

# Carbon-carbon double-bond formation in the intermolecular acetonitrile reductive coupling promoted by a mononuclear titanium(II) compound. Preparation and characterization of two titanium(IV) imido derivatives

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borate<sup>21</sup> were prepared as described in the literature.

**9-Fluoro-*o*-carborane.** The iodonium salt **1** (1.50 g; 3.5 mmol) was added portionwise to a stirred mixture of KF (1.0 g; 17.2 mmol), 18-crown-6 ether (1.34 g; 5.1 mmol), and dry chloroform (10 mL). The exothermic reaction was complete within 1–5 min. The liquid phase was analyzed by GLC and then evaporated, and the residue was chromatographed on alumina (benzene–hexane, 1:3) to give 0.52 g (93%) of 9-fluoro-*o*-carborane, mp 287–288 °C (from benzene–hexane; sealed tube). The compound was found to be identical with an authentic sample.<sup>5,6</sup>

**9-Fluoro-*m*-carborane.** A mixture of **2** (0.70 g; 1.62 mmol), NaHF<sub>2</sub> (0.30 g; 4.84 mmol), water (7 mL), and dichloromethane (7 mL) was vigorously stirred under reflux for 6 h. Internal standard (chlorobenzene) was added, and the organic layer was analyzed by GLC and GC–MS. The organic phase was evaporated, and the residue was chromatographed on silica gel (40–100 mesh; hexane) to give 9-fluoro-*m*-carborane (0.23 g; 89%), mp 267–268 °C (hexane; sealed tube). The compound was found to be identical with an authentic sample.<sup>5,6</sup>

**2-Fluoro-*p*-carborane.** A mixture of **7** (0.7 g; 1.6 mmol), NaF (0.2 g; 4.8 mmol), water (4 mL), and dichloromethane (5 mL) was vigorously stirred at 25 °C for 35 min. The organic phase was separated off, filtered through a short alumina plug, and evaporated. The residue (a mixture of iodobenzene and 2-fluoro-*p*-carborane) was dissolved in dry CCl<sub>4</sub> (5 mL), and the solution was saturated with Cl<sub>2</sub> at 5 °C and then evaporated, to give the mixture of iodobenzene dichloride and the fluoro-carborane. The latter was extracted with pentane [the yield of PhICl<sub>2</sub> left was 0.31 g (70%)], and the pentane solution was filtered through an alumina plug and evaporated to dryness. Vacuum sublimation of the residual solid gave 0.26 g (99.5%) of analytically pure 2-fluoro-*p*-carborane, mp 256 °C (sealed tube). Anal. Calcd for C<sub>2</sub>H<sub>11</sub>B<sub>10</sub>F: F, 11.71. Found: F, 11.74.

**Reactions of 2–6 with NaF.** A mixture of aryl(*m*-carboran-9-yl)-iodonium tetrafluoroborate (0.62 mmol), NaF (0.08 g; 1.9 mmol), water (2 mL), and chloroform (2 mL) was vigorously stirred under reflux for 2.5 h. Internal standard (chlorobenzene) was added, and the organic phase was analyzed by GLC and GC–MS.

**Reactions of 3–6 with NaCl.** A mixture of aryl(*m*-carboran-9-yl)-iodonium tetrafluoroborate (0.24 mmol), NaCl (0.04 g; 1.9 mmol), water (1 mL), and chloroform (1 mL) was vigorously stirred under reflux for 2.5 h. Internal standard (iodobenzene) was added, and the organic layer was analyzed by GLC.

**Reaction of 2 with Trimethylammonium 7,9-Dicarba-*nido*-undecaborate.** A solution of **2** (0.84 g; 1.94 mmol) and trimethylammonium dicarba-*nido*-undecaborate (0.44 g; 2.11 mmol) in acetone (8 mL) was refluxed for 4 h. The resulting solution was analyzed by GLC and then evaporated to dryness. The residue was chromatographed on silica gel (40–100 mesh; hexane) to give 0.26 g (50%) of 9-iodo-*m*-carborane, mp 110–112 °C (hexane; see ref 2).

**Registry No.** **1**, 81353-28-8; **2**, 81353-33-5; **3**, 99506-45-3; **4**, 99506-39-5; **5**, 99506-41-9; **6**, 99506-43-1; **7**, 88242-78-8; 9-*o*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>F, 73050-36-9; 9-*m*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>F, 73050-37-0; 2-*p*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>F, 22762-43-2; 9-*m*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>I, 17157-02-7.

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### Carbon–Carbon Double-Bond Formation in the Intermolecular Acetonitrile Reductive Coupling Promoted by a Mononuclear Titanium(II) Compound. Preparation and Characterization of Two Titanium(IV) Imido Derivatives

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#### Introduction

Reactions forming carbon–carbon bonds are among the most fundamental organic chemical transformations mediated by

early-transition-metal complexes. Today, reductive couplings and insertion reactions are successfully used with a considerable number of transition metals, to form C–C bonds through either catalytic or stoichiometric reactions.<sup>1</sup> While the insertion reactions are the most versatile chemical pathway for polymerization processes,<sup>1a,2</sup> reductive couplings are target of continuous studies for regio- and stereoselective metal-promoted organic syntheses.<sup>3</sup> Group 4 transition metals seem to be especially versatile for this second class of reactions,<sup>1a,4</sup> reductive couplings being documented for the large majority of unsaturated organic compounds (dienes,<sup>5</sup> olefins,<sup>6</sup> acetylenes,<sup>7</sup> isocyanides,<sup>8</sup> nitriles,<sup>9</sup> and carbon monoxide<sup>10</sup>). We were especially interested in defining the chemical reactivity of (TMEDA)<sub>2</sub>TiCl<sub>2</sub> (TMEDA = *N,N,N',N'*-tetramethylethylenediamine),<sup>11</sup> which is one of the rare examples of low-valent titanium complexes.<sup>12,13</sup> In this paper we describe the reaction

- (1) (a) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982. (b) Wilkinson, G. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, England, 1987.
- (2) See, for example: (a) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (b) Boor, J. *Ziegler-Natta Catalysts and Polymerization*, Academic Press: New York, 1979. (c) Fisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. G.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (d) Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479. (e) Watson, P. J. *Am. Chem. Soc.* **1982**, *104*, 337. (f) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (g) Hedden, D.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1647. (h) Jordan, R. F.; LaPointe, R. E.; Chandrasekar, S. B.; Echols, S. F.; Willet, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (i) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902.
- (3) See for example: (a) Erker, G.; Dorf, U. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 777. (b) Tikkanen, W. R.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646. (c) Heck, R. F. *Organotransition Metal Chemistry*; Academic Press: New York, 1974. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. L.; Finke, R. J. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (e) Bird, C. *Transition Metal Intermediates in Organic Synthesis*; Academic Press: New York, 1967. (f) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (g) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (h) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (i) Durfee, L. D.; McMullen, A. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 1463. (j) Walsh, P. J.; Hollander, F. J.; Bergman, B. G. *J. Am. Chem. Soc.* **1990**, *112*, 894. (k) Buchwald, S. L.; Kreutzer, K. A.; Fisher, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4600. (l) Fryzuk, M. D.; Haddad, T. S.; Retting, S. J. *Organometallics* **1988**, *7*, 1224.
- (4) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -hafnium Compounds*; Ellis Horwood Ltd.: Chichester, England, 1986.
- (5) (a) Yasuda, H.; Kajihara, K.; Nagasuna, K.; Mashima, K.; Nakamura, A. *Chem. Lett.* **1981**, 719. (b) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 915. (c) Yasuda, H.; Okamoto, T.; Yamamoto, H.; Nakamura, A. *Shokubai* **1986**, *97*. (d) Brauer, D. J.; Kruger, C. *Organometallics* **1982**, *1*, 207.
- (6) (a) Cohen, S. A.; Auburn, P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. (b) Demersman, B.; Coupance, P. L.; Dixneuf, P. U. *J. Organomet. Chem.* **1985**, *297*, C35. (c) Wielstra, Y.; Gambarotta, S.; Chiang, M. Y. *Organometallics* **1988**, *7*, 1866. (d) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 15. (e) Pez, G. J. *Chem. Soc., Chem. Commun.* **1977**, 560.
- (7) (a) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (b) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376. (c) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Am. Chem. Soc.* **1985**, *107*, 3717. (d) Famili, A.; Faronna, M. F.; Thanedar, S. *J. Chem. Soc., Chem. Commun.* **1983**, 435. (e) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L.; Chiang, M. Y. *Organometallics* **1989**, *8*, 2696.
- (8) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1988**, *110*, 1319.
- (9) (a) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1985**, *5*, 443. (b) De Boer, E. J. M. *J. Organomet. Chem.* **1978**, *153*, 53.
- (10) (a) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *103*, 146. (b) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (c) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (d) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712.
- (11) Edema, J. J. H.; Duchateau, R.; Gambarotta, S.; Hynes, R.; Gabe, E. *Inorg. Chem.* **1991**, *30*, 154.

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with a few unsaturated nitrogen-containing organic substrates (nitriles, azo compounds, and azides). The main interest in the reactivity with these substrates results from the rarity of the organic functionality which may be generated (diiminato,<sup>9</sup> enediiminato,<sup>14</sup> enediimido,<sup>15</sup> imido,<sup>16</sup> or azido) depending on (i) the number of electrons transferred by the transition metal to the organic substrate and (ii) the reducing power of the transition metal.

### Experimental Section

All operations were performed under an inert atmosphere (N<sub>2</sub> or Ar) by using standard Schlenk techniques, or in a nitrogen-filled drybox (Braun MB-200). TMEDA was chromatographed over Al<sub>2</sub>O<sub>3</sub> and distilled from melted potassium. (TMEDA)<sub>2</sub>TiCl<sub>2</sub> was prepared according to the published procedure.<sup>13</sup> Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out at the Microanalytical Department of the State University of Groningen. NMR spectra were recorded on a Varian Gemini 200-MHz instrument. A <sup>13</sup>C solid state magic-angle spinning NMR spectrum (complex 1) was obtained under cross-polarization magic-angle-spinning and high-power proton-decoupling conditions at 45.267 MHz on a Bruker CXP-180 spectrometer. The sample was sealed under vacuum into a glass ampule, which fitted tightly into a 7-mm-o.d. ceramic rotor. The spectrum was obtained using a rotation speed of 1650 Hz. Chemical shifts are reported in ppm from TMS with hexamethylbenzene as an external chemical shift reference, the methyl resonances being assigned a chemical shift of 16.9 ppm.

[*trans*-NC(Me)=(Me)CN]TiCl<sub>2</sub>(TMEDA)<sub>2</sub>·CH<sub>3</sub>CN (1). Solid TiCl<sub>2</sub>(TMEDA)<sub>2</sub> (4.0 g, 11.4 mmol) was added to neat acetonitrile (50 mL) at -60 °C. The mixture was stirred and allowed to warm slowly to room temperature (4 h). Air-sensitive orange crystals separated from the resulting red solution of 1 upon concentration and cooling to -30 °C (2.3 g, 3.9 mmol, 34% yield). Anal. Calcd (found) for C<sub>18</sub>H<sub>41</sub>N<sub>7</sub>Ti<sub>2</sub>Cl<sub>4</sub>: C, 36.45 (36.38); H, 6.97 (6.77); N, 16.53 (16.38); Ti, 16.14 (16.09); Cl, 23.91 (23.77). IR (Nujol, KBr, cm<sup>-1</sup>): 2920 (s), 2250 (m), 1485 (sh), 1460 (s), 1440 (sh), 1405 (w), 1380 (m), 1365 (m), 1355 (w), 1320 (s), 1295 (m), 1280 (m), 1240 (m), 1210 (w), 1195 (w), 1170 (w), 1125 (m), 1100 (m), 1070 (s), 1050 (s), 1020 (s), 995 (s), 950 (s), 940 (m), 800 (s), 770 (s), 725 (w), 675 (s), 600 (m), 510 (s), 490 (m), 450 (s), 415 (m), 385 (s), 350 (s). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 200 MHz, 25 °C): δ 2.88 (s, 2 H, TMEDA CH<sub>2</sub>), 2.69 (s, 6 H, TMEDA CH<sub>3</sub>), 2.05 (s, 3 H, eneiimido CH<sub>3</sub>). <sup>13</sup>C NMR (solid, 1650 Hz spinning): δ 162.9 (C-N), 58.9 (CH<sub>2</sub>), 54.3 and 46.7 (Me groups), 16.3 (CH<sub>3</sub>).

**Hydrolysis of 1.** A suspension of 1 (1 g, 1.68 mmol) in dry toluene (25 mL) was treated with distilled water (7.2 μL) and stirred until the brown color of the suspension disappeared. The white solid was filtered out, and the colorless toluene solution was slowly concentrated to a very

**Table I.** Crystal Data and Structural Analysis Results

complex	1	2
formula	C <sub>18</sub> H <sub>41</sub> N <sub>7</sub> Cl <sub>4</sub> Ti <sub>2</sub>	C <sub>12</sub> H <sub>21</sub> N <sub>3</sub> Cl <sub>2</sub> Ti
space group	C2/c	P2 <sub>1</sub> /c
cryst syst	monoclinic	monoclinic
Z	4	4
a, Å	27.948 (9)	12.617 (3)
b, Å	7.964 (2)	9.002 (2)
c, Å	14.777 (4)	14.441 (4)
β, deg	117.60 (4)	106.42 (2)
V, Å <sup>3</sup>	2914.8 (14)	1573.2 (6)
D <sub>calcd</sub> , g cm <sup>-3</sup>	1.352	1.377
μ <sub>calcd</sub> , cm <sup>-1</sup>	9.31	5.30
λ[radiation (Mo Kα)], Å	0.71073	0.71073
T, K	295	291
R <sup>a</sup>	0.049	0.034
R <sub>w</sub> <sup>b</sup>	0.061	0.042

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}.$$

**Table II.** Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 1

atom	x	y	z	B(eq), Å <sup>2</sup>
Ti1	0.16065 (6)	0.02086 (8)	0.00963 (6)	2.43 (3)
Cl1	0.03709 (9)	0.0274 (1)	0.11452 (8)	3.24 (5)
Cl2	0.1907 (1)	-0.2391 (1)	0.0002 (1)	4.36 (6)
N1	0.2742 (3)	0.0503 (4)	0.1047 (3)	2.8 (2)
N2	0.2447 (3)	0.0457 (4)	-0.1118 (3)	3.2 (2)
N3	0.1408 (3)	0.2700 (4)	-0.0247 (3)	2.8 (2)
C1	0.3512 (3)	0.0477 (5)	0.1945 (3)	2.7 (2)
C2	0.3376 (4)	-0.0498 (5)	0.2659 (3)	3.5 (2)
C3	0.4129 (5)	-0.0542 (6)	0.3545 (4)	4.3 (2)
C4	0.5058 (5)	0.0361 (7)	0.3754 (4)	4.8 (3)
C5	0.5199 (4)	0.1327 (6)	0.3076 (4)	4.5 (3)
C6	0.4423 (4)	0.1406 (5)	0.2171 (4)	3.7 (2)
C7	0.3631 (4)	0.0067 (6)	-0.0726 (4)	4.7 (2)
C8	0.1969 (5)	-0.0472 (6)	-0.1991 (4)	4.9 (3)
C9	0.0390 (4)	0.3220 (5)	-0.0947 (4)	4.6 (2)
C10	0.1531 (5)	0.3554 (5)	0.0661 (4)	5.0 (3)
C11	0.2377 (4)	0.2054 (6)	-0.1439 (4)	4.0 (2)
C12	0.2358 (4)	0.3072 (5)	-0.0630 (4)	3.7 (2)

**Table III.** Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 2

atom	x	y	z	U(eq), Å <sup>2</sup>
Ti	0.3666 (1)	0.0737 (1)	0.8271 (1)	27 (1)
Cl1	0.3265 (1)	-0.0944 (2)	0.9033 (1)	53 (1)
Cl2	0.3536 (10)	-0.1246 (2)	0.7007 (1)	52 (1)
N1	0.3402 (1)	0.3040 (7)	0.8842 (4)	48 (2)
N2	0.3617 (2)	0.2691 (6)	0.7163 (3)	44 (2)
N3	0.4340 (2)	0.0793 (6)	0.9069 (3)	34 (2)
C1	0.3809 (3)	0.2942 (11)	0.9927 (5)	75 (4)
C2	0.2868 (3)	0.4501 (9)	0.8827 (6)	77 (4)
C3	0.3387 (4)	0.4323 (9)	0.8210 (7)	84 (5)
C4	0.3716 (3)	0.2521 (9)	0.7714 (7)	76 (4)
C5	0.4034 (3)	0.2674 (10)	0.6823 (5)	61 (3)
C6	0.3085 (3)	0.0703 (7)	0.6244 (5)	66 (3)
C7	0.4886 (2)	0.2298 (8)	0.9743 (4)	33 (2)
C8	0.5211 (2)	0.9340 (21)	0.9888 (5)	57 (3)
N4	0.0000	0.3309 (10)	0.2500	150 (5)
C9	0.0000	0.7946 (19)	0.2500	91 (4)
C10	0.0000	0.6217 (15)	0.2500	73 (3)

<sup>a</sup> Equivalent isotropic U defined as one-third of the trace of the orthogonalized U<sub>ij</sub> tensor.

small volume. Colorless crystals of tetramethylpyrazine separated during the evaporation (0.055 g, 0.40 mmol, 47%). The identification of the product was carried out by either an X-ray crystal structure<sup>17</sup> or comparison of the NMR spectrum with that of an analytically pure sample.

- (12) (a) Cloke, F. G. N.; Lappert, M. F.; Lawless, G. A.; Swain, A. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1667. (b) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339. (c) Cotton, F. A.; Kibala, P. A.; Roth, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 298. (d) Chi, K. M.; Frerichs, S. R.; Philson, S. B.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1190 and references cited therein. (e) Blackburn, D. W.; Chi, K. M.; Frerichs, S. R.; Tinkham, M. L.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 437. (f) Gardner, T. G.; Girolami, G. S. *Organometallics* **1987**, *6*, 2551. (g) Ellis, J. E.; Chi, M. K. *J. Am. Chem. Soc.* **1990**, *112*, 6022.
- (13) (a) Jensen, J. A.; Wilson, S. R.; Schultz, A. J.; Girolami, G. S. *J. Am. Chem. Soc.* **1987**, *109*, 8094. (b) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720. (c) Calderazzo, F.; Pallavicini, P.; Pampaloni, G. *J. Chem. Soc., Dalton Trans.* **1990**, 1813 and references cited therein. (d) Fisher, M. B.; James, E. J.; McNese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941 and references cited therein. (e) Ellis, J. E.; Frerichs, S. R.; Chi, M. K. *Organometallics* **1990**, *9*, and references cited therein. (f) Cotton, F. A.; Kibala, P. A.; Wojtczak, W. A. *J. Am. Chem. Soc.* **1991**, *113*, 1462. (g) Gambarotta, S.; Chiang, M. Y. *J. Chem. Soc., Chem. Commun.* **1987**, 698.
- (14) (a) Cotton, F. A.; Roth, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 3734. (b) Esjornson, F.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2821.
- (15) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525.
- (16) (a) Hill, J. E.; Proilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (b) Proilet, R. D.; Zambrano, C. H.; Fanwick, P. E.; Nash, J. J.; Rothwell, I. P. *Inorg. Chem.* **1990**, *29*, 4364. (c) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (d) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (e) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 894.

- (17) The structure of tetramethylpyrazine has been reported in the literature.<sup>20</sup> However, although confirming the same structure, we have found considerably different cell parameters: monoclinic, P2<sub>1</sub>/c, a = 5.481 (2) Å, b = 6.936 (3) Å, c = 10.302 (3) Å, β = 99.90 (3)°, V = 385.82 (2) Å<sup>3</sup>, Z = 4, R = 0.043 (R<sub>w</sub> = 0.019) for 71 parameters and 426 significant reflections out of 566 unique reflections.

Table IV. Selected Bond Distances (Å) and Angles (deg)

Compound 1			
Ti1-N1	1.702 (4)	Ti1-N2	2.302 (4)
Ti1-Cl1	2.462 (2)		
N1-Ti1-Cl1	92.0 (1)	Cl1-Ti1-N3	93.4 (1)
N1-Ti1-N2	97.8 (2)	Ti1-N1-C1	164.2 (3)
Cl1-Ti1-Cl2	77.44 (5)		
Compound 2			
Ti1-N3	1.699 (4)	N3-C7	1.384 (5)
Ti-N1	2.280 (6)	C7-C7a	1.337 (10)
Ti-Cl1	2.343 (2)	C7-C8	1.518 (8)
Cl1-Ti1-Cl2	93.7 (1)	N3-C7-C8	116.4 (4)
Cl1-Ti1-N1	88.4 (2)	C7a-C7-C8	121.6 (5)
Cl1-Ti1-N3	107.3 (4)	C7a-C7-N3	121.9 (6)
Ti1-N3-C7	175.2 (4)		

(TMEDA)Ti(NPh)Cl<sub>2</sub> (2). Neat azobenzene (0.6 g, 3.3 mmol) was added to a suspension of TiCl<sub>2</sub>(TMEDA)<sub>2</sub> (2.3 g, 6.5 mmol) in THF (75 mL) at -90 °C. The mixture was stirred while warming it slowly to -30 °C, when a deep red color developed. Once all the purple crystals of starting material were dissolved, the resulting deep red solution was allowed to warm to room temperature. Deep orange crystals of 2 separated upon concentration and cooling to -30 °C (1.6 g, 4.85 mmol, 74%). Anal. Calcd (found) for C<sub>12</sub>H<sub>21</sub>N<sub>3</sub>Cl<sub>3</sub>Ti: C, 44.20 (44.18); H, 6.49 (6.37); N, 12.89 (12.44); Ti, 14.68 (14.09); Cl, 21.74 (21.77). IR (Nujol, KBr, cm<sup>-1</sup>): 1570 (m), 1505 (w), 1460 (s), 1375 (m), 1310 (s), 1290 (w), 1275 (w), 1235 (w), 1170 (w), 1160 (w), 1120 (m), 1100 (w), 1065 (s), 1040 (s), 1020 (m), 1010 (s), 1000 (s), 970 (s), 950 (s), 900 (m), 800 (s), 760 (s), 680 (m), 590 (m), 525 (s), 505 (m), 440 (w), 390 (m), 365 (s). <sup>1</sup>H NMR (THF-*d*<sub>6</sub>, 200 MHz, 25 °C): δ 6.98 (s, 1 H, phenyl), 6.97 (s, 1 H, phenyl), 6.95 (s, 2 H, phenyl), 6.68 (m, 1 H, phenyl), 2.73 (broad singlet, 16 H, CH<sub>3</sub> and CH<sub>2</sub>, TMEDA). <sup>13</sup>C NMR (THF-*d*<sub>6</sub>, 75.43 MHz, 17 °C): δ 160.48 (C, phenyl) 128.52, 124.03, 122.07 (phenyl), 69.03 (CH<sub>2</sub>, TMEDA), 59.37, 56.74 (CH<sub>3</sub>, TMEDA).

**X-ray Crystallography. Complex 1.** A deep orange crystal was sealed in a glass capillary and mounted on a Siemens R3m/V diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Cell constants and orientation matrix were obtained from a least-squares refinement of the setting angles of 25 reflections in the range 5.4 <  $\theta$  < 23.2. The data were collected at room temperature using the  $\omega$  scan technique to a maximum 2 $\theta$  value of 55.0°. Semi-empirical absorption corrections were applied to the data. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using the Siemens SHELXTL PLUS program. Full-matrix least-squares refinement with anisotropic thermal parameters of 133 parameters and 1576 reflections out of 3367 converged to  $R = 0.049$  ( $R_w = 0.061$ ). Non-hydrogen atoms of the acetonitrile molecule were isotropically refined. Hydrogen atoms were introduced at their calculated positions in the last refinement cycle. Neutral-atom scattering factors were taken from Cromer and Waber.<sup>18</sup> Details on crystal data and structure solution and refinement are given in Table I. Atomic coordinates and isotropic thermal parameters are reported in Table II. Relevant bond distances and angles are given in Table IV.

**Complex 2.** A red block-shaped crystal sealed in a glass capillary was mounted on a Rigaku AFC6S diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Cell constants and orientation matrix for data collection, obtained from a least-squares refinement of 21 carefully centered reflections in the range 38.27 <  $\theta$  < 39.76°, corresponded to a monoclinic cell. The data were collected at 23 °C using the  $\omega$ -2 $\theta$  scan technique to a maximum 2 $\theta$  value of 47.0°. Of the 2628 reflections which were collected, 2502 were unique. The intensities of three representative reflections, which were measured every 150 reflections, remained constant throughout data collection, indicating crystal and instrument stability (no decay correction was applied). Azimuthal scans of several reflections indicated no need for absorption corrections. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1536 observed reflections [ $I > 3.00\sigma(I)$ ] and 163 variable parameters. Convergence was reached at  $R = 0.034$  ( $R_w = 0.042$ ). Neutral-atom scattering factors were taken from Cromer and Waber.<sup>18</sup> Anomalous dispersion effects were included in  $F_o$ . Details on crystal data collection and structure solution and refinement are reported in Table I. Atomic coordinates and isotropic thermal parameters are given in

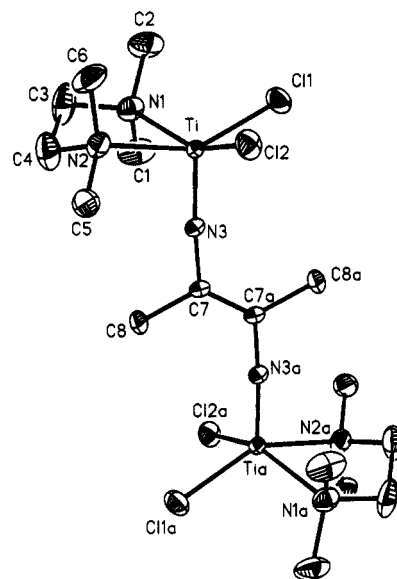


Figure 1. ORTEP drawing of 1 showing the labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

### Scheme I

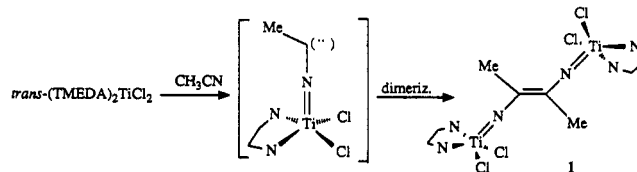


Table III. Relevant bond distances and angles are reported in Table IV. All calculations were performed using the TEXSAN<sup>19</sup> crystallographic software package of the Molecular Structure Corp., using a Digital VAX computer.

### Results and Discussion

The reaction of (TMEDA)<sub>2</sub>TiCl<sub>2</sub> in neat acetonitrile proceeds at -30 °C to produce deep orange crystals of [*trans*-NC(Me)=C(Me)N][TiCl<sub>2</sub>(TMEDA)]<sub>2</sub> (1) (Scheme I).

The structure of 1, as demonstrated by X-ray diffraction analysis, consists of two square-pyramidal TiCl<sub>2</sub>(TMEDA) fragments linked together by a *trans*-[N-C(Me)=C(Me)-N]<sup>4-</sup> moiety (Figure 1). The Ti-N distance formed by the nitrogen atoms of the eneimidato group is very short [Ti-N = 1.699 (4) Å], suggesting some triple bond character. The C-N distance [C7-N3 = 1.384 (5) Å] and the C-C distance [C7-C7a = 1.337 (10) Å] are in agreement with the proposed formulation and indicate a considerable electronic delocalization over the organic fragment. The geometry around the transition metal is best described as slightly distorted square-pyramidal with an axial eneimido group. Two chlorine and two nitrogen atoms from one molecule of TMEDA bound to the basal plane [Cl1-Ti-Cl2 = 93.7 (1)°; Cl1-Ti-N1 = 88.4 (2)°; N1-Ti-N2 = 77.8 (2)°] reaching normal values of the Ti-Cl [Ti-Cl1 = 2.343 (2) Å] and Ti-N [2.280 (6) Å] distances.

Complex 1 is diamagnetic, and consistent <sup>1</sup>H NMR data could be obtained only in CD<sub>3</sub>CN solution due to its extremely poor solubility in the common inert organic solvents. Fast decomposition was observed in chlorinated and coordinating solvents (THF, pyridine, DMF). <sup>13</sup>C NMR spectra were recorded in the solid state, due to the very poor solubility of the sample and its limited thermal stability at room temperature.

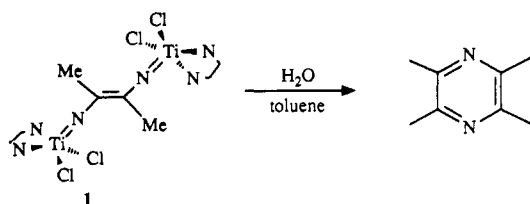
Formation of the dimetallic 1 proceeds probably via transfer of two electrons from the metal center to a coordinated molecule of CH<sub>3</sub>CN (Scheme I). The resulting carbene-like species forms

(18) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

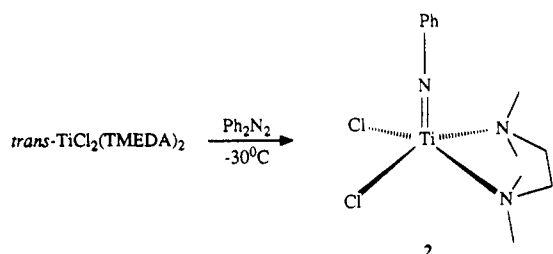
(19) Texsan-Textray Structure Analysis Package. Molecular Structure Corp., 1985.

(20) Braam, A. W. M.; Eshuis, A.; Vos, A. *Acta Crystallogr.* **1951**, *37*, 730.

Scheme II



Scheme III



the final product via either direct dimerization or reaction with a second molecule of acetonitrile and unreacted starting Ti(II) complex. The solution NMR data, consistent with the solid-state formulation, suggest that the reaction cannot be reversed. There was no evidence for the presence of the cis isomer either in the pure sample or in the mother liquor. We find this selectivity remarkable, when one considers that no significant steric hindrance is present in complex 1. This complex provides the first case where the four-electron reductive coupling of acetonitrile takes place on a mononuclear system, this kind of transformation having so far been observed only with multiply bonded di- or polymetallic systems.<sup>14,15</sup>

Attempts to demetallate the organic fragment via hydrolysis gave moderate yield (47%) of tetramethylpyrazine (TMP) as a colorless crystalline material (Scheme II).<sup>17</sup> This compound could be isolated only when the hydrolysis was carried out under inert atmosphere with the use of 4 equiv of water. Intractable mixtures have been obtained in all the other cases. It is difficult to rationalize the unexpected formation of this heterocyclic compound during the hydrolysis since the cyclic structure imply rearrangement of the  $[N-C(Me)=C(Me)-N]^{4-}$  moiety from the trans to the cis configuration. Attempts to isolate and identify the inorganic residue failed.

The stability of the Ti-N multiple bond, as suggested by the very short Ti-N distance, is probably high and is likely the thermodynamic driving force for the preliminary reduction of  $CH_3CN$ . In agreement with this hypothesis, the Ti-imido function can be easily formed with other organic precursors. The reaction of  $(TMEDA)_2TiCl_2$  with azobenzene for example, proceeds at  $-30^\circ C$  in THF to form the corresponding  $(TMEDA)Cl_2Ti=NPh$  (**2**) in good yield (Scheme III). The ease of this reaction is in contrast to the hard pyrolytic conditions employed for the preparation of  $(ArO)_2Ti(NPh)py_2$ ,<sup>16</sup> underlying the versatility of  $TiCl_2(TMEDA)_2$  as a synthetic tool. Furthermore, the presence of two "reactive" chlorine atoms in **1** and **2** is especially desirable for further reactivity studies, including toward reduction and alkylation reactions. The structure of **2**, as demonstrated by X-ray analysis, shows the monomeric complex basically isostructural with the monomeric fragment of **1** forming comparable bond distances and angles (Figure 2). The Ti=N distance [Ti-N = 1.702 (6) Å] is slightly shorter than in the previously reported  $(ArO)_2Ti(NPh)(py)_2$ ,<sup>16a</sup> probably as a result of decreased steric hindrance. There is no prohibitive steric hindrance in complex **2**; therefore, we suggest that the unusual pyramidal geometry, generally observed among group 4 metal imidates,<sup>16</sup> may be determined by electronic factors.

Finally the reaction of  $(TMEDA)_2TiCl_2$  with  $Me_3SiN_3$  led to the formation in low yield of the thermally unstable  $(TMEDA)TiCl_2N_3$  as a light blue crystalline solid. The characteristic absorption at  $\nu = 1980\text{ cm}^{-1}$  of the IR spectrum suggested the

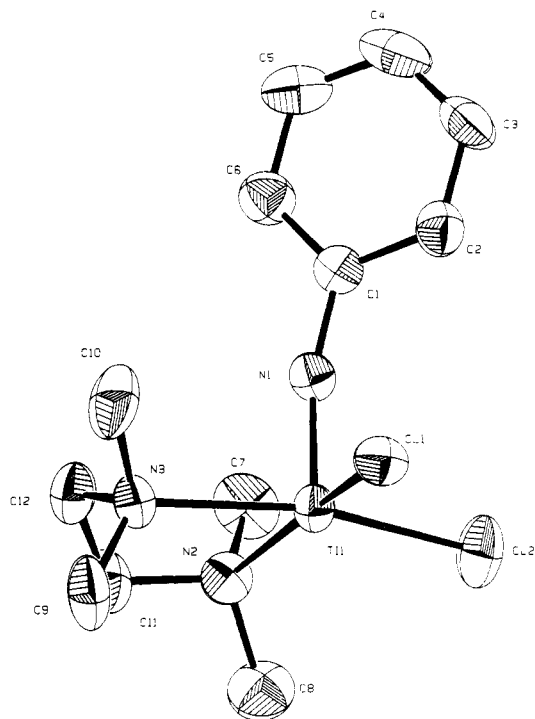


Figure 2. ORTEP drawing of **2** showing the labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

presence of a bent terminally bonded azido group.

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**Supplementary Material Available:** Tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **1** and **2** (21 pages); tables listing observed and calculated structure factors for **1** and **2** (24 pages). Ordering information is given on any current masthead page.

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### Simple Syntheses and Alkylation Reactions of 3-Iodo-*o*-carborane and 9,12-Diiodo-*o*-carborane<sup>1</sup>

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Although 3-chloro-,<sup>2a,b</sup> 3-bromo-,<sup>2c</sup> and 3-fluoro-*o*-carborane<sup>2b</sup> are all known, 3-iodo-*o*-carborane (**1**) is not. In this note, we first describe a modification of our recent recipe for 3-bromo-*o*-carborane<sup>2c</sup> that produces **1** in good yield and purity. Next, we report an extension of our route to 9-iodo-*o*-carborane<sup>3</sup> to give

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- (2) (a) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V. *J. Organomet. Chem.* **1969**, *16*, 371. (b) Roscoe, J. S.; Kongpricha, S. *Inorg. Chem.* **1970**, *9*, 1561. (c) Li, J.; Jones, M., Jr. *Inorg. Chem.* **1990**, *29*, 4162.
- (3) (a) Andrews, J. S.; Zayas, J.; Jones, M., Jr. *Inorg. Chem.* **1985**, *24*, 3715. (b) See also: Zakharkin, L. I.; Ol'shevskaya, V. A.; Poroshina, T. Yu.; Balagurova, E. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1987**, *57*, 1800.