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C–H bond activation and C–N coupling reactions of methylacetylenes and allenes with an imidotitanium complex

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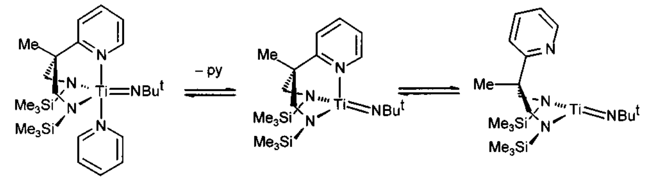
Reaction of an imidotitanium complex, stabilized by a tridentate diamidopyridine ligand, with the methyl acetylenes MeC_2Me and MeC_2Ph led to C–H-activation of the substrate and subsequent C–N coupling to give azatitanatetracycles which may be viewed as dimetallated enamines; the same compounds were obtained in reactions with the allenes Me(H)C=C=CH$_2$ and Ph(H)C=C=CH$_2$.

We have shown previously that the coordination of the diamidopyridine ligand system developed previously by us[1] to titanium leads to stable monomeric imidotitanium complexes such as **1**.[2] Compound **1** posseses labile pyridine and pyridyl functionalities that, under appropriate reaction conditions, may dissociate to yield an unsaturated and highly reactive imido complex of the type hitherto generally only accessible *via* irreversible thermolysis of certain precursors.[3] The facile accessibility and stability of **1** and its homologues has allowed us to undertake a systematic investigation into their reactivity, in particular C–N coupling with unsaturated hydrocarbons.



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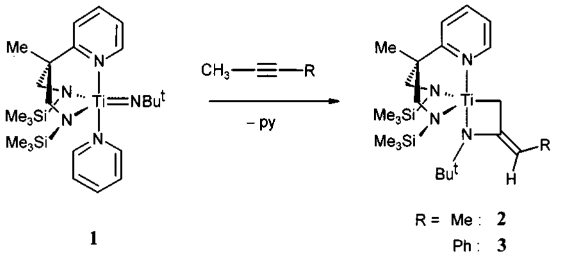
Heating compound **1** dissolved in neat but-2-yne or 1-phenylpropyne at 80 °C for 10 days in a sealed tube led to its complete conversion to the novel complexes **2** and **3** (Scheme 1), respectively which were isolated by direct crystallization from the reaction mixture (yields: **2** 73%, **3** 70%).

Neither **2** nor **3** contain the auxiliary pyridine ligand present in the starting material and the ^{1}H and ^{13}C NMR spectra indicate a transformation of a methyl group of the acetylene substrate.§Thus, new resonances for a metal bound CH$_2$ group were observed [δ(^{1}H/^{13}C) **2**: 1.77/62.4; **3**: 2.03/63.6] as well as those for an olefinic CH unit [δ(^{1}H/^{13}C) **2**: 4.76/86.7; **3**: 5.86/96.4]. This led to the formulation of the reaction products as depicted in Scheme 1. Unambiguous evidence for this new structural type was obtained from a single crystal X-ray structure analysis of **2** the result of which is depicted in Figure 1.¶



Scheme 1

The coordination geometry of the molecule is distorted trigonal bipyramidal. The two amido functions of the tripodal ligand as well as the alkyl C-atom C(45) occupy the equatorial sites while the pyridyl N-atom and the amido-N atom derived from the imido ligand represent the axial ligating atoms. The N(4)–Ti vector is significantly tilted towards the equatorial plane [N(4)–Ti–C(45) 67.6(2)°] as a consequence of the small bite angle of the coordinated chelating metalla-enamine. The bond lengths and interbond angles within the C–N-coupled organic fragment clearly support its interpretation as a metallated enamine with C(45)–C(46) 1.515(9) Å and C(46)–N(4) 1.404(8) Å representing single bonds and C(46)–C(47) 1.338(9) Å being consistent with a C–C-double bond. The {TiN(Bu^t)C(=CHR)CH$_2$} metalla-azetidine fragment in **2** and **3** is the first crystallographically authenticated example of this structural unit. Related oxo-metallacyclic species (*i.e.* metallaoxetanes) have only recently been fully characterized, namely [Ti(η^5-C$_5$Me$_5$)$_2${OC(=CH$_2$)CH$_2$}],[4a] [Mo(NBu^t)$_2$Cl{OC(=CHPPh$_3$)CPh$_2$}],[4b] and [Ru(PMe$_3$)$_4${OC(=CHBu^t)CH$_2$}].[4c] Interestingly, the latter two complexes have a *Z*-configuration for the exocyclic C=C bond, whereas the configuration in **2** and **3** is *E*, presumably due to the steric influence of the N-*tert*-butyl group.

Although the conversion to the reaction products **2** and **3** proceeds slowly it is remarkably selective and could be monitored by ^{1}H NMR spectroscopy in C$_6$D$_6$. The fact that no deuterium was incorporated into the products suggests that the

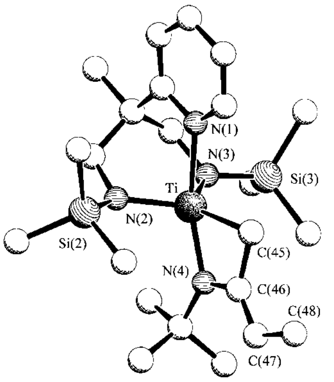
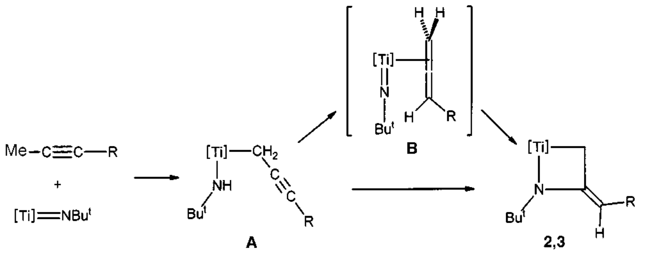


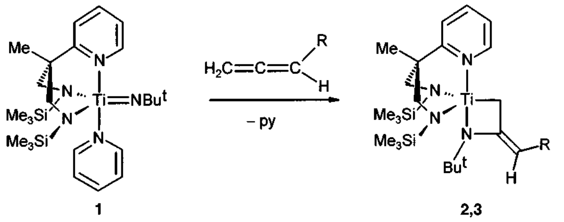
Fig. 1 Molecular structure of [TiL(NBu^t)C(CH$_2$)CHMe] **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–N(3) 1.890(5), Ti–N(2) 1.903(5), Ti–N(4) 1.949(6), Ti–C(45) 2.149(7), Ti–N(1) 2.232(6), N(4)–C(46) 1.404(8), C(45)–C(46) 1.515(9), C(46)–C(47) 1.338(9), C(47)–C(48) 1.532(9), N(3)–Ti–N(2) 110.5(3), N(3)–Ti–N(4) 107.3(3), N(2)–Ti–N(4) 106.3(2), N(3)–Ti–C(45) 121.6(3), N(2)–Ti–C(45) 127.1(3), N(4)–Ti–C(45) 67.6(2), N(3)–Ti–N(1) 86.1(2), N(2)–Ti–N(1) 83.9(2), N(4)–Ti–N(1) 158.3(2), C(45)–Ti–N(1) 90.9(3), C(46)–C(45)–Ti 88.2(4), C(47)–C(46)–N(4) 131.3(7), C(47)–C(46)–C(45) 125.6(7), N(4)–C(46)–C(45) 103.0(6), C(46)–C(47)–C(48) 123.7(8).



Scheme 2

hydrogen transfer involving the reaction medium does not take place. A reasonable reaction mechanism based on these results is depicted in Scheme 2.

In a first reaction step (formation of intermediate **A**) the Me-group of the methyl acetylene adds across the Ti=NR bond generating an R(H)N-amido ligand and a Ti–alkyl unit.|| Such C–H bond activation reactions of transiently generated imido compounds have been studied extensively by Wolczanski and others in recent years.[3] In a proposed second step, H atom transfer to an acetylene C-atom leads to the re-formation of the imido unit and a π-bonded allene ligand (**B**).** These fragments couple in the third and final step to give the four-membered azatitanacycle present in **2** and **3**. Supporting evidence for this third step was obtained independently by reacting compound **1** with 1-methylallene and 1-phenylallene, respectively. In both cases the same reaction products (*i.e.* **2** and **3**, respectively) as those described above were obtained (Scheme 3). We would like to point out that, alternatively, intermediate **A** may also be directly converted to the metallacycle.



Scheme 3

The reactions of **1** with MeC≡CR and $CH_2{=}C{=}CHR$ to form **2** and **3** are the first examples of such transformations in transition metal chemistry. Although reactions of imido complexes with internal alkynes to form metallacycles $[L_nM\{N(R)C(R){=}CR\}]$ are known,[7] no examples of the activation of sp^3 C–H bonds in preference to forming the simple cyclization products have been described.[8] The reaction of **1** with allenes to form a metalla-azetidine is the first fully characterized example of this type for imido complexes, although very recently the reaction of $[Ti(\eta^5\text{-}C_5Me_5)_2(O)(py)]$ with allene to form $[Ti(\eta^5\text{-}C_5Me_5)_2\{OC({=}CH_2)CH_2\}]$ was described.[4a]

In the more general context of organic synthesis *via* organometallics, the remarkable products of a C–N coupling reaction may be viewed as dimetallated enamines. In view of the known chemistry of *mono*-metallated enamines[9] as well as the reactive patterns established for Ti–C units,[10] a rich and varied organic chemistry is expected to derive from these preliminary results.

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Notes and references

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§ *Selected spectroscopic data*: **2**: ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 0.04 [18H, s $Si(CH_3)_3$], 1.00 (3H, s, CH_3), 1.77 (2H, s, CH_2), 1.81[9H, s, $NC(CH_3)_3$], 2.22 [3 H, d, ^2J(HH) 6.3 Hz, CH_3], 3.08 [2H, d, ^2J(HH) 12.8 Hz, CH*H*NSi], 3.70 [2H, d, ^2J(HH) 12.7 Hz, C*H*HNSi], 4.76 [1H, q, ^3J(HH) 6.4 Hz, CH], 6.51 (1H, m, H^5 C_5H_4N), 6.80 [1H, d, $^3J(H^6H^5)$ 7.9 Hz, H^3 C_5H_4N], 7.03 [1H, virtual td H^4 C_6H_4N, $^3J(H^4H^5)$ 7.7 $^3J(H^4H^3)$ 7.9 $^4J(H^4H^6)$ 1.7 Hz], 8.59 (1H, d, $^3J(H^6H^5)$ 5.4 Hz, H^6 C_5H_4N). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 0.06 [$Si(CH_3)_3$], 13.6 (CH_3), 23.3 (CH_3), 30.4 [NC(*C*H$_3$)$_3$], 46.5 [*C*(CH$_2$NSiMe$_3$)$_2$], 62.4 (CH_2), 56.4 (N*C*Me$_3$), 63.5 (*C*H$_2$NSiMe$_3$), 86.7 (CH), 120.6 (C^3 C_5H_4N), 121.7 (C^5 C_5H_4N), 138.3 (C^4 C_5H_4N), 140.7 [*C*=C(HMe), 145.7 (C^6 C_5H_4N), 159.8 (C^2 C_5H_4N). **3**: ^{1}H NMR (200 MHz, C_6D_6, 295 K): = δ −0.03 (s, 18H, $SiMe_3$), 0.97 (s, 3H, CCH_3), 1.81 (s, 9 H, Bu^t), 2.03 (s, 2 H, CH_2), 3.03 [d, 2H, ^3J(HH) 12.8 Hz, CHHN], 3.71 (d, 2 H, CH*H*N), 5.86 [s, 1 H, C=C*H*(C_6H_5)], 6.50 [ddd, 1H, H^5, C_5H_4N, $^3J(H^5H^4)$ 7.6 $^3J(H^5H^6)$ 5.6 $^3J(H^5H^3)$ 1.2 Hz], 6.76 [dd, 1H, H^3, C_5H_4N, $^3J(H^3H^4)$ 7.9 Hz], 6.95–7.06 (m, 2 H, H^4, C_5H_4N and H^4, C_6H_5), 7.37 (2H, H^{3,5}, C_6H_5), 7.79 (2H, H^{2,6}, C_6H_5), 8.42 (ddd, H^6, C_5H_4N). $\{^1H\}^{13}C$ NMR (50.3 MHz, C_6D_6, 295 K): δ 0.0 [$Si(CH_3)_3$], 23.4 (C*C*H$_3$), 30.6 [NC(*C*H$_3$)$_3$], 47.5 (*C*CH$_3$), 56.2 [N*C*(CH$_3$)$_3$], 58.0 (*C*H$_2$), 63.6 (*C*H$_2$N), 96.4 [C=*C*H(C_6H_5)], 120.4 (C^3, C_5H_4N), 121.4 (C^4, C_6H_5), 122.0 (C^5, C_5H_4N), 127.9 (C^{2,6}, C_6H_5), 128.3 (C^{3,5}, C_6H_5), 138.7 (C^4, C_5H_4N), 144.23 (C^1, C_6H_5), 145.8 (C^6, C_5H_4N), 147.7 [*C*=CH(C_6H_5)], 159.5 (C^2, C_5H_4N). Correct elemental analyses were obtained for both compounds.

¶ *Crystal data* for [TiL(NBu^t)C(CH$_2$)CHMe] **2**: $C_{23}H_{44}N_4Si_2Ti$, M = 480.70, monoclinic, space group $C2/c$, a = 28.721(7), b = 10.450(2), c = 18.866(4) A, β = 100.50(2)° V = 5567 A^3, Z = 8, $F(000)$ = 2080, T = 223(2) K, μ = 0.410 mm^{-1}; Siemens P4 diffractometer, 4176 measured data, semi-empirical absorption corrections (ψ-scans, relative T_{max} 0.799 and T_{min} 0.682), 3391 independent reflections, R_{int} = 0.0893, R_1 0.0665, wR_2 = 0.0983 [$I > 2\sigma(I)$], S = 0.0862. Hydrogen atoms were included in calculated positions and anisotropic displacement parameters were assigned to all other atoms. CCDC 182/1050.

|| Since the reversible addition of alkynes to M=NR or M=O bonds is established, we cannot rule out the reversible aza–titanacyclobutene intermediate prior to C–H activation.[5,6]

** Similar intermediates involving alkenes or alkynes η^2-bound to metal–imido complexes have been proposed previously.[5]

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