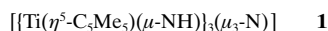


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- [10] Dialysis was carried out in a stirred cell with a 5000 nominal molecular weight limit polyethersulfone ultrafiltration membrane, using a pressure of 5 atm to force over 1 L of water through the sample. Low-molecular-weight compounds such as free cyclodextrin and **7** are rapidly removed by this procedure.
- [11] We have no information on the relative orientation of the cyclodextrin units in **4**, **8**, and **11**; our schematic representation is not intended to imply that all the macrocycles point the same way.
- [12] Disodium 1-iodonaphthalene-3,6-disulfonate (**5**) was prepared in 86% yield by treatment of the diazonium salt of disodium 1-aminonaphthalene-3,6-disulfonate with KI.
- [13] Electrophoresis was performed in 12% urea-PAGE gels, using the Bio-Rad minigel system, with 5 M urea in the separating gel at pH 8.8, at 100 V.
- [14] GPC solvent: aqueous 100 mM Tris/HCl, 100 mM NaCl, pH 8; molecular weight markers: 12.4–67 kDa from Sigma.

[{Ti(η^5 -C₅Me₅)(μ -NH)}₃(μ_3 -N)}]: An Efficient Entry to Single and Double Cube-Type Nitrido Complexes**

Angel Abarca, Avelino Martín, Miguel Mena,* and Carlos Yélamos

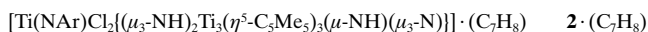
Group 4 tetrametallic derivatives of the formula [(ML_n)₄(μ_3 -E)₄] with cube-type cores remain extremely rare and are limited to halide-bridged [{TiL}₄(μ_3 -Cl)₄] (L = η^8 -C₈H₈,^[1] Me₃^[2]), chalcogenide-bridged [{Ti(η^5 -C₅H₄R)}₄(μ_3 -S)₄],^[3] and imido-bridged [{Ti(η^5 -C₅H₅)₄(μ_3 -NSnMe₃)₄] complexes.^[4] Our first contributions in this field were the preparation of the singular nitrido and alkylidyne complexes [{Ti(η^5 -C₅Me₅)(μ_3 -E)}₄] (E = N^[5], CH^[6]), which contained an almost perfect T₄E₄ cube. A possible synthetic strategy to access this type of compounds would involve the incorporation of different metal complex fragments in a cuboidal core such as [Ti₃(μ -NH)₃(μ_3 -N)],^[7] in a similar way to that reported for [M₃(μ -S)₃(μ_3 -S)] species.^[8–10] In this context, we have recently determined that the preorganized^[11] “organometallic ligand” **1** is able to displace mesitylene or carbonyl ligands in



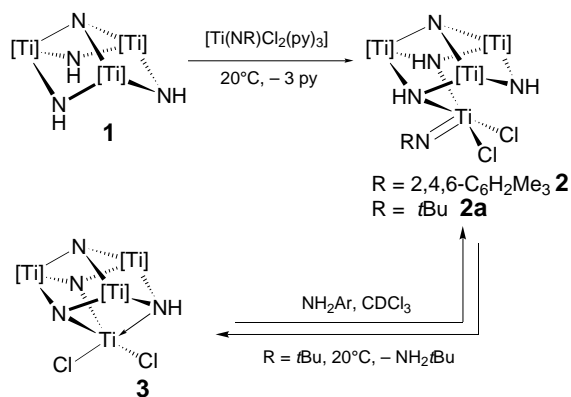
[Mo(CO)₃(1,3,5-Me₃C₆H₃)] or [M(CO)₆], respectively,^[12] and also reacts, by N–H activation, with tris(dimethylamido)cyclopentadienyltitanium(IV) compounds^[13] to give azametallocubane complexes. Herein we describe the reactions of **1** with several d⁰ imido- and amidotitanium and -zirconium com-

plexes that yield new cube-type derivatives and, for the first time, metal corner-shared double cube nitrido complexes. This synthetic method should be generally applicable and thus make the Ti₃N₄ core a very versatile building block for heterometal cluster chemistry and for molecular precursors of new ternary nitrides MTi_xN_y.

Reaction of complex **1** with [Ti(NAr)Cl₂(py)₃] (Ar = 2,4,6-C₆H₂Me₃)^[14] in toluene at room temperature results in displacement of the pyridine (py) ligands and formation of **2**·(C₇H₈) in 51% yield (Scheme 1). Analogous treatment of **1** with the *tert*-butylimido derivative [Ti(N*t*Bu)Cl₂(py)₃]^[14] in toluene afforded the complex **3** as a green precipitate in 82%

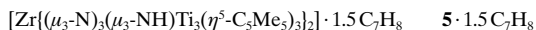


yield.^[15] The addition of 2,4,6-trimethylaniline (1 equiv) to a solution of **3** in CDCl₃ at room temperature gave **2** within several days. Complexes **2** and **3** were characterized by spectral and analytical methods, as well as by an X-ray structure determination in the case of **2** (vide infra).

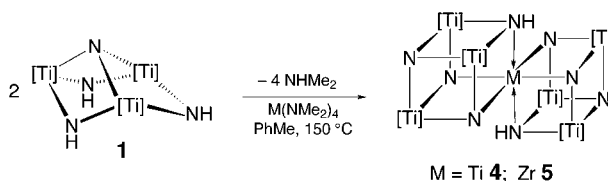


Scheme 1. Synthesis of **2** and **3** from **1**. [Ti] = Ti(η^5 -C₅Me₅).

Treatment of **1** with tetrakis(dimethylamido)titanium(IV) or -zirconium(IV) in toluene at 150 °C afforded the corner-shared double cube complexes **4**·2C₇H₈ and **5**·1.5C₇H₈, respec-



tively, as dark green crystals in 69 and 60% yield, respectively (Scheme 2). Complex **5**·1.5C₇H₈ was also prepared in 53% yield through the reaction of **1** with the imido derivative [Zr(NAr')(NHAr')₂(py)₂] (Ar' = 2,6-C₆H₃iPr₂)^[16] in toluene at 90 °C. Once isolated complexes **4** and **5** are not soluble in



Scheme 2. Synthesis of **4** and **5** from **1**. [Ti] = Ti(η^5 -C₅Me₅).

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common solvents, precluding their characterization by NMR spectroscopy. Their IR spectra showed ν_{NH} vibrations at 3353 and 3345 cm^{-1} , respectively.

The X-ray crystal structures of **2**, **4**, and **5** were determined in order to establish the geometry around the metal centers and the bonding modes of the imido and nitrido ligands.^[17] Crystals of **2** bear one toluene molecule per titanium compound. The molecular structure of **2** consists of a distorted cube core (Figure 1).^[18] The incorporated titanium atom Ti4

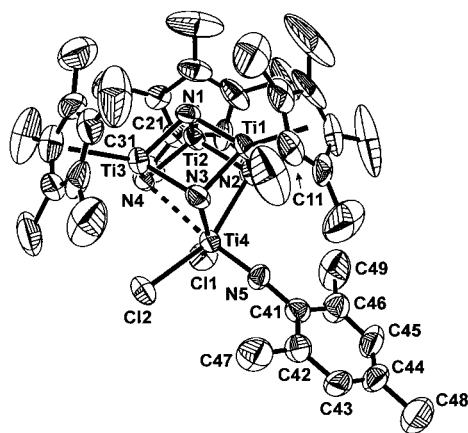


Figure 1. Structure of complex **2** (thermal ellipsoids at the 50% probability level). The C_7H_8 solvent molecule has been omitted for clarity. Selected lengths [\AA] and angles [$^\circ$]: Ti4–N2 2.263(8), Ti4–N3 2.304(9), Ti4 \cdots N4 2.602(7), Ti4–N5 1.695(8), Ti4–Cl1 2.365(3), Ti4–Cl2 2.373(3), Ti4 \cdots Ti(av) 3.143(3); Ti4–N5–C41 171.6(7), Cl1–Ti4–Cl2 98.3(1), N2–Ti4–N3 76.5(3), N2–Ti4–Cl1 92.4(2), N2–Ti4–Cl2 155.9(2), N2–Ti4–N4 75.3(3), N2–Ti4–N5 98.2(3), N3–Ti4–N4 75.2(3), N3–Ti4–N5 103.6(3), N3–Ti4–Cl1 155.8(2), N3–Ti4–Cl2 85.2(2), N4–Ti4–N5 173.6(3).

exhibits an apparent octahedral geometry with a “missing vertex”; the Ti4 \cdots N4 distance is 2.602(7) \AA . Ti4 is bound to two chlorine, one linear arylimido ligand, and two imido groups of the incomplete cube core [$\text{Ti}_3(\mu\text{-NH})_3(\mu_3\text{-N})$]. The angle subtended at the arylimido nitrogen atom (Ti4–N5–C41 171.6(7) $^\circ$) and the Ti4–N5 bond length (1.695(8) \AA) are in the normal range for other imidotitanium complexes,^[19, 20] in which the ArN^{2-} ligand acts as a six-electron donor. The extremely strong *trans* influence of the arylimido group rationalizes the noncoordination of the third imido group of the cuboidal system (N5–Ti4–N4 173.6(3) $^\circ$). The bond lengths between Ti4 and the nitrogen atoms of the NH groups are similar (Ti4–N2 2.263(8) and Ti4–N3 2.304(9)) and analogous to values for Ti–N distances in other titanium(IV) complexes with amino ligands.^[13, 21–23] Analogous Ti–N bond lengths and a similar *trans* influence of the imido ligands have been reported for a family of macrocyclic d^0 imidotitanium complexes [$\text{Ti}(\text{N}t\text{Bu})\text{Cl}_2(\text{L})$] ($\text{L} = [9]\text{aneN}_3$, $\text{Me}_3[9]\text{aneN}_3$, and $\text{Me}_2[9]\text{aneN}_2\text{S}$).^[24]

Complex **4** crystallizes with two toluene molecules. The structure shows two cubes with a common titanium vertex (Figure 2). This titanium center exhibits a six-coordinate geometry, in which the nitrogen atoms lie at the vertices of a trigonal antiprism. The two “[$(\mu_3\text{-N})_3(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3$]” ligands adopt a mutually staggered conformation which may correspond to the minimization of the steric repulsion of the bulky pentamethylcyclopentadienyl ligands. The N–Ti–N an-

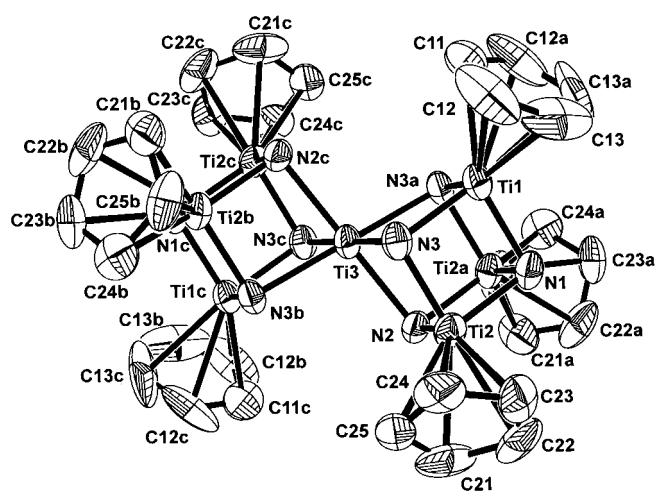


Figure 2. Structure of complex **4** (thermal ellipsoids at the 50% probability level). The methyl groups of the pentamethylcyclopentadienyl ligands as well as the C_7H_8 solvent molecules have been omitted for clarity. Selected lengths [\AA] and angles [$^\circ$]: Ti3–N2 2.125(9), Ti3–N3 2.122(6), Ti1–N1 1.931(7), Ti3–Ti 2.948(2), Ti1 \cdots Ti1 2.800(2); N1–Ti3–N1 81.1(3), N1–Ti3–N2 99.0(3). Subscript 1 means an atom of the same Ti_3N_4 unit, and subscript 2 means an atom of a second Ti_3N_4 unit, average values.

gles between the central atom and each tridentate ligand are 81.1(3) $^\circ$, while the N–Ti–N *cis* angles between the two ligands span 99.0(3) $^\circ$. The Ti3–N bond lengths are the same within the experimental error (2.122(6) and 2.125(9) \AA), and range between those in amido-^[25–27] and aminotitanium(IV) complexes.^[13, 21–23] The tridentate ligands display similar Ti–N (av 1.931(7) \AA) and Ti–Ti (2.800(2) \AA) lengths to those determined for **1**.^[7]

Complex **5** (Figure 3) shows a similar geometry to that of **4** with a more elongated trigonal antiprism environment for the central zirconium atom due to the different atomic radii. Thus, the Zr–N bonds in complex **5** are longer than the Ti3–N bond in **4** (≈ 0.1 \AA), the angles between zirconium and the nitrogen

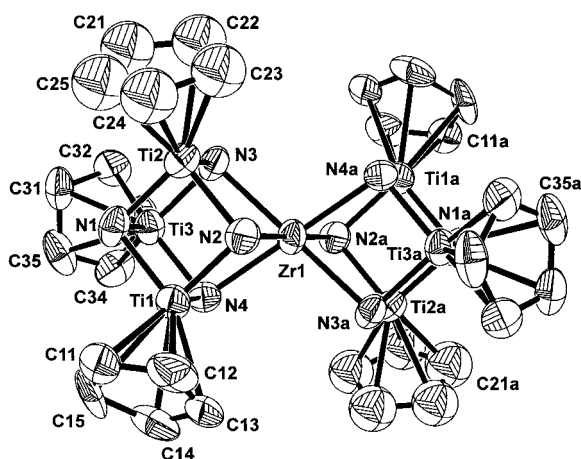


Figure 3. Structure of complex **5** (thermal ellipsoids at the 50% probability level). The methyl groups of the pentamethylcyclopentadienyl ligands as well as the C_7H_8 solvent molecules have been omitted for clarity. Selected lengths [\AA] and angles [$^\circ$]: Zr1–N2 2.233(11), Zr1–N3 2.234(11), Zr1–N4 2.237(11), Ti1–N1 1.94(1), Ti1 \cdots Ti1 2.802(4), Zr1 \cdots Ti 3.072(3); N1–Zr1–N1 77.8(4), N1–Zr1–N2 102.2(4). Subscript 1 means an atom of the same Ti_3N_4 unit, and subscript 2 means an atom of a second Ti_3N_4 unit, average values.

atoms of the same tridentate ligand ($\approx 3.3^\circ$ less in **5**) are narrower, and the angles between the *cis* nitrogen atoms of the two ligands and zirconium ($\approx 3.2^\circ$ more in **5**) are wider.

In summary, we have examined the reactions of the incomplete cube compound **1** with a variety of titanium and zirconium d^0 complexes. The results indicate that the $[\text{Ti}_3\text{N}_4]$ core of **1** is capable of displacing labile ligands bound to inorganic derivatives by coordination of the NH groups as in the formation of complex **2**. However, the stability of the resulting adducts depends on the other ligands linked to the incorporated metal. If the N–H bonds of the organometallic ligand **1** are activated by metal–imido or metal–amido linkages, the elimination of organic molecules and formation of nitrido groups bridging the metal centers takes place.

Experimental Section

2· C_7H_8 : A 100-mL Schlenk flask was charged with **1** (0.50 g, 0.82 mmol), $[\text{Ti}(\text{NC}_6\text{H}_2\text{Me}_3)\text{Cl}_2(\text{py})_3]$ (0.40 g, 0.82 mmol), and toluene (50 mL). The reaction mixture was stirred at room temperature for 24 h, then the resultant brown solution was concentrated to about 25 mL under reduced pressure. The solution was filtered and cooled to -10°C for 20 h to afford brown crystals of **2**· C_7H_8 (0.40 g, 51%). IR (KBr): $\tilde{\nu} = 3343$ (s) cm^{-1} $\nu(\text{NH})$; ^1H NMR (300 MHz, C_6D_6 , 20°C): $\delta = 11.90$ (s br., 3H; NH), 6.66 (s, 2H; $\text{C}_6\text{H}_2\text{Me}_2\text{Me}$), 2.86 (s, 6H; $\text{C}_6\text{H}_2\text{Me}_2\text{Me}$), 2.16 (s, 3H; $\text{C}_6\text{H}_2\text{Me}_2\text{Me}$), 1.93 (s, 45H; C_5Me_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 20°C): $\delta = 156.6$, 133.2, 129.1, 127.3 ($\text{C}_6\text{H}_2\text{Me}_2\text{Me}$), 123.5 (C_5Me_5), 20.9 ($\text{C}_6\text{H}_2\text{Me}_2\text{Me}$), 19.4 ($\text{C}_6\text{H}_2\text{Me}_2\text{Me}$), 12.4 (C_5Me_5); elemental analysis calcd for $\text{C}_{46}\text{H}_{67}\text{N}_5\text{Cl}_2\text{Ti}_4$ (%): C 58.01, H 7.09, N 7.35; found: C 58.16, H 7.21, N 7.06.

3: A 100-mL Schlenk flask was charged with **1** (1.00 g, 1.64 mmol), $[\text{Ti}(\text{NtBu})\text{Cl}_2(\text{py})_3]$ (0.70 g, 1.64 mmol), and toluene (50 mL). After the mixture had been stirred at room temperature for 48 h, the brown solution was separated from a fine green powder. The powder was washed with hexane (40 mL) and vacuum-dried for 3 h to afford **3** (0.98 g, 82%). IR (KBr): $\tilde{\nu} = 3240$ (s) cm^{-1} $\nu(\text{NH})$; ^1H NMR (300 MHz, CDCl_3 , 20°C): $\delta = 13.46$ (s br., 1H; NH), 2.15 (s, 15H; C_5Me_5), 2.07 (s, 30H; C_5Me_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 20°C): $\delta = 123.3$ (C_5Me_5), 12.3 (C_5Me_5), 12.0 (C_5Me_5) (one C_5Me_5 resonance signal was not found due to the low solubility or to the coincidence with that at $\delta = 123.3$); elemental analysis calcd for $\text{C}_{30}\text{H}_{46}\text{N}_4\text{Cl}_2\text{Ti}_4$ (%): C 49.69, H 6.39, N 7.73; found: C 49.70, H 6.53, N 7.30.

4· $2\text{C}_7\text{H}_8$: A 200-mL Carius tube was charged with **1** (0.50 g, 0.82 mmol), $[\text{Ti}(\text{NMe}_2)_4]$ (0.09 g, 0.41 mmol), and toluene (60 mL). The tube was flame-sealed and heated at 150°C for 30 h. The reaction mixture was allowed to cool to room temperature overnight to afford green crystals of **4**· $2\text{C}_7\text{H}_8$ (0.41 g, 69%). IR (KBr): $\tilde{\nu} = 3353$ (m), 2972 (m), 2906 (s), 2855 (s), 2719 (w), 1604 (w), 1494 (m), 1436 (s), 1373 (s), 1156 (w), 1079 (w), 1023 (m), 803 (s), 730 (s), 703 (vs), 687 (vs), 668 (vs), 612 (vs), 522 (w), 475 (m), 445 (s), 435 (s) cm^{-1} ; elemental analysis calcd for $\text{C}_{74}\text{H}_{108}\text{N}_8\text{Ti}_7$ (%): C 61.51, H 7.53, N 7.76; found: C 61.71, H 7.53, N 7.96.

5· $1.5\text{C}_7\text{H}_8$: Method A: In a similar way to the preparation of **4**, **1** (0.40 g, 0.66 mmol) and $[\text{Zr}(\text{NMe}_2)_4]$ (0.09 g, 0.34 mmol) were heated at 150°C to afford green crystals of **5**· $1.5\text{C}_7\text{H}_8$ (0.28 g, 60%). Elemental analysis calcd for $\text{C}_{70.5}\text{H}_{104}\text{N}_8\text{Ti}_6\text{Zr}$ (%): C 58.72, H 7.27, N 7.77; found: C 58.98, H 7.39, N 7.47. Method B: A 100-mL ampoule (Teflon stopcock) was charged with **1** (0.30 g, 0.49 mmol), $[\text{Zr}(\text{NAr}')(\text{NHAr}')_2(\text{py})_2]$ ($\text{Ar}' = 2,6\text{-C}_6\text{H}_3\text{iPr}_2$) (0.19 g, 0.24 mmol), and toluene (25 mL). After heating at 90°C for 2 d, the green solution was allowed to cool to room temperature overnight to afford green crystals of **5**· $1.5\text{C}_7\text{H}_8$ (0.19 g, 53%). IR (KBr): $\tilde{\nu} = 3345$ (m), 2908 (s), 2855 (s), 1604 (w), 1495 (m), 1436 (s), 1374 (s), 1024 (m), 804 (vs), 729 (s), 694 (vs), 662 (vs), 647 (s), 611 (vs), 531 (w), 486 (s), 470 (m), 447 (s), 431 (s) cm^{-1} ; elemental analysis calcd for $\text{C}_{70.5}\text{H}_{104}\text{N}_8\text{Ti}_6\text{Zr}$ (%): C 58.72, H 7.27, N 7.77; found: C 58.35, H 7.26, N 7.72.

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- [15] A complex analogous to **2** was characterized following this reaction by NMR spectroscopy in $[\text{D}_2]$ dichloromethane. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra after 10 min showed complete reaction and formation of $[\text{Ti}(\text{NtBu})\text{Cl}_2((\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-NH})(\mu_3\text{-N}))]$ (**2a**). This complex decomposed within hours to give **3** and *tert*-butylamine elimination. NMR data for **2a**: ^1H NMR (300 MHz, CD_2Cl_2 , 20°C): $\delta = 11.95$ (s br., 3H; NH), 2.14 (s, 45H; C_5Me_5), 1.02 (s, 9H; CMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2 , 20°C): $\delta = 123.4$ (C_5Me_5), 69.2 (CMe_3), 31.3 (CMe_3), 12.7 (C_5Me_5).
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- [17] X-ray crystal structure determinations of complexes **2**, **4**, and **5**: Brown crystals of compound **2** and green crystals of **4** and **5** were obtained from toluene solutions. All data were collected on an Enraf Nonius CAD4 diffractometer at room temperature, $\text{MoK}\alpha = 0.71073 \text{ \AA}$. All the structures were solved by using the WINGX^[20] package by direct methods (SHELXS-97), and refined by least-squares against F^2 (SHELXL-97).^[20] X-ray crystal structure data for $\text{C}_{46}\text{H}_{67}\text{Cl}_2\text{N}_5\text{Ti}_4$ (**2**· C_7H_8): $0.40 \times 0.35 \times 0.32 \text{ mm}^3$, triclinic, $P\bar{1}$, $a = 11.065(2)$, $b = 14.598(2)$, $c = 16.530(3) \text{ \AA}$, $\alpha = 71.45(1)$, $\beta = 78.33(1)$, $\gamma = 80.59(1)^\circ$, $V = 2464.8(6) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.283 \text{ Mg m}^{-3}$. Intensity measurements were performed by ω - 2θ scans in the range $4^\circ < 2\theta < 44^\circ$ for **2**; of the 6247 measured reflections, 5957 were independent; $R1 = 0.073$ and $wR2 = 0.194$ (for 3168 reflections with $F > 4\sigma(F)$). The values of $R1$ and $wR2$ are defined as $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$. Largest difference peak and hole 1.037 and $-0.486 \text{ e \AA}^{-3}$, respectively. All non-hydrogen atoms, except those of the solvent, were anisotropically refined. X-ray crystal structure data for $\text{C}_{74}\text{H}_{108}\text{N}_8\text{Ti}_7$ (**4**· $2\text{C}_7\text{H}_8$): $0.35 \times 0.33 \times 0.30 \text{ mm}^3$, orthorhombic, $Pnmm$, $a = 14.389(1)$, $b = 15.405(1)$, $c = 16.550(1) \text{ \AA}$, $V = 3668.5(4) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.308 \text{ Mg m}^{-3}$. Intensity measurements were performed by ω - 2θ scans in the range $4^\circ < 2\theta < 44^\circ$ for **4**; of the 4565 measured reflections, 2340 were independent; $R1 = 0.090$ and $wR2 = 0.270$ (for 1478 reflections with $F > 4\sigma(F)$). Largest difference peak and hole 1.138 and $-0.648 \text{ e \AA}^{-3}$, respectively. All non-hydrogen atoms, except those of the solvent and C14, C15, and C16 (carbon atoms of methyl groups of one pentamethylcyclopentadienyl ring), were anisotropically refined. X-ray crystal structure data for $\text{C}_{70.5}\text{H}_{104}\text{N}_8\text{Ti}_6\text{Zr}$ (**5**· $1.5\text{C}_7\text{H}_8$): $0.43 \times 0.38 \times 0.32 \text{ mm}^3$, monoclinic, $P2_1/n$, $a = 14.480(1)$, $b = 15.408(1)$, $c = 16.579(1) \text{ \AA}$, $\beta = 90.12(1)^\circ$, $V = 3698.9(4) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.295 \text{ Mg m}^{-3}$. Intensity measurements were performed by ω scans in the range $5^\circ < 2\theta < 43^\circ$; of the 4532 measured reflections, 4327 were independent; $R1 = 0.107$ and $wR2 = 0.283$ (for 2253 reflections with $F > 4\sigma(F)$). All non-hydrogen atoms, except

those of the solvent and the carbon atoms of the C21–C30 pentamethylcyclopentadienyl ring, were anisotropically refined. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-144326, CCDC-144327, and CCDC-144328. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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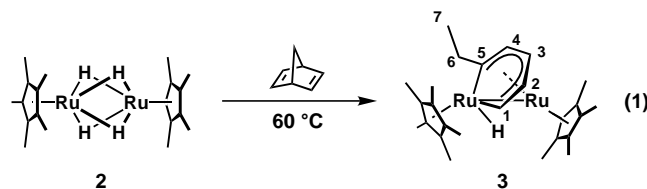
Novel Mode of C–C Bond Cleavage of Norbornadiene on a Dinuclear Ruthenium Complex**

Yasuhiro Ohki and Hiroharu Suzuki*

The activation of C–C bonds by transition metal complexes has attracted considerable attention in the field of organometallic chemistry due to its applicability to industrial processes such as petroleum refining and cracking. Most of the reported examples of C–C bond activation by transition metal complexes involve highly strained systems, pre-aromatic organic substrates such as alkylated cyclopentadienes,^[1] or intramolecular ligand activation in which the C–C bond is favorably oriented towards the metal center.^[2] In the last ten

years, we have intensively studied substrate activation on a multimetallic site and reported a novel selective C–C bond cleavage of cyclopentadiene on a trinuclear ruthenium pentahydride complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ (**1**).^[3] As well as this triruthenium cluster, the dinuclear ruthenium tetrahydride $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}]_2(\mu\text{-H})_4$ (**2**) has been shown to provide an active species for multimetallic activation and to undergo cleavage of various types of bonds such as $\text{C}(\text{sp}^2)\text{-H}$, Si-H , and $\text{P-C}(\text{aryl})$ bonds under mild conditions.^[4] We have now focussed our attention on the activation of C–C bonds by a dinuclear complex and have examined the reaction of **2** with a variety of 1,3- and 1,4-cyclic dienes because these dienes have geometries suitable for coordination to a dimetallic site. We report herein an unprecedented type of selective carbon–carbon bond cleavage of norbornadiene by the dinuclear ruthenium tetrahydride complex **2**.

Treatment of **2** with three equivalents of norbornadiene in toluene at 60°C resulted in the formation of the dinuclear 2-ethylruthenacyclohexadienyl complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}]_2(\mu\text{-}\eta^5:\eta^1\text{-C}_5\text{H}_4\text{C}_2\text{H}_5)(\text{H})$ (**3**) as the result of a C–C bond cleavage [Eq. (1)] (yield ca. 65% from ^1H NMR data). The



new complex **3** was isolated as a red crystalline solid in 44% yield by column chromatography on neutral alumina, and identified on the basis of the ^1H and ^{13}C NMR, and $^{13}\text{C}\text{-}^1\text{H}$ HETCOR spectra. The ^{13}C NMR spectrum exhibited two characteristic signals for bridging alkenyl carbons, C1 and C5, at $\delta = 168.1$ ($J_{\text{C,H}} = 141.9$ Hz) and $\delta = 186.2$, respectively. The gated ^{13}C NMR spectrum showed three doublets at $\delta = 91.1$ ($J_{\text{C,H}} = 156.3$ Hz, C2), $\delta = 85.8$ ($J_{\text{C,H}} = 159.5$ Hz, C3), and $\delta = 90.2$ ($J_{\text{C,H}} = 151.0$ Hz, C4) for the carbon atoms of the ruthenacycle, and the chemical shifts were comparable to those observed in the related η^5 -cyclohexadienylruthenium complexes.^[5] A resonance signal due to the hydrogen atom attached to the α -carbon (C1) appeared at $\delta = 9.33$ in the ^1H NMR spectrum. The two hydrogen atoms on C6 are diastereotopic and their resonance signals appeared at $\delta = 2.38$ and $\delta = 3.18$.

There are two possible modes of C–C bond cleavage that account for the formation of the ruthenacycle **3**. One involves C–C bond cleavage at C1–C2 and C4–C5 of norbornadiene. The other pathway involves the C1–C2 and C4–C7 bond cleavage (Scheme 1). The latter mode of C–C bond cleavage is observed in the protonation of $[(\eta^5\text{-C}_5\text{R}_5)\text{Co}(\eta^1\text{-norbornadiene})]$.^[6] To elucidate the reaction pathway to **3**, complex **2** was allowed to react with 7-methylnorbornadiene^[7] under similar conditions to those with norbornadiene. This reaction generated the analogous ruthenacycle $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}]_2(\mu\text{-}\eta^5:\eta^1\text{-C}_5\text{H}_3\text{CH}_3\text{C}_2\text{H}_5)(\text{H})$ (**4**) in which a methyl group was bound to C4 [Eq. (2)]. Complex **4** was isolated as a red

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