H, adamantyl), 2.99 (s, 2 H, CH$_2$), 5.71 (s, 10 H, Cp). ^{13}C NMR: δ 33.7, 37.5, 40.4, 41.0 (adamantyl), 42.7 (CH$_2$), 112.6 (d, J_{CH} = 172.4 Hz, Cp), 165.6 (s, C═N). High-resolution EI-MS (90 eV): calcd for $C_{29}H_{32}N_2Ti$ 514.2827, found 514.2804. Anal. Calcd for $C_{33}H_{42}N_2Ti$: C, 77.02; H, 8.23; N, 5.44. Found: C, 76.96; H, 8.39; N, 5.12.

X-ray Analysis of 10. Crystal data are presented in Table I. Data were collected at 130 K on a Siemens R3m/V diffractometer using Mo Kα radiation (λ = 0.71073 Å) with a highly oriented graphite crystal monochromator for 2θ = 0.0–46.0°, using a constant ω scan speed of 58.6° min^{-1} and an ω scan range of 1.00° over the index ranges $0 \le h \le 12$, $-17 \le k \le 1$, $-18 \le l \le 18$, giving 8997 independent reflections [4569 reflections with $I \ge 3\sigma(I)$]. Background measurements were performed with a stationary crystal and a stationary counter at ±1.00° offsets from peak, each for 50.0% of the total scan time. Two standard reflections were measured every 198 reflections. Solution and refinement details are summarized in Table VI. Two molecules of the complex make up the asymmetric unit. Final atomic coordinates and equivalent isotropic displacement coefficients are presented in Table VII, and representative bond lengths and angles are presented in Tables VIII and IX. Anisotropic displacement coefficients, hydrogen atom coordinates and isotropic displacement coefficients, and observed and calculated structure factors are provided in the supplementary material.

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Supplementary Material Available: Tables of positional parameters for hydrogen atoms and thermal parameters for **7b** and **10** (10 pages); tables of observed and calculated structure factors for **7b** and **10** (41 pages). Ordering information is given on any current masthead page.