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Reductions of β-Diketiminato−Titanium(III) Complexes

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The reductions of (Nacnac)Ti(III) complexes (Nacnac = (HC(CMeNC$_6$H$_3$(i-Pr)$_2$)$_2$) are examined. Treatment of (Nacnac)TiCl$_2$ with K/Na alloy in the presence of CH$_2$(PPh$_2$)$_2$ afforded the dark red product [K(C(Me)CHC(Me)NAr)Ti(NAr)(μ-H)]$_2$ (**2**). This Ti(III)-imido-hydride complex is a product of Nacnac ligand cleavage. The Ti(III) species (Nacnac)CpTiCl (**3**) and (Nacnac)(C$_5$Me$_4$H)TiCl (**4**) were prepared and characterized. While compound **3** was readily alkylated with n-BuLi to give (Nacnac)CpTiBu (**5**), reduction of **3** with Na/K gave the dinitrogen complex ((Nacnac)CpTi)$_2$(μ-η^2-N$_2$) (**6**). In contrast, treatment of **4** with t-BuLi or n-BuLi or Na/K amalgam afforded the ligand cleavage product (C$_5$Me$_4$H)[(ArNC(Me)CHC(Me)]Ti(NAr) (**7**). Compounds **2**−**7** are crystallographically characterized. The effects of the nature of the ancillary ligands on the course of these reactions are considered.

Introduction

β-Diketiminate ligand (Nacnac) complexes have been the subject of a considerable renaissance in recent years. For example, these ligands have been used in main group[1−8] and lanthanide[3,9−12] chemistry, as well as a variety of transition metal chemistry.[7,13−46] A number of recent studies have focused on the formation of low-coordinate β-diketiminato transition metal complexes.[7,13−25,47−49] For example, Warren and co-workers

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(1) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *Organometallics* **2005**, *24*, 1184−1188.

(2) Dove, A. P.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2004**, 570−578.

(3) Avent, A. G.; Caro, C. F.; Hitchcock, P. B.; Lappert, M. F.; Li, Z.; Wei, X.-H. *Dalton Trans.* **2004**, 1567−1577.

(4) El-Kaderi, H. M.; Xia, A.; Heeg, M. J.; Winter, C. H. *Organometallics* **2004**, *23*, 3488−3495.

(5) Harder, S. *Organometallics* **2002**, *21*, 3782−3787.

(6) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S.; Sablong, R. *Chem. Commun.* **2002**, 1920−1921.

(7) Ding, Y.; Ma, Q.; Roesky, H. W.; Herbst-Irmer, R.; Uson, I.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2002**, *21*, 5216−5220.

(8) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806−4811.

(9) Hitchcock, P. B.; Lappert, M. F.; Protchenko, A. V. *Chem. Commun.* **2005**, 951−953.

(10) Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Herbst-Irmer, R.; Walfort, B.; Stalke, D. *Organometallics* **2003**, *22*, 2279−2283.

(11) Zhang, Y.; Yao, Y.-M.; Luo, Y.-J.; Shen, Q.; Cui, Y.; Yu, K.-B. *Polyhedron* **2003**, *22*, 1241−1247.

(12) Hitchcock, P. B.; Lappert, M. F.; Tian, S. *Dalton Trans.* **1997**, 1945−1952.

(13) Smith, K. M. *Organometallics* **2005**, *24*, 778−784.

(14) Vela, J.; Vaddadi, S.; Cundari, T. R.; Smith, J. M.; Gregory, E. A.; Lachicotte, R. J.; Flaschenriem, C. J.; Holland, P. L. *Organometallics* **2004**, *23*, 5226−5239.

(15) Eckert, N. A.; Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2004**, *43*, 3306−21.

(16) Gregory, E. A.; Lachicotte, R. J.; Holland, P. L. *Organometallics* **2005**, *24*, 1803−1805.

(17) Eckert, N. A.; Bones, E. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2003**, *42*, 1720−5.

(18) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752−15753.

(19) Andres, H.; Bominaar, E. L.; Smith, J. M.; Eckert, N. A.; Holland, P. L.; Munck, E. *J. Am. Chem. Soc.* **2002**, *124*, 3012−25.

(20) Vela, J.; Smith Jeremy, M.; Lachicotte Rene, J.; Holland Patrick, L. *Chem. Commun.* **2002**, 2886−7.

(21) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Organometallics* **2002**, *21*, 4808−4814.

(22) Jazdzewski, B. A.; Holland, P. L.; Pink, M.; Young, V. G., Jr.; Spencer, D. J. E.; Tolman, W. B. *Inorg. Chem.* **2001**, *40*, 6097−6107.

(23) Randall, D. W.; DeBeer George, S.; Holland, P. L.; Hedman, B.; Hodgson, K. O.; Tolman, W. B.; Solomon, E. I. *J. Am. Chem. Soc.* **2000**, *122*, 11632−11648.

(24) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270−7271.

(25) Puiu, S. C.; Warren, T. H. *Organometallics* **2003**, *22*, 3974−3976.

(26) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416−24.

(27) Aboulkacem, S.; Tyrra, W.; Pantenburg, I. *Z. Anorg. Allge. Chem.* **2003**, *629*, 1569−1574.

(28) Amisial, L. D.; Dai, X.; Kinney, R. A.; Krishnaswamy, A.; Warren Timothy, H. *Inorg. Chem.* **2004**, *43*, 6537−9.

(29) Basuli, F.; Kilgore, U. J.; Brown, D.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2004**, *23*, 6166−6175.

(30) Dai, X.; Kapoor, P.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 4798−4799.

(31) Doherty, J. C.; Ballem, K. H. D.; Patrick, B. O.; Smith, K. M. *Organometallics* **2004**, *23*, 1487−1489.

(32) Franceschini, P. L.; Morstein, M.; Berke, H.; Schmalle, H. W. *Inorg. Chem.* **2003**, *42*, 7273−7282.

(33) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132−2133.

(34) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622−5623.

(35) Holland, P. L.; Rodgers, K. R.; Tolman, W. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 1139−1142.

(36) Knight, L. K.; Piers, W. E.; Fleurat-Lessard, P.; Parvez, M.; McDonald, R. *Organometallics* **2004**, *23*, 2087−2094.

(37) Lauterwasser, F.; Hayes, P. G.; Braese, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234−2237.

(38) MacAdams, L. A.; Kim, W.-K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952−960.

(39) Neculai, A. M.; Roesky, H. W.; Neculai, D.; Magull, J. *Organometallics* **2001**, *20*, 5501−5503.

(40) Nikiforov, G. B.; Roesky, H. W.; Magull, J.; Labahn, T.; Vidovic, D.; Noltemeyer, M.; Schmidt, H.-G.; Hosmane, N. S. *Polyhedron* **2003**, *22*, 2669−2681.

(41) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752−15753.

(42) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222−9223.

(43) Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108−2109.

(44) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307−6321.

(45) Vela, J.; Stoian, S.; Flaschenriem Christine, J.; Munck, E.; Holland Patrick, L. *J. Am. Chem. Soc.* **2004**, *126*, 4522−4523.

(46) Wiencko, H. L.; Kogut, E.; Warren, T. H. *Inorg. Chim. Acta* **2003**, *345*, 199−208.

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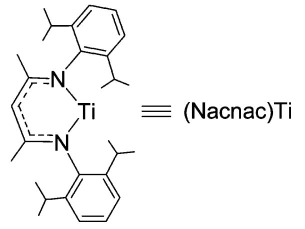
Scheme 1. Nacnac Ligand Structure



have described three-coordinate β-diketiminato-nickel[25] and -cobalt[30] complexes derived from Ni(I) and Co(I) precursors, while Holland and co-workers[41] have described the chemistry of a three-coordinate β-diketiminato-iron hydride complex. Our interests in related chemistry have focused on the synthesis and chemistry of low-valent β-diketiminato complexes. In our first report of efforts in this area, we recently described the complex [(Nacnac)Ni)$_2$(μ-η^3-η^3-C_6H_5Me)], which acts as a synthon for a variety of β-diketiminato Ni(I) complexes,[50] while a subsequent report described the reactivity of Ni(I) and Fe(I) species with primary phosphines.[51] Low-valent early metal complexes have drawn limited attention to date, although Mindiola and co-workers have described β-diketiminato Zr complexes.[29] They showed that reduction of such species led to β-diketiminato ligand cleavage reactions and the formation of Zr-imido complexes. The Mindiola group has also recently probed the chemistry of β-diketiminato-Ti-alkylidenes.[52,53] In this article, we examine the reduction chemistry of (Nacnac)Ti(III) complexes (Scheme 1) resulting in the formation of a Ti-dinitrogen complex as well as products of β-diketiminato ligand cleavage reactions. The nature of these products and the impact of ancillary ligands on the reaction course are discussed.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubbs-type solvent purification system manufactured by Innovative Technology. Deuterated solvents were purified using the appropriate techniques. All organic reagents were purified by conventional methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All NMR spectra were recorded in C_6D_6 at 25 °C. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. EPR spectra were recorded on an X-band Bruker ESP 300E spectrometer equipped with an electromagnet capable of providing a magnetic field from 50 G to 15 kG, a gaussmeter, and a microwave counter. Typical measurement conditions were microwave power 20 mW, microwave frequency 9.7 GHz, modulation amplitude 3.830 G, and 4K data points covering a sweep range of 4000 G. IR spectra were recorded on a Bruker FTIR spectrometer. Combustion analyses were done in-house employing a Perkin-Elmer CHN analyzer. In this paper, the abbreviation Nacnac refers to the β-diketiminate ligand (HC($CMeNC_6H_3$(i-Pr)$_2$)$_2$ and Ar = $CMeNC_6H_3$(i-Pr)$_2$. The compound (Nacnac)$TiCl_2$ (**1**) was prepared by known methods.[40,54]

Synthesis of [(η^2-ArNC(Me)CHC(Me))(ArN)Ti(μ-H)]$_2$K$_2$, 2. Compound **1** (1.072 g, 2.0 mmol), $CH_2(Ph_2P)_2$ (0.768 g, 2.0 mmol), and K/Na alloy (0.234 g K, 6.0 mmol; 0.066 g Na, 2.8 mmol) were combined in toluene (15 mL) at 25 °C and stirred for one week. After filtration and concentration to 5 mL in vacuo, dark red crystals of **2** (0.12 g) were obtained upon standing of this solution at −35 °C. Further concentration to 3 mL and standing at −35 °C yielded more crystals of **2**. Total yield of crystalline product: 0.23 g (23%). IR (Nujol) (cm^{-1}): 1954 (br w), 1883 (br w), 1810 (br w), 1716 (w), 1698 (w), 1684 (w), 1653 (br w), 1575 (s), 1463 (s), 1432 (s), 1407 (s), 1378 (s), 1356 (m), 1323 (s), 1254 (s), 1210 (m), 1177 (m), 1136 (m), 1094 (s), 1041 (m), 1025 (m), 999 (m), 917 (s), 795 (m), 744 (s), 696 (s), 603 (m), 502 (m), 480 (m), 421 (m). EPR(C_7H_8): $g = 1.918$. Anal. Calcd for $C_{58}H_{84}N_4Ti_2K_2$ (1011.3): C 68.9, H 8.4. Found: C 68.5, H 7.5. (N analysis was performed repeatedly on crystalline samples and was consistently low. This is attributed to the formation of TiN.)

Synthesis of (Nacnac)CpTiCl, 3, and (Nacnac)(C_5Me_4H)TiCl, 4. These compounds were prepared in a similar fashion, and thus one preparation is detailed. THF (25 mL) was added to the mixture of **1** (2.144 g, 4.0 mmol) and CpLi (0.288 g, 4.0 mmol) at 25 °C. Stirring was continued overnight, and the solvent was removed. Toluene (20 mL) was added, and the suspension was stirred for 0.5 h. After filtration and subsequent concentration (to 10 mL) in vacuo, the resulting deep brown solution was kept at −35 °C overnight to isolate dark red crystals of **3** (1.25 g). After concentration of the filtrate to 3 mL, the solution was kept at −35 °C for 3 days. An additional crop of **3** (0.81 g) was formed. Yield: 2.06 g (91%). IR (Nujol): 1923 (w), 1868 (w), 1837 (w), 1796 (w), 1772 (m), 1697 (m), 1650 (m), 1519 (s), 1460 (s), 1374 (s), 1310 (s), 1250 (s), 1168 (m), 1100 (m), 1014 (s), 927 (m), 849 (m), 800 (s), 764 (m), 728 (m), 699 (w), 669 (w), 640 (w), 522 (m), 446 (m) cm^{-1}. EPR: 1.973. Anal. Calcd for $C_{34}H_{46}ClN_2Ti$ (566.1): C 72.1, H 8.2, N 5.0. Found: C 72.3, H 8.7, N 5.0. **4**: Yield 2.9 g (78%). IR (Nujol): 1924 (w), 1861 (w), 1796 (w), 1624 (w), 1532 (s), 1434 (s), 1382 (s), 1312 (s), 1274 (s), 1249 (s), 1173 (s), 1110 (s), 1097 (s), 1057 (m), 1020 (s), 969 (m), 922 (s), 846 (s), 794 (s), 761 (s), 727 (m), 698 (m), 638 (m), 613 (m), 563 (w), 522 (s), 492 (w), 459 (m), 441 (m) cm^{-1}. EPR: 1.954. Anal. Calcd for $C_{38}H_{54}ClN_2Ti$ (622.20): C 73.4, H 8.8, N 4.5. Found: C 73.5, H 8.8, N 4.6.

Synthesis of (Nacnac)CpTiBu, 5. n-BuLi (2.5 M in hexane; 0.4 mL, 1.0 mmol) was added to a solution of **3** (0.57 g, 1.0 mmol) in toluene (10 mL) at 25 °C. Stirring was continued overnight, and the solution was filtered and subsequently concentrated to 5 mL in vacuo. The resulting deep brown solution was kept at −35 °C overnight to isolate dark red crystals of **5** (0.45 g). After concentration of the filtrate to 3 mL, the solution was kept at −35 °C for 3 days. An additional crop of **5** (0.09 g) was formed. Yield: 0.54 g (92%). IR (Nujol): 1923 (w), 1860 (w), 1797 (w), 1716 (w), 1682 (w), 1622 (w), 1603 (w), 1580 (w), 1529 (s), 1459 (s), 1436 (s), 1381 (s), 1311 (s), 1277 (m), 1253 (s), 1190 (w), 1168 (m), 1056 (m), 1040 (m), 1020 (s), 959 (m), 930 (s), 867 (w), 849 (m), 794 (s), 757 (m), 728 (m), 698 (m), 623 (m), 601 (w), 542 (w), 522 (m), 445 (m) cm^{-1}. EPR: 1.967. Anal. Calcd for $C_{38}H_{55}N_2Ti$ (587.76): C 77.7, H 9.4, N 4.8. Found: C 77.9, H 9.6, N 4.6.

Synthesis of ((Nacnac)CpTi)$_2$(μ-η^2-N_2), 6. Toluene (15 mL) was added to the mixture of **3** (0.580 g, 1.00 mmol) and K/Na alloy (0.030 g K, 0.77 mmol; 0.011 g Na, 0.48 mmol) at 25 °C and was stirred for one week. After filtration and subsequent concentration (to 5 mL) in vacuo, the resulting deep red solution was kept at −35 °C for one week to isolate dark red crystals of **6** (0.22 g). After concentration of the filtrate to 3 mL, the solution was kept at

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(47) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416−14424.

(48) Zhang, D.; Jin, G.-X.; Weng, L.-H.; Wang, F. *Organometallics* **2004**, *23*, 3270−3275.

(49) Kogut, E.; Wiencko Heather, L.; Zhang, L.; Cordeau Douglas, E.; Warren Timothy, H. *J. Am. Chem. Soc.* **2005**, *127*, 11248−11249.

(50) Bai, G.; Wei, P.; Stephan, D. W. *Organometallics* **2005**, *24*, 5901−5908.

(51) Bai, G.; Wei, P.; Das, A.; Stephan, D. W. *Dalton Trans.* **2006**, 0000.

(52) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 1886−1906.

(53) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 3321−3334.

(54) Budzelaar, P. H. M.; Oort, A. B. v.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485.

Table 1. Crystallographic Data

	2	**3**	**4**	**5**	**6**·2C_6H_6·THF	**7**
formula	$C_{58}H_{86}K_2N_4Ti_2$	$C_{34}H_{46}ClN_2Ti$	$C_{38}H_{54}ClN_2Ti$	$C_{38}H_{55}N_2Ti$	$C_{78}H_{106}N_6OTi_2$	$C_{38}H_{54}N_2Ti$
fw	1013.30	566.08	622.18	587.74	1239.49	586.73
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	*Pnma*	$P\bar{1}$	$P\bar{1}$
a (Å)	11.920(4)	10.2513(10)	10.6011(14)	17.009(3)	12.4323(15)	10.2831(19)
b (Å)	15.273(5)	25.950(3)	12.4442(16)	20.219(3)	14.2063(17)	11.695(2)
c (Å)	15.817(5)	12.4811(12)	14.6844(19)	10.0920(15)	21.938(3)	16.354(3)
α (deg)			105.829(2)		94.297(2)	74.933(2)
β (deg)	90.312(7)	105.8820(10)	94.417(2)		103.003(2)	73.761(2)
γ (deg)			106.856(2)		97.792(2)	70.496(2)
V (Å^3)	2879.6(16)	3193.5(5)	1757.8(4)	3470.6(9)	3718.1(8)	1749.4(6)
Z	2	4	2	4	2	2
d(calc) (gcm^{-1})	1.164	1.177	1.175	1.125	1.107	1.114
μ (mm^{-1})	0.460	0.379	0.347	0.273	0.260	0.271
no. of data collected	13 924	30 470	17 021	31 899	36 087	16 635
R(int)	0.0794	0.0480	0.0378	0.0507	0.0929	0.0675
no. of data $F_o^2 > 3\sigma(F_o^2)$	4206	5622	6179	3141	13 015	6137
no. of variables	306	343	379	205	712	370
R	0.0561	0.0575	0.0555	0.0475	0.0845	0.0655
R_w	0.1399	0.1408	0.1465	0.1223	0.2137	0.1467
GOF	1.016	1.045	1.025	1.061	0.971	1.025

−35 °C for 3 days. An additional crop of **6** (0.10 g) was formed. Yield: 0.32 g (59%). IR (Nujol): 1935 (w), 1866 (w), 1799 (w), 1697 (w), 1620 (w), 1582 (m), 1526 (s), 1497 (s), 1462 (s), 1436 (s), 1422 (s), 1384 (s), 1367 (s), 1344 (s), 1312 (s), 1278 (m), 1256 (s), 1231 (m), 1187 (m), 1170 (s), 1105 (s), 1056 (m), 1041 (m), 1018 (sw), 964 (m), 930 (s), 898 (m), 852 (m), 796 (s), 759 (s), 728 (m), 717 (m), 837 (w) 626 (m), 603 (w), 542 (w), 527 (m), 510 (w), 455 (m) cm^{-1}. ^{1}H NMR: 7.21−6.99 (m, *Ar*), 5.96 (s, 5 H, *Cp*), 5.68 (s, 1 H, *γ*-C*H*), 3.74 (sept, $^3J_{HH}$ = 7 Hz, 1 H, C*H*Me$_2$), 3.30 (sept, $^3J_{HH}$ =7 Hz, 1 H, C*H*Me$_2$), 2.90, 2.89 (d sept, $^3J_{HH}$ =7 Hz, 2 H, C*H*Me$_2$), 1.85, 1.84 (ds, 6 H, C*Me*), 1.77 (d, $^3J_{HH}$ = 7 Hz, 3 H, CH*Me*$_2$), 1.38, 1.36, 1.35 (td, $^3J_{HH}$ = 6 Hz, 9 H, CH*Me*$_2$), 1.22, 1.21 (dd, $^3J_{HH}$ = 6, 6 Hz, 9 H, CH*Me*$_2$), 1.14 (d, $^3J_{HH}$ = 7 Hz, 3 H, CH*Me*$_2$). ^{13}C NMR: 166.9, 166.4 (N*C*), 149.8, 147.7, 145.5, 143.8, 142.4, 141.4, 125.9, 125.0, 124.8, 124.8, 124.0, 112.6 (*Ar*), 105.2 (*γ*-*C*), 28.6, 28.5, 27.7, 27.1 (*C*HMe$_2$), 27.0, 26.3, 26.3, 26.0, 25.8, 25,7, 25.6, 25.4 (CH*Me*$_2$), 24.9, 24.6 (NC*Me*). Anal. Calcd for $C_{68}H_{92}N_6Ti_2$ (1089.29): C 75.0, H 8.5, N 7.7. Found: C 75.2, H 8.9, N 6.9.

Synthesis of (C_5Me_4H)[(ArNC(Me)CHC(Me)]Ti(NAr), 7. Method A: THF (25 mL) was added to the mixture of **1** (2.144 g, 4.0 mmol) and Me_4HC_5Li (0.513 g, 4.0 mmol) at 25 °C and stirred for 8 h. *t*-BuMgBr (2.0 M in ether; 2 mL, 4.0 mmol) was added to the above mixture. The resulting reddish-brown solution was stirred overnight. After removal of THF, toluene (20 mL) was added, and the suspension was stirred for 0.5 h. After filtration and subsequent concentration (to ca. 5 mL) in vacuo, hexane (10 mL) was added. The resulting deep red solution was kept at −35 °C overnight to isolate dark red crystals of **7** (1.12 g). After removal of the solvents, hexane (5 mL) was added, and the solution was kept at −35 °C for 3 days. An additional crop of **7** (0.25 g) was formed. Yield: 1.37 g (58%). Method B: Toluene (30 mL) was added to a mixture of **4** (0.622 g, 1.00 mmol) and K/Na alloy (0.030 g K, 0.77 mmol; 0.011 g Na, 0.48 mmol) at room temperature. The mixture was stirred for one week at this temperature. After filtration and subsequent concentration (to 5 mL) in vacuo, the resulting deep red solution was kept at −35 °C for one week to isolate dark red crystals of **7** (0.20 g). After concentration of the filtrate to 3 mL, the solution was kept at −35 °C for 3 days. An additional crop of **7** (0.07 g) was formed. Yield: 0.27 g (46%). Method C: Treatment of **4** with 1 equiv of *n*-BuLi led also to **7** in a yield similar to that in method A. IR (Nujol): 1897 (w), 1792 (w), 1693 (w), 1582 (m), 1528 (m), 1460 (s), 1416 (s), 1377 (s), 1342 (s), 1280 (s), 1253 (s), 1179 (m), 1104 (m), 1027 (s), 959 (m), 920 (m), 880 (s), 794 (s), 679 (m), 605 (m), 525 (m) cm^{-1}. ^{1}H NMR: 7.05−6.82 (m, 6 H, *Ar*), 6.44, 6.43, 6.43, 6.42 (s, 1 H, Me$_4$C$_5$*H*), 5.61 (s, 1 H, *C*MeC*H*CMe), 3.90 (sept, $^3J_{HH}$ = 7 Hz, 2 H, C*H*Me$_2$), 3.70 (sept, $^3J_{HH}$ = 7 Hz, 1 H, C*H*Me$_2$), 2.82 (sept, $^3J_{HH}$ = 7 Hz, 1 H, C*H*Me$_2$), 2.48, 2.47 (ds, 3 H, TiC*Me*), 2.11 (s, 3 H, *Me*$_4$C$_5$H), 2.09 (s, 3 H, *Me*$_4$C$_5$H), 1.99 (s, 3 H, *Me*$_4$C$_5$H), 1.90 (s, 3 H, *Me*$_4$C$_5$H), 1.54 (s, 3 H, NC*Me*), 1.34 (d, $^3J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.27 (d, $^3J_{HH}$ = 7 Hz, 3 H, CH*Me*$_2$), 1.01 (d, $^3J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 0.94 (dd, $^3J_{HH}$ = 7 and 7 Hz, 6 H, CH*Me*$_2$), 0.80 (d, $^3J_{HH}$ = 7 Hz, 3 H, CH*Me*$_2$). ^{13}C NMR: 252.8 (Ti*C*Me), 178.7 (N*C*), 155.9 (*Ar*), 145.0, 144.6, 143.5, 140.8, 127.4, 126.9, 125.9, 123.9, 122.8, 122.7, 121.5, 121.3, 121.0, 119.7 (*Ar* or *C*Me of Me$_4$C$_5$H), 111.3 (Ti*C*Me), 31.2 (*C*H of Me$_4$C$_5$H), 28.2, 28.1, 27.8 (*C*HMe$_2$), 25.7, 25.6, 24.9, 24.5, 24.3 (CH*Me*$_2$), 24.3(NC*Me*), 24.0 (TiC*Me*CHCMe), 13.9, 13.7, 12.7, 12.5 (*Me*$_4$C$_5$H). Anal. Calcd for $C_{38}H_{54}N_2Ti$ (586.75): C 77.8, H 9.3, N 4.8. Found: C 77.9, H 9.4, N 4.6.

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1448 frames with 10 s exposure times (4.5° < 2*θ* < 45−50.0°). The observed extinctions were consistent with the space groups in each case. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement were performed using the SHELXTL solution package.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[55] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on *F*, minimizing the function $w(F_o - F_c)^2$, where the weight *w* is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. In the case of compound **1** the methyl group of toluene was modeled by a 50:50 two-site disorder. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H atom

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(55) Cromer, D. T.; Waber, J. T. *Int. Tables X-ray Crystallogr.* **1974**, *4*, 71−147.

contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information.

Results and Discussion

The reaction of **1**[40,54] with K/Na alloy was performed in toluene at 25 °C. The reaction mixture was stirred for 1 week and then concentrated and cooled to −35 °C. Efforts to isolate a product from this reduction led only to oils that could not be characterized. Similarly addition of donor ligands including PMe_3 and pyridine afforded no isolable solids. However, execution of the reduction in the presence of $CH_2(PPh_2)_2$, followed by concentration of the solution and standing at −35 °C, afforded dark red crystals of a new product, **2**. A second crop of **2** was obtained following isolation of the crystals and further standing at −35 °C, to give an overall yield of 23%. Crystals of **2** redissolved in toluene at 25 °C gave rise to an EPR resonance at $g = 1.918$, with a line width of about 20 G, typical of Ti(III) compounds.[56,57] IR data for **2** showed considerable changes in the fingerprint region in comparison to the IR spectrum of the precursor complex **1**,[54] suggesting the presence of ligand fragments. NMR data revealed only broad resonances and thus were not informative. It is noteworthy that removal of the solvent from the mother liquor gave a red oil, which was confirmed to be **2** by EPR spectroscopy, suggesting that the relatively low isolated yield of **2** is due to difficulties in crystallizing this compound.

The structure of **2** was unambiguously determined by an X-ray crystallographic study. Suitable crystals of **2** were obtained by recrystallization from toluene, and the structural solution revealed the formulation as [K(C(Me)CHC(Me)NAr)-Ti(NAr)(μ-H)]$_2$ (Figure 1). Despite the fact that the observation of an EPR signal for **2** suggests a momeric formulation in solution, this species is a centrosymmetric dimer in the solid state. The two Ti centers are each coordinated to a terminal imido and ene-imine fragments and bridged by two hydrides. The two K cations are situated between the pairs of arene rings on imide and ene-imine fragments (Figure 1).

The imido fragment in the asymmetric unit of **2** gives rise to a Ti−N bond length of 1.770(4) Å and a Ti−N−C angle of 175.3(3)°. This Ti−N bond distance is slightly longer than the corresponding Ti−N imido bond length of 1.729(4) Å in the Ti(IV)-imido species (PhNC(Me)C(Me)NPh)$TiCl_2$(NAr)(py),[58] consistent with the respective oxidation states.[58] The planar ene-imine fragment gives rise to a Ti−N distance of 2.029(3) Å. The Ti−C(3) bond distance is 2.189(4) Å, consistent with a formal σ-bond. The Ti−C distances to the carbons α and β to C(3) are 2.343(4) and 2.352(4) Å, respectively. These data together with the N(1)−C(1) and C−C distances in the ene-imine fragment of 1.400(5), 1.380(6), and 1.414(6) Å, respectively, are consistent with a π-interaction between Ti and the ene-imine unit analogous to that described for the Zr(IV) species [(C(*t*-Bu)CHC(*t*-Bu)NAr)ZrCl(THF)(NAr)].[29]

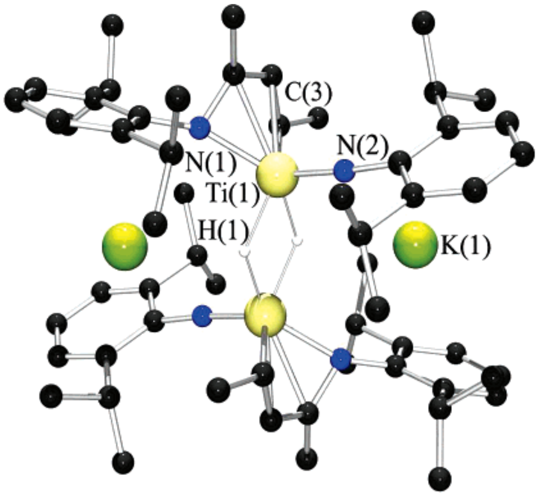

Figure 1. POV-ray drawing of the dimeric structure of **2**. Hydrogen atoms except for the hydrides are omitted for clarity. Color scheme: Ti: wheat, N: blue, K: yellow-green, C: black; H: light-grey. Selected bond distances (Å) and angles (deg): Ti(1)−N(2) 1.770(4), Ti(1)−N(1) 2.029(3), Ti(1)−C(1) 2.343(4), Ti(1)−C(2) 2.352(4), Ti(1)−C(3) 2.189(4), Ti(1)−K(1) 3.5432(17), Ti(1)−H(1) 1.824(3), Ti(1)−H(1)′ 1.818(3), N(1)−C(1) 1.400(5), N(1)−C(6) 1.435(5), C(1)−C(2) 1.380(6), C(2)−C(3) 1.414(6), N(1)−K(1) 3.042(4), N(2)−K(1) 2.807(3), N(2)−Ti(1)−N(1) 125.48(14), Ti(1)−H(1)−Ti(1)′ 115.9(3)°, N(2)−Ti(1)−C(3) 116.17(19), N(1)−Ti(1)−C(3) 86.79(15), N(2)−Ti(1)−C(1) 105.86(16), N(1)−Ti(1)−C(1) 36.47(14), C(3)−Ti(1)−C(1) 66.65(16), N(2)−Ti(1)−C(2) 103.55(15), N(1)−Ti(1)−C(2)65.83(14), C(3)−Ti(1)−C(2) 36.05(16), C(1)−Ti(1)−C(2) 34.17(14), C(1)−N(1)−C(6) 117.0(3), C(1)−N(1)−Ti(1) 84.1(2), C(6)−N(1)−Ti(1) 156.5(3), Ti(1)−N(2)−C18) 175.3(3), C(2)−C(1)−N(1) 119.1(4).

The hydride atoms in **2** were located and refined. The $Ti_2(\mu\text{-}H)_2$ core is planar with Ti−H distances of 1.824(3) and 1.818(3) Å and Ti−H−Ti′ angles of 115.9(3)°. This geometry results in a Ti−Ti′ separation of 3.0872(16) Å. These metric parameters in **2** compare with the Ti−H distances, Ti−H−Ti′ angles, and Ti−Ti′ separations of 1.77(3) Å, 1.88(3) Å, 107(2)°, and 2.931(3) Å found in [$(Me_3SiNCH_2CH_2)_2NSiMe_3$)Ti($\mu$-H)]$_2$[59] and 1.90(3) Å, 113.9(14)°, and 3.2288(18) Å found in [(Indenyl)$_2$-(CH_2CH_2)Ti(μ-H)]$_2$.[60] In addition, the Ti−Ti′ separation in the paramagnetic product **2** is much longer than that found in the triply hydride-bridged diamagnetic compound [$Li_3(THF)_2(Et_2O)$-(Ti(*t*-BuC_6H_2O($C_6H_2CH_2$(*t*-Bu)MeO)$_2$))$_2$(μ-H)$_3$] (2.6210(10) Å).[61]

The K^+ ions are positioned between the arene rings of imido and ene-imine fragments on the opposing Ti atoms (Figure 1). This positioning gives rise to K−N distances of 2.807(3) and 3.042(4) Å, which compares with the K−N distances of 2.8484(12), 2.770(3), and 2.803(3) Å seen in $KC(SiMe_3)_2(SiMe_2NMe_2)$[62] and [K[N($SiMe_3$)$_2$)]$_2$, respectively.[63] The K is positioned nearly symmetrically with respect to the *ipso* and *alpha* carbons with K−C distances of 2.884(3), 3.200(5), and 3.3311(5) Å, respectively. With respect to the imido-aryl group the K approaches isopropyl carbons at distances of 2.938(4), 3.100(5), and 3.304(5) Å, respectively. The latter K−C approach also results in a K-isopropyl hydrogen approach of 2.894(4) Å. These K−C distances are in the range seen in the benzoid radical salt [(18-crown-6)K(η^6-C_6H_5Me)], where the K−C distances range from 3.044(5) to 3.311 Å,[64] or in LuCH($SiMe_3$)$_2$(μ-Cl)K(η^6-

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(56) Dick, D. G.; Stephan, D. W. *Organometallics* **1991**, *10*, 2811−16.

(57) Sung, R. C. W.; Courtenay, S.; McGarvey, B. R.; Stephan, D. W. *Inorg. Chem.* **2000**, *39*, 2542−2546.

(58) McInnes, J. M.; Blake, A. J.; Mountford, P. *Dalton Trans.* **1998**, 3623−3628.

(59) Love, J. B.; Clark, H. C. S.; Cloke, F. G. N.; Green, J. C.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1999**, *121*, 6843−6849.

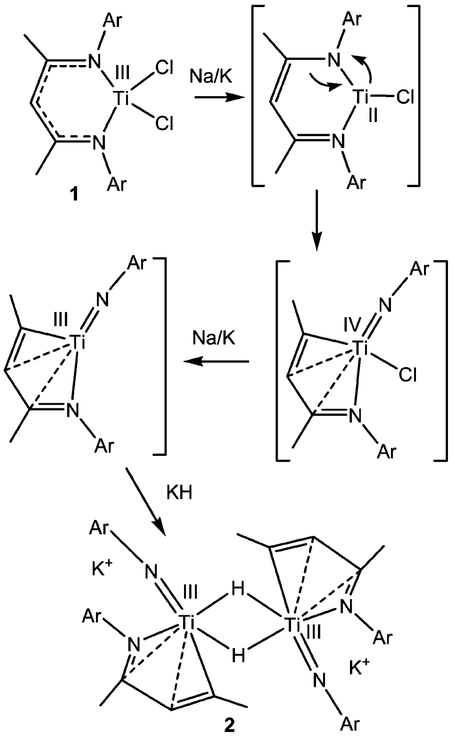
(60) Xin, S.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1994**, *116*, 11562−11563.

(61) Matsuo, T.; Kawaguchi, H. *Organometallics* **2003**, *22*, 5379.

(62) Al-Juaid, S. S.; Eaborn, C.; El-Hamruni, S.; Farook, A.; Hitchcock, P. B.; Hopman, M.; Smith, J. D.; Clegg, W.; Izod, K.; O’Shaughnessy, P. *Dalton Trans.* **1999**, 3267−3273.

(63) Tesh, K. F.; Hanusa, T. P.; Huffman, J. C. *Inorg. Chem.* **1990**, *29*, 1584−1586.

Scheme 2. Proposed Mechanism of Formation of 2



$C_6H_5Me)_2$, where the K−centroid distances are reported to be 3.003 and 3.128 Å.[65] The Ti−K separations are 3.5432(17) and 3.7482(19) Å, while the approach of K to the proximal bridging hydride is 2.272 Å.

Relatively few Ti-hydride compounds have been isolated and fully characterized. The cyclopentadienyl complexes $[Cp_2Ti(\mu\text{-}H)]_2$,[66] $[(IndenylCH_2)_2Ti(\mu\text{-}H)]_2$,[60] $[CpTi(\mu\text{-}H)(\mu\text{-fulvalene})]_2$,[67] $[(C_5Me_4Ph)_2Ti(\mu\text{-}H)_2]_2Mg$, and $(C_5Me_4Ph)[C_5Me_4(o\text{-}C_6H_4)]Ti(\mu\text{-}H)_2Mg(THF)_2$[68] are known, while the known nonmetallocene Ti-hydride complexes include $[TiH((Me_3SiNCH_2CH_2)_2NSiMe_3)]_2$,[59] $[Li_3(THF)_2(Et_2O)(Ti(t\text{-}BuC_6H_2O(C_6H_2CH_2(t\text{-}Bu)MeO)_2))_2(\mu\text{-}H)_3]$,[61] and $Ti(t\text{-}Bu_2CHNC_6H_3(t\text{-}Bu)(\mu\text{-}H)Mg(THF)_2)_2(\mu\text{-}Cl)$.[69] Thus, compound **2** represents a rare example of such nonmetallocene Ti(III)-hydride species containing Ti−C bonds.

The reaction mechanism affording **2** is the subject of speculation (Scheme 2). Related recent work by Mindiola and co-workers[29] described the reduction of the Zr(IV) species $(HC(C(Me)Ar)_2)ZrCl_3$, which results in ligand cleavage and formation of the Zr(IV) product $[(C(t\text{-}Bu)CHC(t\text{-}Bu)NArZrCl(THF)(NAr)]$. It is proposed that reduction of the Ti(III) compound $(HC(C(Me)NAr)_2)TiCl_2$ proceeds in a similar fashion through a transient Ti(II) species $(HC(C(Me)NAr)_2)TiCl$, which effects oxidative ligand cleavage to give an intermediate Ti(IV) compound $[(C(Me)CHC(Me)NAr)TiCl(NAr)]$ (Scheme 2). This compound is again reduced by excess reductant and trapped by KH to give **2**. Similar ligand rupture has been reported for related Ti(III)-alkylidene complexes employing the *t*-Bu-substituted Nacnac ligand.[52] The source of the hydride is thought to be the reaction of K/Na with $CH_2(PPh_2)_2$, although this could not be unambiguously confirmed.

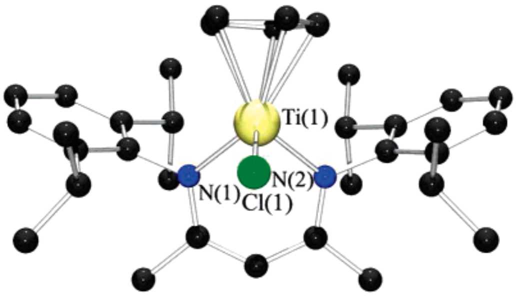


Figure 2. POV-ray drawing of **3**. Hydrogen atoms are omitted for clarity. Color scheme: Ti: wheat, Cl: green, N: blue, C: black. Selected bond distances (Å) and angles (deg): Ti(1)−N(1) 2.086(2), Ti(1)−N(2) 2.088(3), Ti(1)−Cl(1) 2.2997(13), N(1)−Ti(1)−N(2) 87.41(10), N(1)−Ti(1)−Cl(1) 101.03(8), N(2)−Ti(1)−Cl(1) 102.69(8), N(1)−Ti(1)−C(37) 108.4(2).

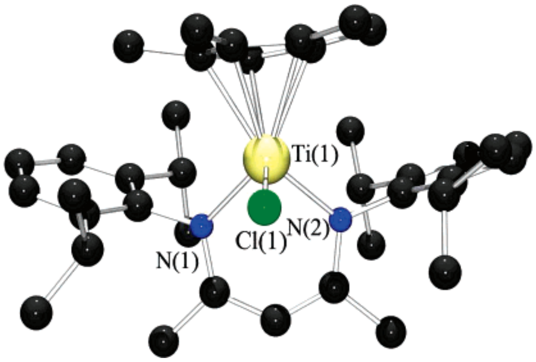


Figure 3. POV-ray drawing of **4**. Hydrogen atoms are omitted for clarity. Color scheme: Ti: wheat, Cl: green, N: blue, C: black. Selected bond distances (Å) and angles (deg): Ti(1)−N(2) 2.119(3), Ti(1)−N(1) 2.125(2), Ti(1)−Cl(1) 2.3049(10), N(2)−Ti(1)−N(1) 86.14(10), N(2)−Ti(1)−Cl(1) 99.94(8), N(1)−Ti(1)−Cl(1) 100.00(7).

In an effort to further explore the relationship between reduction and ligand cleavage, new Ti(III) species were prepared. Compound **1** was reacted with CpLi or $(C_5Me_4H)Li$ to give deep red crystals of compounds formulated as (Nacnac)CpTiCl (**3**) and $(Nacnac)(C_5Me_4H)TiCl$ (**4**) in 91 and 92% yield, respectively. These compounds give rise to EPR signals with *g* values of 1.975 and 1.955, respectively, typical of Ti(III) species. Crystallographic studies of these compounds confirmed the anticipated pseudo-tetrahedral geometries at Ti. In the case of compound **3** (Figure 2) the Ti−N distances were found to be 2.086(2) and 2.088(3) Å, while the Ti−Cl distance was observed to be 2.2997(13) Å. The corresponding distances in **4** (Figure 3) are 2.119(3), 2.125(2), and 2.3049(10) Å. The slightly longer distances in **4** were consistent with the greater electron donation from (C_5Me_4H) in comparison to the Cp ligand. The bite angles for the Nacnac ligands in **3** and **4** were similar at 87.41(10)° and 86.14(10)°, respectively.

Alkyllithium reagents are known in some cases to act as reductants; however, reaction of **3** with *n*-BuLi proceeds in a straightforward fashion to effect alkylation at Ti. Red crystals of **5** are isolated in 92% yield. The EPR spectrum of **5** shows a slight shift in the *g* value, suggesting a new Ti(III) derivative. X-ray crystallographic studies of **5** confirmed the formulation as (Nacnac)CpTiBu (Figure 4). Similar to **3**, the geometry at Ti is pseudotetrahedral with a Ti−N bond length of 2.0873(18) Å and $Ti-C_{butyl}$ distance of 2.142(4) Å. The Ti−N bond lengths are longer in **5** than those seen in **3**, consistent with

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(64) Hitchcock, P. B.; Lappert, M. F.; Protchenko, A. V. *J. Am. Chem. Soc.* **2001**, *123*, 189−190.

(65) Schaverien, C. J.; Mechelen, J. B. v. *Organometallics* **1991**, *10*, 1704−1709.

(66) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1969**, *91*, 7301.

(67) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1970**, *92*, 6182.

(68) Kupfer, V.; Thewalt, U.; Horacek, M.; Petrusova, L.; Mach, K. *Inorg. Chem. Commun.* **1999**, *2*, 540−544.

(69) Mokuolu, Q. F.; Duckmanton, P. A.; Blake, A. J.; Wilson, C.; Love, J. B. *Organometallics* **2003**, *22*, 4387.

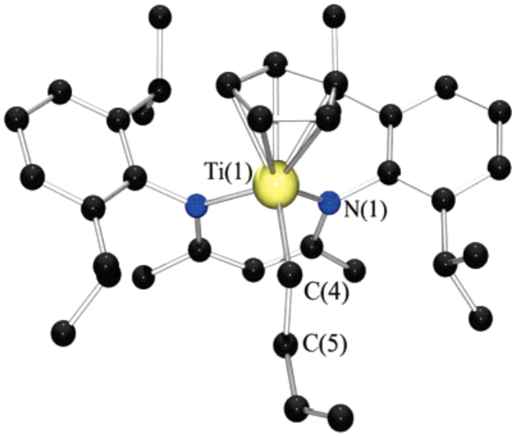
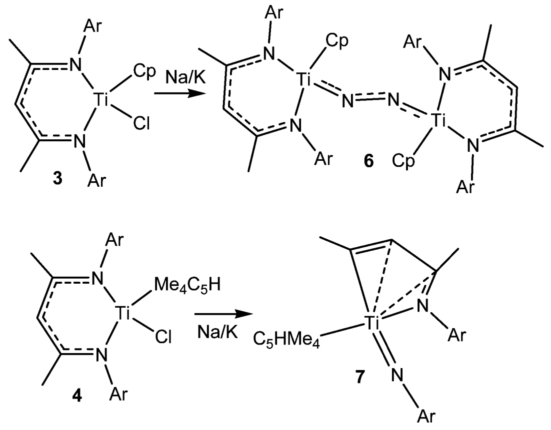


Figure 4. POV-ray drawing of **5**. Hydrogen atoms are omitted for clarity. Color scheme: Ti: wheat, N: blue, C: black. Selected bond distances (Å) and angles (deg): Ti(1)−N(1) 2.0873(18), Ti(1)−C(4) 2.142(4), N(1)−Ti(1)−N(1)′ 88.74(10), N(1)−Ti(1)−C(4) 104.90(9).

Scheme 3. Reductions of 3 and 4



stronger sigma donation from the alkyl group in **5**. This also results in a corresponding increase in the Nacnac ligand bite angle in **5** to 88.74(10)°. Notably this Ti(III)-alkyl compound **5** proved to be remarkably stable under thermal duress. On standing in solution at 120 °C for 24 h, **5** showed no evidence of degradation. Apparently, the Lewis acidity of the Ti(III) center is insufficient to initiate β-hydride abstraction and liberation of butene, at least under these conditions. A related Ti(III) alkyl species, recently reported by Miniola and coworkers, exhibits similar stablity.[53]

Compound **4** reacts with the stronger reductant Na/K amalgam to afford the isolation of the new dark red species **6** in 59% yield. ^{1}H and ^{13}C{^{1}H} NMR characterization of **6** reveals that it is a diamagnetic compound with resonances attributable to intact Nacnac and Cp ligands. As these data were not conclusive in the structural determination, X-ray crystallography was used to determine that **6** is in fact formulated as ((Nacnac)CpTi)$_2$(μ-η^2-N$_2$), **6** (Scheme 3). In this species, dinitrogen bridges the two Ti centers, each of which is coordinated to Cp and Nacnac ligands (Figure 5). The Ti−N bond lengths in **6** for the Nacnac ligands average 2.121(5) Å, slightly longer than those in the precursor **3**. The corresponding Nacnac ligand bite angles were found to be 89.90(18)° and 90.48(18)°, again slightly larger than that found in **3**. The Ti−N distances for the bridging dinitrogen moiety average 1.803(5) Å, while the N−N distance is 1.273(6) Å. While this latter distance is consistent with significant reduction of the N−N triple bond in free N$_2$ (1.0975 Å), it is much shorter than the N−N single bond in hydrazine (1.46 Å). The N−N distance in **6** is similar to those seen in [((Me$_2$NC(N*i*-Pr)$_2$)$_2$Ti]$_2$(N$_2$) (1.28(1) Å),[70] [(PhCNSiMe$_3$)$_2$)$_2$Ti]$_2$(N$_2$) (1.275(6) Å),[71] [((Me$_3$Si)$_2$N)TiCl(TMEDA)]$_2$(N$_2$) (1.289(9) Å),[72] and [((Me$_3$Si)$_2$N)TiCl(py)]$_2$(N$_2$) (1.263(7) Å)[73] and significantly longer than those in titanocene derivatives [Cp′$_2$Ti]$_2$(N$_2$) (Cp′ = Cp* 1.165 Å,[74,75] Me$_4$C$_5$H 1.170(4) Å[76]). While these similarities suggest a bonding description involving delocalization over the TiN$_2$Ti fragment in **6**, it is also noteworthy that this moiety is nonlinear, with Ti−N−N angles of 165.9(4)° and 162.6(4)°, respectively, presenting a *transoid* disposition. Significant reduction of the N$_2$ fragment is also consistent with the stability of **6**, even on storage under N$_2$ for several months at 30 °C.

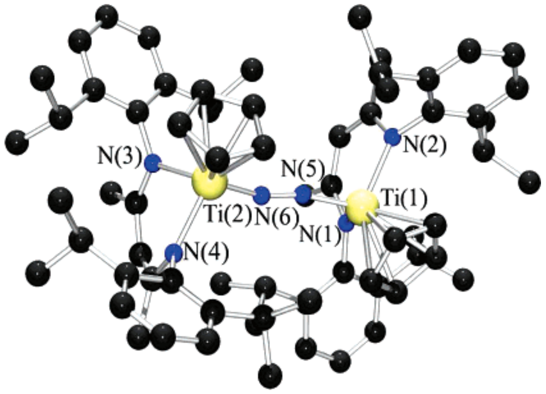


Figure 5. POV-ray drawing of **6**. Hydrogen atoms are omitted for clarity. Color scheme: Ti: wheat, N: blue, C: black. Selected bond distances (Å) and angles (deg): Ti(1)−N(5) 1.801(5), Ti(1)−N(2) 2.128(5), Ti(1)−N(1) 2.129(4), Ti(2)−N(6) 1.806(5), Ti(2)−N(4) 2.111(5), Ti(2)−N(3) 2.116(5), N(5)−N(6) 1.273(6), N(5)−Ti(1)−N(2) 107.81(18), N(5)−Ti(1)−N(1) 100.89(18), N(2)−Ti(1)−N(1) 89.90(18), N(6)−Ti(2)−N(4) 108.83(18), N(6)−Ti(2)−N(3) 104.24(18), N(4)−Ti(2)−N(3) 90.48(18), N(6)−N(5)−Ti(1) 165.9(4), N(5)−N(6)−Ti(2) 162.6(4).

Attempts to effect reduction of **4** in reactions analogous to those achieved with **3** were undertaken. Reactions of **4** with *t*-BuLi or *n*-BuLi or Na/K amalgam all led to the formation and isolation of the same new product **7** in yields ranging from 46 to 58%. ^{1}H NMR data for **7** reveal signals at 6.42 ppm attributable to the Me$_4$C$_5$H ligand. The resonances at 1.34, 1.27, 1.01, 0.94, and 0.80 ppm are attributable to isopropyl methyl groups, suggesting that the Nacnac ligand symmetry has been disrupted. An X-ray crystallographic study of **7** confirmed that the Nacnac ligand had undergone C−N bond scission, affording (C$_5$Me$_4$H)[(ArNC(Me)CHC(Me)]Ti(NAr) (Scheme 3, Figure 6). In this species the Nacnac ligand has been cleaved to imido and ene-imine fragments similar to those seen in **2**. In contrast to **2**, however, **7** is monomeric, presumably a result of the inclusion of the sterically demanding substituted cyclopentadienyl ligand. The Ti−N bond lengths for these fragments were found to be 2.202(3) and 1.730(3) Å, respectively. The Ti−N

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(70) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6952.

(71) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893.

(72) Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986.

(73) Beydoun, N.; Duchateau, R.; Gambarotta, S. *Chem. Commun.* **1992**, 244.

(74) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(75) Sanner, R. D.; Duggan, M. D.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358.

(76) de Wolf, J. M.; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. *Organometallics* **1996**, *15*, 4977.

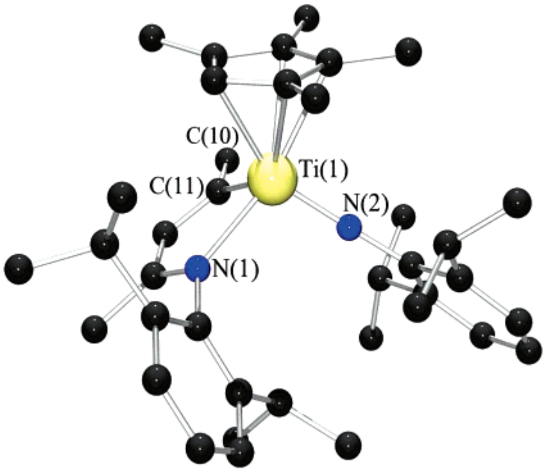

Figure 6. POV-ray drawing of **7**. Hydrogen atoms are omitted for clarity. Color scheme: Ti: wheat, N: blue, C: black. Selected bond distances (Å) and angles (deg): Ti(1)−N(1) 2.202(3), Ti(1)−N(2) 1.730(3), Ti(1)−C(11) 2.160(4), N(2)−Ti(1)−C(11) 106.95(14), N(2)−Ti(1)−N(1) 101.87(12), C(11)−Ti(1)−N(1) 78.88(14), C(27)−N(2)−Ti(1) 178.1(3).

bond length for the imido group is similar to that seen in the Ti-imido species Ti(NAr)(NC_5H_5)(PhNCMeCMeNPh) by Mountford and co-workers.[58] This and the linear geometry at N are consistent with the formal Ti−N double-bond character. The geometry of the ene-imine fragment is similar to that observed for the species [(C(*t*-Bu)CHC(*t*-Bu)NAr)ZrCl(THF)(NAr)][29] reported recently by Mindiola and co-workers.

The mechanism of formation of **7** is the subject of speculation. It is reasonable to suggest that reduction of the precursor **4** generates a putative Ti(II) species "(Me_4C_5H)Ti(Nacnac)". This view is supported to some extent by the isolation of **6**, as **6** represents the interception of the putative Ti(II) species "CpTi(Nacnac)" by N_2. In the parallel reactions of **4**, the species "(Me_4C_5H)Ti(Nacnac)" is not intercepted by N_2. This variation in N_2 binding is reminencent of the recent Zr chemistry reported by Chirik and co-workers, although in that case, use of tetramethylcyclopentadienyl ligands allowed interception of N_2 complexes.[77−79] Presumably in the present Ti case, an analogous N_2 complex would be destabilized by the steric conflict generated by the required proximity of substituted cyclopentadienyl ligands on the Ti centers. In addition, the Ti center in the transient species "(Me_4C_5H)Ti(Nacnac)" is more election rich than in the Cp analogue, prompting internal redox chemistry and reductive ligand cleavage with concurrent oxidation of the metal center. A similar mechanism has been put forward by Mindiola et al. for a closely related Zr system.[29]

Summary

Reductions of (Nacnac)Ti(III) complexes generating transient "(Nacnac)Ti(II)" species result in the Nacnac ligand cleavage products **2** and **7**. This view is supported by the isolation of **6**, which is best described as the product of N_2 interception of the putative Ti(II) species. It is clear that both the electronic and steric nature of ancillary ligands play a role in determining the course of such reduction reactions. We are continuing to study related chemistry of reduced Nacnac complexes.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(77) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 7901−7911.

(78) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 14051−14061.

(79) Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291−10304.