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Cycloaddition Reactions of the Titanium Imide $[Ti(NBu^t)\{MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}(py)]$ with Bu^tCP and MeCN

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The diamidopyridine-supported titanium imide $[Ti(NBu^t)(L)(py)]$ [**1**, L = $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$] undergoes a [2+2] cycloaddition reaction with Bu^tCP to form the mononuclear product $[Ti\{N(Bu^t)PC(Bu^t)\}(L)]$ (**2**). In contrast, reaction of **1** with MeCN affords the binuclear derivative $[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2]$ (**3**), which contains a doubly deprotonated *N-tert*-butylacetamidinate ligand. Compound **3** undergoes a quantitative cycloreversion reaction at elevated temperatures yielding MeCN and $[Ti(NBu^t)(L)]$ (**4**).

Introduction

One of the main stimuli in the study of transition metal imido compounds $[M(NR)L_n]$ (R typically is an alkyl or aryl substituent; L_n represents a supporting ligand set) is the reactivity of the M═NR linkage itself, toward organic substrates.[1] (Although for ease of representation we have shown metal−imido linkages as "M═NR", the formal M−N bond order in many complexes $[M(NR)(L_n)]$ is generally best thought of as three (pseudo-σ^2 π^4 triple bond) rather than as two.[1]) Work by Bergman, Wolczanski, and others has established that group 4 compounds in particular may have very reactive imido groups that can activate sp^3- and sp^2-hybridized C−H bonds[2] as well as undergo coupling reactions with, for example, alkenes,[2c,3] allenes,[4] alkynes,[3,5] imines,[6] isocyanides,[7] isocycanates, carbodiimides, and CO_2.[8]

As part of an ongoing study of early transition metal amide[9] and imide[10] chemistry we described the diamidopyridine-supported titanium imide $[Ti(NBu^t)(L)(py)]$ [**1**, L = $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$], which also possesses a reactive Ti═NBu^t linkage that undergoes a number of the reactions mentioned above.[4,7] In this contribution we report the reactions of **1** with the phosphaalkyne Bu^tCP and with MeCN.[11,12] Despite the well-established reactivity of metal imides with alkynes, corresponding reactions with the phosphaalkyne RCP and nitrile RCN analogues have received very little attention. There are only two reports[13] of the reaction of imides with RCP substrates, and only in one report has a metal-containing product been isolated.[13b] No coupling reactions of "simple" metal imides $[M(NR)L_n]$ (i.e., where R = alkyl or aryl) with nitriles have yet been described, although the *vinyl*imides $[TiCp_2\{NC({=}CH_2)R\}(PMe_3)]$ (R = Bu^t, adamantyl) couple with RCN (R = Bu^t, adamantyl) via *both* the imido *and* pendant vinyl functionalities to form 1,3-diazatitanacyclohexadiene

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products $[TiCp_2\{NC(Bu^t)C(H)C(Bu^t)N(H)\}]$ in which the imide *and* conjugated vinyl moiety have been activated by RCN.[14]

Experimental Section

General Methods and Instrumentation. General methods for the purification of solvents, manipulation and characterization of air-sensitive compounds, and instrumentation used in our laboratories have been described previously.[15−17]

Literature Preparations. The compounds $[Ti(NBu^t)(L)(py)]$ (**1**) and Bu^tCP were prepared according to previously described methods.[7,18,19]

$[Ti\{N(Bu^t)PC(Bu^t)\}(L)]$ (2). To a stirred solution of $[Ti(NBu^t)(L)(py)]$ (0.276 g, 0.65 mmol) in toluene (15 mL) was added Bu^tCP (0.130 g, 1.3 mmol) dropwise. Upon addition, the yellow reaction mixture turned orange and was stirred for 24 h. Removal of the solvent under reduced pressure and recrystallization of the resulting orange residue from hexanes yielded orange crystals of **2**. Yield: 0.202 g, (49%).

Crystals suitable for X-ray analysis were grown from a slowly cooled and concentrated hexane solution at −45 °C. The following NMR assignments have the $C(Me)(CH_2NSiMe_3)_2$ substituent of the pyridyl ring in the 2-position. ^1H NMR (C_6D_6, 300.1 MHz): 8.50 (1 H, br d, H^6), 7.24 (1 H, m, H^4), 7.12 (1 H, m, H^3), 6.61 (1 H, m, H^5), 4.47 (2 H, m, CH_aH_b), 4.18 (2 H, m, CH_aH_b), 1.64 (3 H, s, NC_5H_4CMe), 1.44 (9 H, s, NBu^t), 1.32 (9 H, d, $^4J_{PH} = 3.4$, PBu^t), 0.02 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): 166.2 (C^2), 149.2 (C^6), 135.5 (C^4), 122.0 (C^5), 121.0 (C^3), 62.8 (CH_2), 61.4 (d, $^2J_{PC} = 11.0$, $NCMe_3$), 53.3 ($C(CH_2NSiMe_3)_2$), 43.3 (d, $^2J_{PC} = 15.36$, $PCCMe_3$), 34.7 (d, $^3J_{PC} = 12$, $PCCMe_{3,}$ Hz), 34.4 (d, $^3J_{PC} = 7.6$, $NCMe_3$), 25.2 (Me of L), 1.5 ($SiMe_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): 201.2. EI-MS: m/z (%) 526 (10) $[M]^+$, 426 (23) $[M - (PCBu^t)]^+$, 411 (100) $[M - (PCBu^t) - (Me)]$. Anal. Found (calcd for $C_{24}H_{47}N_4PSi_2Ti$): C, 54.1 (54.7); H, 9.1 (9.0); N, 10.5 (10.6).

$[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2]$ (3). To a solution of $[Ti(NBu^t)(L)(py)]$ (300 mg, 0.59 mmol) in benzene (5 mL) at room temperature was added MeCN (35 mg, 45 μL, 0.86 mmol). The solution was heated to 45 °C for 17 h, after which all volatiles were removed under reduced pressure. The resulting yellow solid (**3**) was washed with pentane (2 × 3 mL) and dried in vacuo. Yield: 205 mg (74%).

Yellow crystals of **3** suitable for X-ray diffraction were obtained from a saturated pentane solution at 5 °C over a period of 48 h. NMR assignments refer to the labeling scheme given below and were made using 1- and 2-D homo- and heteronuclear correlation and NOE spectroscopies.

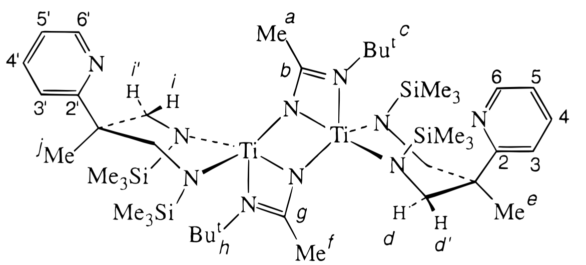

Table 1. X-ray Data Collection and Processing Parameters for $[Ti\{N(Bu^t)PC(Bu^t)\}(L)]$ (2) and $[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2]$ (3)

	2	3
empirical formula	$C_{24}H_{47}N_4PSi_2Ti$	$C_{42}H_{82}N_{10}Si_4Ti_2$
fw	536.7	935.34
temp/°C	−100(2)	−50(2)
crysta descrip	orange block	yellow block
cryst dimens/mm	0.30 × 0.30 × 0.20	0.44 × 0.26 × 0.24
wavelength/Å	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a/Å	10.1495(12)	10.555(3)
b/Å	10.325(2)	27.615(4)
c/Å	14.487(3)	18.551(8)
α/deg	84.292(16)	
β/deg	86.632(12)	103.23(3)
γ/deg	83.411(14)	
V/Å^3	1498.9(5)	5264(3)
Z	2	4
d(calcd)/Mg m^{-3}	1.17	1.180
abs coeff/mm^{-1}	0.440	0.432
total no. of reflns	5268	8110
no. of unique reflns	5268	6442
R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.036$, $wR_2 = 0.084$	$R_1 = 0.0654$, $wR_2 = 0.1353$
R indices (all data)	$R_1 = 0.047$, $wR_2 = 0.089$	$R_1 = 0.1260$, $wR_2 = 0.1787$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w\,(F_o^2 - F_c^2)^2/\Sigma(w(F_o^2)^2\}^{1/2}$.

^1H NMR (C_6D_6, 500.0 MHz): 8.50, (2 × 1 H, 2 × overlapping d, H^6 & $H^{6'}$), 7.26, (2 × 1 H, 2 × overlapping d, H^3 & $H^{3'}$), 7.11, (2 × 1 H, 2 × overlapping m, H^4 & $H^{4'}$), 6.60, (2 × 1 H, 2 × overlapping m, H^5 & $H^{5'}$), 4.95, (2 H, d, $^2J = 13.5$, H^i), 4.37, (2 H, d, $^2J = 14.0$, $H^{d'}$), 4.21, (2 H, d, $^2J = 14.0$, H^d), 3.30, (2 H, d, $^2J = 13.5$, $H^{i'}$), 2.49, (3 H, s, Me^a), 2.30, (3 H, s, Me^f), 1.63, (3 H, s, Me^j), 1.52, (9 H, s, $^tBu^h$), 1.34, (3 H, s, Me^e), 1.07, (9 H, s, $^tBu^c$), 0.35, (36 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) (C_6D_6, 125.7 MHz, 298 K): 184.0, 183.7 (C^b & C^g), 167.8, 166.1 (C^2 & $C^{2'}$), 149.1, 149.0 (C^6 & $C^{6'}$), 136.0, 135.4 (C^4 & $C^{4'}$), 122.2, 121.0, 120.9, 120.6 ($C,^5$ $C^{5'}$, C^3 & $C^{3'}$), 64.8 ($CH_2{}^i$), 62.3 ($CH_2{}^d$), 52.8, 52.6, 52.5, 52.4 (CMe_3 of $^tBu^c$, CMe_3 of $^tBu^h$, CMe^e, CMe^j), 32.7 (Me of $^tBu^h$), 32.2 (Me of $^tBu^c$), 28.9 (Me^e), 27.0 (Me^a), 26.6 (Me^f), 21.5 (Me^j), 2.1 ($SiMe_3$), 2.0 ($SiMe_3$). IR (NaCl plates, Nujol, cm^{-1}): 1631 (w), 1589 (m), 1571 (w), 1347 (w), 1246 (s), 1199 (s), 1152 (w), 1078 (w), 1047 (m), 1023 (s), 996 (m), 953 (w), 919 (m), 901 (w), 848 (s), 785 (w), 773 (w), 723 (w), 688 (w), 667 (w), 632 (m), 613 (m), 585 (w), 556 (w), 523 (w), 510 (w), 463 (w). Anal. Found (calcd for $C_{42}H_{82}N_{10}Si_4Ti_2$): C, 53.9 (53.9); H, 8.8 (8.8); N, 14.5 (15.0).

Cycloreversion Reaction of $[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2]$ (3). $[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2]$ (**3**) was heated in a sublimation tube at 155 °C and 1 × 10^{-6} mbar (dynamic vacuum) over 4 h. The sublimate $[Ti(NBu^t)(L)]$ (**4**) was identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[20] Yield of **4**: 90%. In a separate experiment a pure sample of **3** was heated at 180 °C under a dynamic vacuum of 1 × 10^{-2} mbar. In-line monitoring (mass spectrometry) of the volatiles produced showed the formation of MeCN.

Crystal Structure Determination of $[Ti\{N(Bu^t)PC(Bu^t)\}(L)]$ (2) and $[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2]$ (3). Crystal data collection and processing parameters are given in Table 1. For both **2** and **3** crystals were mounted in an inert oil and cooled in a cold N_2 gas stream. Diffraction data were collected using monochromated Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer for **2** and on a Siemens P4 four-circle diffractometer for **3**. Lorentz−polarization and absorption corrections based on ψ-scans were applied to the data. The positions of the non-hydrogen atoms were located by direct methods and subsequent Fourier-difference syntheses. Refine-

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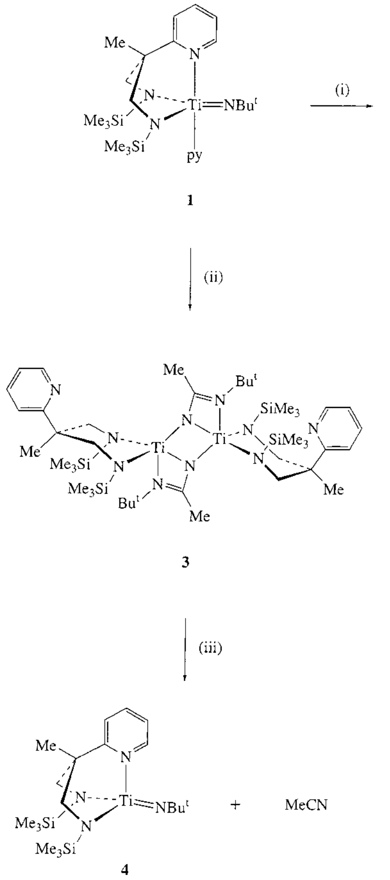
Scheme 1[a]



[a] Reagents and conditions: (i) Bu^{t}CP (2 equiv), toluene, rt, 24 h, 49%; (ii) MeCN (1.5 equiv), benzene, 45 °C, 17 h, 74%; (iii) 155−185 °C, 1 × 10^{-6} mbar, 4 h, 90%.

ment was based on F^2 using SHELXL-97 for **2** and SHELXTL for **3**.[21] Hydrogen atoms were placed in calculated positions. Non-hydrogen atoms were assigned anisotropic displacement parameters in the final cycles of full-matrix least-squares refinement.[21]

A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Results and Discussion

We have described the synthesis of [Ti(NBu^t)(L)(py)] [**1**, L = MeC(2-C_5H_4N)(CH_2NSiMe_3)$_2$] previously.[7] The new reactions are summarized in Scheme 1.

Reaction with Bu^{t}CP. [Ti(NBu^t)(L)(py)] (**1**) was treated with 1 equiv of Bu^{t}CP in toluene at room temperature. Removal of the volatiles after 12 h and recrystallization of the residue from hexanes yielded [Ti{N(Bu^t)PC(Bu^t)}(L)] (**2**) as an orange microcrystalline product. The molecular structure is shown in Figure 1; selected bond lengths and angles are listed in Table 2.

The compound [Ti{N(Bu^t)PC(Bu^t)}(L)] (**2**) possesses a distorted tetrahedral titanium center (angles at titanium in the range 83.47(8)−121.15(18)°) and features a planar four-membered metallacycle {Ti−N(1)−P−C(1)} (sum of the internal angles = 359.9°). The Ti−N and Ti−C distances are within the ranges expected for single bonds (the Ti−N bonds may be augmented by N(p_π)→Ti(d_π) interactions from the near-planar N atoms),[22] whereas the P−C(1) bond length of 1.688(2) Å lies within the range expected for a P=C double bond.[23] These features are consistent with the localized bonding description for **2** shown in Scheme 1. The N(1)−P and P−C(1) distances and associated angles are comparable to those found in the related zirconocene compound [ZrCp$_2${N(Ar)PC(Bu^t)}].[13b]

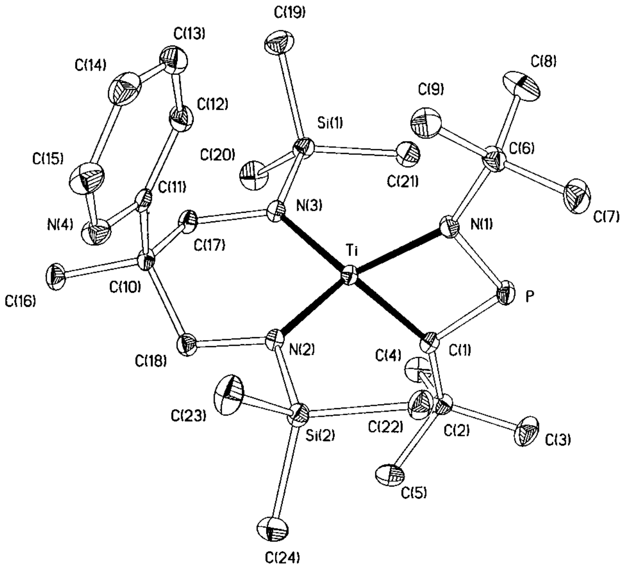


Figure 1. Displacement ellipsoid plot of [Ti{N(Bu^t)PC-(Bu^t)}(L)] (**2**). Hydrogen atoms are omitted, and displacement ellipsoids are drawn at the 35% probability level.

Table 2. Selected Distances (Å) and Angles (deg) for [Ti{N(Bu^t)PC(Bu^t)}(L)] (2)

Distances			
Ti−N(1)	1.908(2)	Ti−N(2)	1.905(2)
Ti−N(3)	1.916(2)	Ti−C(1)	2.029(2)
Ti−P	2.561(1)	P−C(1)	1.688(2)
P−N(1)	1.725(2)		
Bond Angles			
N(2)−Ti−N(1)	118.78(8)	N(2)−Ti−N(3)	101.99(7)
N(1)−Ti−N(3)	121.15(8)	N(2)−Ti−C(1)	114.01(8)
N(1)−Ti−C(1)	83.47(8)	N(3)−Ti−C(1)	117.80(8)
N(2)−Ti−P	126.40(6)	N(1)−Ti−P	42.33(5)
N(3)−Ti−P	131.27(6)	C(1)−Ti−P	41.14(6)
C(1)−P−N(1)	100.43(10	C(1)−P−Ti	52.28(7)
N(1)−P−Ti	48.15(6)		

Figure 1 shows also that the pyridyl fragment is not coordinated to the metal center. This is the first structurally characterized example of the ligand L having bidentate coordination, although this mode has been inferred from ^{1}H NMR spectra in, for example, [Ti(L)(CH_2SiMe_3)$_2$].[19] The titanium center possesses a valence electron count of between 8 and 14 (depending on the extent of N(p_π)→Ti(d_π) lone pair donation), and in this regard it is surprising that the pyridyl moiety is not coordinated. However, such low electron counts are not uncommon in titanium chemistry, and, presumably, the steric crowding around titanium inhibits pyridyl

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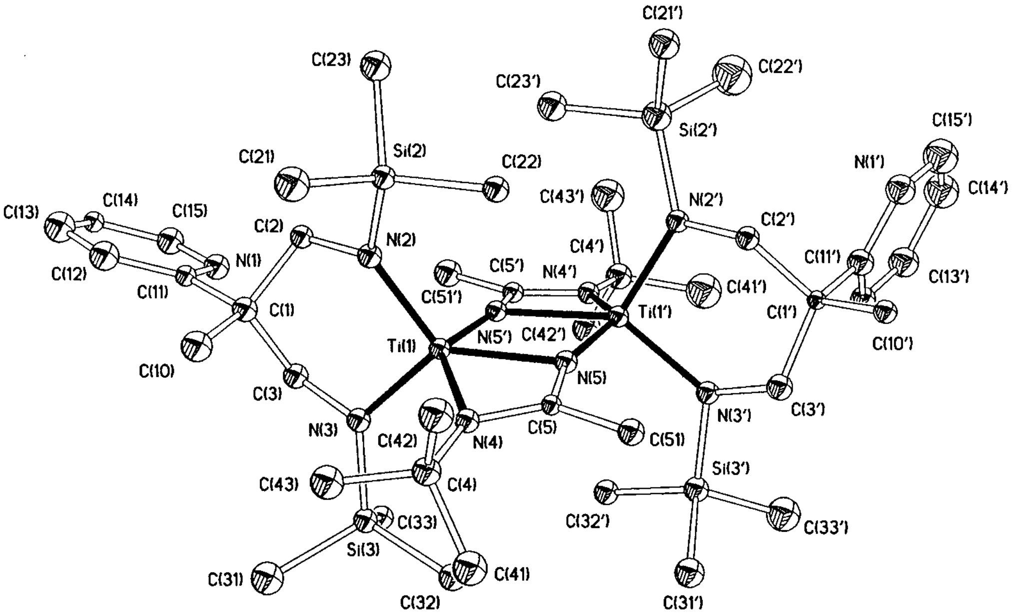


Figure 2. Displacement ellipsoid plot of [$Ti_2\{\mu$-η^2-NC(Me)NBu$^t\}_2$(L)$_2$] (**3**). Hydrogen atoms are omitted, and displacement ellipsoids are drawn at the 20% probability level.

coordination. In addition the Ti−P distance of 2.561(1) Å is well within range for bonding, and compensation of the electronic unsaturation by interaction of the phosphorus lone pair with titanium cannot be disregarded.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data for **2** in C_6D_6 imply that the solid state structure is maintained in solution. The pyridyl group ortho-hydrogen appears as a multiplet at δ 8.50 in the ^{1}H NMR spectrum. This shift is comparable to that of the parent proligand H_2L (δ 8.47) in the same solvent.[19] The EI mass spectrum of **2** features a molecular ion the isotopic distribution of which is consistent with the expected formula.

The compound [Ti{N(Bu^t)PC(Bu^t)}(L)] (**2**) presumably forms via a [2+2] phosphaalkyne-imide cycloaddition reaction. That the phosphorus is bonded to the nitrogen of the imide function (as opposed to titanium) is consistent with the bond polarity of the individual unsaturated reactive sites. This orientation may also be due both to steric repulsion between the imide and phosphaalkyne *tert*-butyl groups and to the preference of titanium to bond to the harder carbon rather than to the softer phosphorus atom. Analogous [2+2] modes of addition were very recently found for transient [ZrCp$_2$(NR)] (R = Bu^t or 2,6-$C_6H_3Pr^i_2$) with Bu^{t}CP.[13b] Furthermore, we have previously found that certain titanium imides, namely, [Ti(NBu^t)Cl$_2$(py)$_3$] and [Ti(NBu^t)(η^8-C_8H_8)], react with 2 equiv of Bu^{t}CP to form 1:2 (Ti:Bu^{t}CP) addition products containing an η^5-Bu^{t}NP(CBu^t)$_2$P ligand that possesses a P_2C_2 ring.[13b] The compound **2**, however, does not react further with an excess of Bu^{t}CP.

Reaction with MeCN. The successful reaction of [Ti(NBu^t)(L)(py)] (**1**) with Bu^{t}CP prompted us to examine its reactions with nitriles. Addition of 1.5 equiv of MeCN to **1** in benzene at room temperature and heating to 45 °C overnight afforded [$Ti_2\{\mu$-η^2-NC(Me)NBu$^t\}_2$(L)$_2$] (**3**) as a bright yellow solid in good yield (see Scheme 1). Titration of an NMR sample of **1** in C_6D_6 with MeCN showed that the reaction proceeds in a 1:1 ratio only.

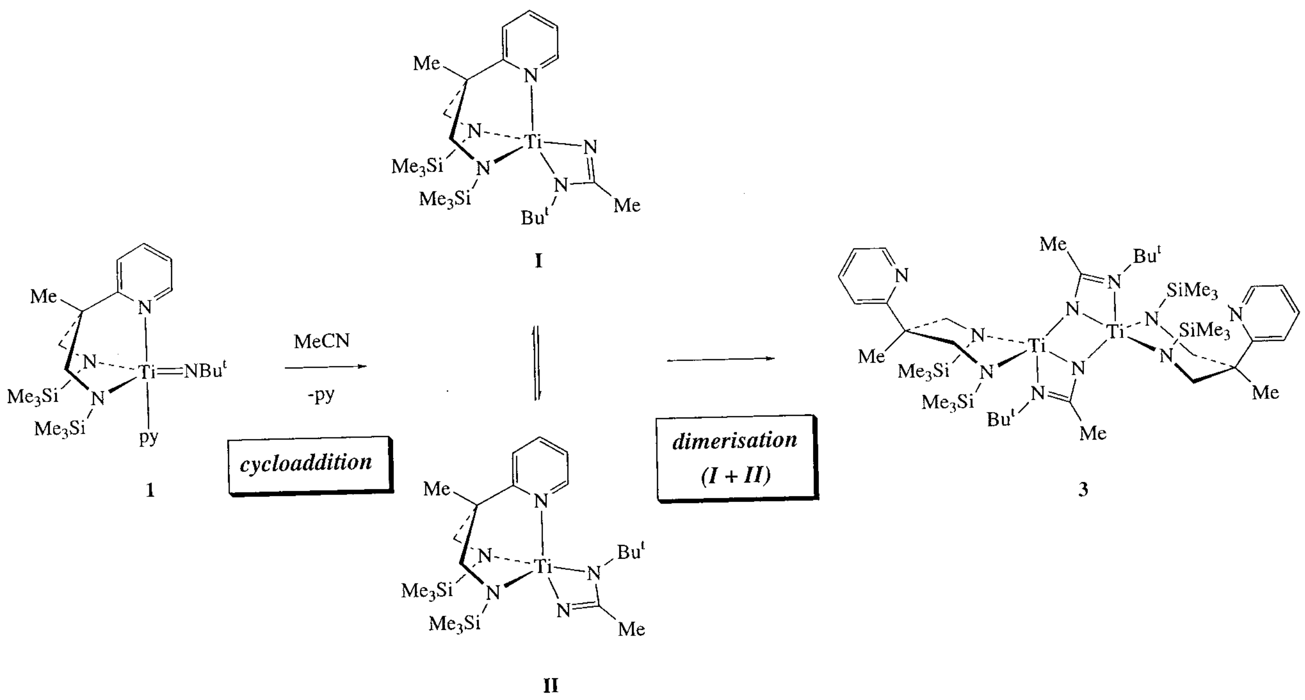
Table 3. Selected Distances (Å) and Angles (deg) for [$Ti_2\{\mu$-η^2-NC(Me)NBu$^t\}_2$(L)$_2$] (3)

Distances			
Ti(1)···Ti(1′)	3.0924(17)	Ti(1′) − N(2′)	1.897(5)
Ti(1)−N(2)	1.904(5)	Ti(1′)−N(3′)	1.928(5)
Ti(1)−N(3)	1.912(5)	Ti(1′)−N(4′)	2.213(5)
Ti(1)−N(4)	2.247(5)	Ti(1′)−N(5′)	2.074(5)
Ti(1)−N(5)	2.062(5)	Ti(1′)−N(5)	1.944(5)
Ti(1)−N(5′)	1.939(5)	N(4′)−C(5′)	1.320(8)
N(4)−C(5)	1.308(8)	N(5′)−C(5′)	1.329(8)
N(5)−C(5)	1.345(8)	Ti(1′)−N(2′)	1.897(5)
Bond Angles			
N(4)−Ti(1)−N(2)	103.4(2)	N(4′)−Ti(1′)−N(2′)	105.1(2)
N(4)−Ti(1)−N(3)	100.3(2)	N(4′)−Ti(1′)−N(3′)	101.6(2)
N(4)−Ti(1)−N(5)	62.1(2)	N(4′)−Ti(1′)−N(5′)	62.4(2)
N(4)−Ti(1)−N(5′)	140.3(2)	N(4′)−Ti(1′)−N(5)	139.6(2)
N(5)−Ti(1)−N(2)	122.6(2)	N(5′)−Ti(1′)−N(2′)	121.5(2)
N(5)−Ti(1)−N(3)	135.1(2)	N(5′)−Ti(1′)−N(3′)	137.4(2)
N(5)−Ti(1)−N(5′)	79.2(2)	N(5′)−Ti(1′)−N(5)	78.8(2)
N(2)−Ti(1)−N(3)	101.0(2)	N(2′)−Ti(1′)−N(3′)	100.3(2)
Ti(1)−N(4)−C(5)	88.3(4)	Ti(1′)−N(4′)−C(5′)	88.6(4)
Ti(1)−N(5)−C(5)	95.4(4)	Ti(1′)−N(5′)−C(5′)	94.4(4)
N(4)−C(5)−N(5)	114.2(6)	N(4′)−C(5′)−N(5′)	114.3(6)
Ti(1)−N(5)−Ti(1′)	101.0(2)	Ti(1)−N(5′)−Ti(1′)	100.7(2)

Extended heating of **3** in the presence of an excess of MeCN at 45 °C failed to promote any further reaction, although heating to temperatures of 60 °C or higher caused decomposition to an unidentified mixture of products over several hours. In contrast, the compound **1** does not react with EtCN or Bu^{t}CN at 80 °C in C_6D_6, but does react slowly with 3 equiv of TolCN (Tol = *p*-tolyl) under the same conditions to form a mixture of at least three products after 2 weeks. This reaction was not pursued on a preparative scale.

The molecular structure of [$Ti_2\{\mu$-η^2-NC(Me)NBu$^t\}_2$(L)$_2$] (**3**) is shown in Figure 2, and selected bond lengths and angles are listed in Table 3. Molecules of **3** comprise two Ti{μ-η^2-NC(Me)NBu^t}(L) fragments linked together via bridging nitrogen atoms N(5) and N(5′). As is the case for [Ti{N(Bu^t)PC(Bu^t)}(L)] (**2**) above, the pyridyl donors of the diamidopyridine ligands are detached from the metal center. The geometry about each titanium atom is at best described as a highly distorted trigonal

Scheme 2. Possible Mechanism for the Formation of [$Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2$] (3)



bipyramid. The "axial" sites are occupied by N(4) and N(5′) about Ti(1), and N(4′) and N(5) about Ti(1′), although the distortion from an ideal trigonal bipyramidal geometry is such that the angles subtended at titanium by the "axial" donors [N(4)−Ti(1)−N(5′) = 140.3(2)° and N(4′)−Ti(1′)−N(5) = 139.6(2)°] are considerably less than 180°. The titanium centers in **3** form part of a "bowed" ladder-type structural motif composed of three four-membered metallocyclic rings. The central ring is folded slightly about the nitrogen bridging atoms (dihedral angles between the TiN_2 planes 4.3°) and the best planes of the two outer rings. Ti(1), N(4) C(5), N(5) and Ti(1′), N(4′) C(5′), N(5′) are at dihedral angles of 7.7° and 10.0°, respectively, to the best plane through Ti_2N_2bridging atoms. The six-membered chelate rings formed by the two diamido ligands adopt chair conformations with the pairs of opposite atoms Ti(1) and C(1) and Ti(1′) and C(1′) lying on opposite sides of the best plane through the other four atoms of their ring [deviations: Ti(1), −0.677; C(1), 0.705; Ti(1′), −0.68; C(1′), 0.64 Å]. The two uncoordinated pyridyl groups of the diamido ligands occupy equatorial [N(1)−C(11)] and axial [(N(1′)−C(11′)] sites of the chelate ring. As a result, the pyridyl arms both lie on the same side of the molecule and so have a *syn* conformation with respect to the Ti(1)···Ti(1′) vector. The two Ti{μ-η^2-NC(Me)NBu^t}(L) fragments are therefore chemically inequivalent.

Examination of the bond lengths associated with the $Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2$ provides an insight into the nature of the bonding in this unit. The mean of the N(4)−C(5) and N(4′)−C(5′) bond lengths (i.e., 1.314(8) Å) is not significantly different from that of the N(5)−C(5) and N(5′)−C(5′) bond lengths (i.e., 1.332(8) Å) and so seems to be consistent with considerable delocalization of π-electron density across the N−C−N unit (cf. η^3-allyl systems). However, the mean Ti(1)−N(4) and Ti(1′)-N(4′) distance of 2.230(5) Å is considerably longer than the mean of the Ti(1)−N(5) and Ti(1′)−N(5′) values, namely, 2.068 Å. Since metal−carbon distances are generally better defined than distances between two light atoms, the data appear generally to support the valence bond interpretation of **3** shown in Scheme 1 in which N(5) and N(5′) are depicted as μ-imido (2−) donors and N(4) and N(4′) as imino (neutral) donors.

The compound **3** can therefore be viewed as a Lewis base adduct of the well-established class of complexes [$Ti_2(\mu\text{-}NR)_2X_4$] (X = amide or alkoxide).[24] The bridging nitrogens do not bind symmetrically to the two titanium centers (e.g., Ti(1)−N(5) = 2.062(5) Å, Ti(1)−N(5′) = 1.939(5) Å). This is perhaps not surprising given the unsymmetrical coordination environment, although we cannot rule out alternative or additional electronic origins. The μ-η^2-NC(Me)NBu^t moieties in **3** may be viewed as doubly deprotonated *N*-*tert*-butylacetamidinate ligands. N,N′-Disubstituted amidinates $RC(NR')_2$ are very well-established versatile, monoanionic ligands in main group-, transition-, and lanthanide-metal chemistry,[25] but a doubly deprotonated N-monosubstituted amidinate ligand has never before been structurally characterized.

The solution NMR data support the solid state structure, and a full assignment is given in the Experimental Section. The data reveal two chemically inequivalent NC(Me)NBu^t and L ligand environments consistent with the *syn* conformation revealed in the solid state. When the reaction between **1** and MeCN was followed by ^{1}H NMR spectroscopy, no evidence for an additional isomeric *anti* form or intermediates was found. The IR spectrum of **3** shows a band at 1631 cm^{-1} (not present in the IR spectrum of **1**) that is consistent with the presence of an imine-type functionality.

Scheme 2 gives a proposed mechanism for the formation of **3**. [Ti(NBu^t)(L)(py)] (**1**) most likely loses pyridine

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(24) See the following, and references therein: Collier, P. E.; Blake, A. J.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1997**, 2911.

(25) For leading references, see: Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403. Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219.

and undergoes a [2+2] cycloaddition to form initially an intermediate of the type **I** (with NBu^t approximately *trans* to the pyridyl nitrogen) or **II** (NBu^t *cis* to pyridyl). Although neither of these intermediates have been directly observed, we have previously isolated analogues of both **I** and **II** via cycloaddition reactions of **1**.[4,18] Thus reaction of **1** with allene gives $[Ti\{CH_2C(=CH_2)NBu^t\}(L)]$ with the NBu^t group approximately *trans* to pyridyl,[4] whereas reaction with ArNCO (Ar = 2,6-C_6H_3-Pr^i_2) gives the ureato product $[Ti\{OC(=NAr)NBu^t\}(L)(py)]$, which has NBu^t *cis* to pyridyl.[18] It is apparent that the MeCN molecule adds to the $Ti=NBu^t$ functionality in a “head-to-tail” manner, contrasting with the “head-to-head” addition of Bu^tCP. This is consistent with the differing polarities of the C≡P and C≡N functional groups in the two substrates and also avoids forming a thermodynamically less favorable N−N bond. Intermediates analogous to **I** and **II** have been proposed in the cycloaddition reactions of transient $[ZrCp_2(E)]$ (E = O or S) with BzCN (Bz = CH_2Ph).[26] In these reactions, however, proposed 1:1 adducts $[ZrCp_2\{NC(Bz)E\}]$ are not isolated but apparently insert a second BzCN into the Zr−N bond to form $[ZrCp_2\{NC(Bz)NC(Bz)E\}]$, which contains a six-membered metallacycle. As mentioned, even in the presence of an excess of MeCN, **1** forms only the dimeric, 1:1 product **3**.

We do not know which of the intermediates **I** and **II** is first formed, but we propose that (unless they are both initially formed in equal quantities) there is a rapid interconversion between the two. Recalling that the X-ray and NMR data show that $[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2]$ (**3**) forms exclusively with the pyridyl groups of each diamidopyridine in a *syn* conformation, it is clear that formation of **3** requires the dimerization of **I** with **II** (since **I** + **I** or **II** + **II** dimerizations would give an isomeric, C_2-symmetric form of **3** with the pyridyls in a mutually *anti* arrangement). The interconversion of **I** and **II** (which formally contain N-monosubstituted acetamidinate ligands) is reminiscent of the highly facile, apparent in-place rotation of N,N′-disubstituted amidinate ligands $RC(NR')_2$ in many of their metal complexes.[27] That **I** and **II** self-trap by dimerization rather than inserting a further MeCN can be attributed to the highly basic and nucleophilic nature of the metallaimino nitrogens. The requirement for a **I** + **II** dimerization is most probably attributable to steric factors.

Cycloreversion Reaction of $[Ti_2\{\mu\text{-}\eta^2\text{-}NC(Me)NBu^t\}_2(L)_2]$ (3). Attempted high-vacuum sublimation of **3** (1×10^{-6} mbar, 155 °C) led to the formation of the pyridine-free imide $[Ti(NBu^t)(L)]$ (**4**) as an orange sublimate in 90% yield (Scheme 1). The compound **4** was characterized by comparison of its ^1H NMR spectrum with that of an authentic sample.[20] In a separate experiment a pure sample of **3** was heated at 180 °C under a dynamic vacuum (1×10^{-2} mbar). In-line monitoring (mass spectrometry) of the volatiles produced showed the formation of MeCN. To establish whether **3** undergoes a detectable cycloreversion reaction in the solution phase (i.e., transiently forming MeCN and **4** or its MeCN adduct), a sample of **3** in C_6D_6 was heated at 60 °C in the presence of CD_3CN. After several days no incorporation of CD_3CN into **3** was observed. Prolonged heating of the sample or heating at elevated temperatures led to the formation of unknown decomposition products. The cycloreversion reaction of **3** has no precedent in organonitrile reaction chemistry, but group 4 imides in general are known to undergo reversible cycloaddition with other unsaturated substrates such as alkenes, alkynes, and imines.[2,3,5,6]

Summary and Conclusions

We have described the first comparitive reactions of a transition metal imide with the two heteroalkyne substrates Bu^tCP and MeCN. In both instances a [2+2] cycloaddition product is formed, but for MeCN the product is self-trapped by an unusual dimerization reaction. The binuclear compound **3** undergoes an unusual and quantitative retrocyclization reaction.

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Supporting Information Available: Details of the X-ray structure determinations of **2** and **3**. Crystallographic files in CIF format for the structure determinations of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000264U

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(26) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761.

(27) For examples, see: Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 3616. Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1982.