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Cube-Type Nitrido Complexes Containing Titanium and Zinc/Copper

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Several azaheterometallocubane complexes containing $[MTi_3N_4]$ cores have been prepared by the reaction of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with zinc(II) and copper(I) derivatives. The treatment of **1** with zinc dichloride in toluene at room temperature produces the adduct $[Cl_2Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**2**). Attempts to crystallize **2** in dichloromethane gave yellow crystals of the ammonia adduct $[(H_3N)Cl_2Zn\{(\mu_3\text{-}NH)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}]$ (**3**). The analogous reaction of **1** with alkyl, (trimethylsilyl)cyclopentadienyl, or amido zinc complexes $[ZnR_2]$ leads to the cube-type derivatives $[RZn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (R = CH_2SiMe_3 (**5**), CH_2Ph (**6**), Me (**7**), $C_5H_4SiMe_3$ (**8**), $N(SiMe_3)_2$ (**9**)) via RH elimination. The amido complex **9** decomposes in the presence of ambient light to generate the alkyl derivative $[\{Me_3Si(H)N(Me)_2SiCH_2\}Zn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**10**). The chloride complex **2** reacts with lithium cyclopentadienyl or lithium indenyl reagents to give the cyclopentadienyl or indenyl zinc derivatives $[RZn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (R = C_5H_5 (**11**), C_9H_7 (**12**)). Treatment of **1** with copper(I) halides in toluene at room temperature leads to the adducts $[XCu\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (X = Cl (**13**), I (**14**)). Complex **13** reacts with lithium bis(trimethylsilyl)amido in toluene to give the precipitation of $[\{Cu(\mu_4\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**15**). Complex **15** is prepared in a higher yield through the reaction of **1** with $[\{CuN(SiMe_3)_2\}_4]$ in toluene at 150 °C. The addition of triphenylphosphane to **15** in toluene produces the single-cube compound $[(Ph_3P)Cu\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**16**). The X-ray crystal structures of **3**, **8**, **9**, and **15** have been determined.

Introduction

An extensive coordination chemistry has been developed with tridentate nitrogen-based ligands. Representative examples are tris(pyrazolyl)borates,[1] tris(pyrazolyl)methanes,[2] triazacyclononanes,[3] triazacyclohexanes,[4] and other tripodal amido ligands,[5] because of their ability to serve as facially coordinating six-electron donors. In this binding mode, the tris(pyrazolyl)hydroborate ligand is formally analogous to the cyclopentadienide (Cp^-) ligand, in that both are uninegative and isolobal. However, the electron-donating ability[6] and the steric profile of the tris(pyrazolyl)hydroborate (Tp) ligand and the substituted (Tp^x) derivatives thereof, are very different.[7] At present, tris(pyrazolyl)hydroborates have become one of the most widely used classes of ligands in inorganic chemistry, giving different reactivity patterns and frequently permitting the isolation of species whose cyclo-

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(1) For general references, see: (a) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College, London, 1999. (b) Pettinari, C.; Santini, C. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Ed.; Elsevier: New York, 2004; Vol. 1, pp 159−210. (c) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.

(2) For recent reviews, see: (a) Bigmore, H. R.; Lawrence, S. C.; Mountford, P.; Tredget, C. S. *Dalton Trans.* **2005**, 635−651. (b) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 525−543.

(3) For reviews, see: (a) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329−436. (b) Schmidt, J. A. R.; Giesbrecht, G. R.; Cui, C.; Arnold, J. *Chem. Commun.* **2003**, 1025−1033.

(4) For a selection of 1,3,5-triazacyclohexane complexes of copper and zinc, see: (a) Fuchs, R.; Klüfers, P. *J. Organomet. Chem.* **1992**, *424*, 353−370. (b) Köhn, R. D.; Seifert, G.; Kociok-Köhn, G. *Chem. Ber.* **1996**, *129*, 1327−1333. (c) Haufe, M.; Köhn, R. D.; Weimann, R.; Seifert, G.; Zeigan, D. *J. Organomet. Chem.* **1996**, *520*, 121−129. (d) Haufe, M.; Köhn, R. D.; Kociok-Köhn, G.; Filippou, A. C. *Inorg. Chem. Commun.* **1998**, *1*, 263−266. (e) Köhn, R. D.; Seifert, G.; Pan, Z.; Mahon, M. F.; Kociok-Köhn, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 793−796. (f) Köhn, R. D.; Pan, Z.; Mahon, M. F.; Kociok-Köhn, G. *Chem Commun.* **2003**, 1272−1273. (g) Köhn, R. D.; Pan, Z.; Mahon, M. F.; Kociok-Köhn, G. *Dalton Trans.* **2003**, 2269−2275. (h) Köhn, R. D.; Pan, Z.; Haufe, M.; Kociok-Köhn, G. *Dalton Trans.* **2005**, 2793−2797.

(5) For recent reviews, see: (a) Gade, L. H. *Acc. Chem. Res.* **2002**, *35*, 575−582. (b) Gade, L. H. *J. Organomet. Chem.* **2002**, *661*, 85−94.

(6) Tellers, D. M.; Skoog, S. J.; Bergman, R. G.; Gunnoe, T. B.; Harman, W. D. *Organometallics* **2000**, *19*, 2428−2432.

(7) (a) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419−513. (b) Sandford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5384−5389 and references therein.

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pentadienyl relatives are highly reactive.[1] In comparison, the chemistry of tris(pyrazolyl)methane ligands, the neutral analogues of the anionic tris(pyrazolyl)hydroborates, has been underdeveloped, although this area is currently a subject of active research.[2] The neutral 1,4,7-triazacyclononane (R_3tacn)[3a] and 1,3,5-triazacyclohexane (R_3tach)[4] ligands are also widely used as fac-coordinating N_3-donor ligands in transition metal complexes, and more recently, monoanionic triazacyclononane (R_2tacn^-) ligands have demonstrated their ability to support novel organometallic chemistry with main group and early transition metals.[3b]

In the past few years, we have been involved in the study of the coordination chemistry of the trinuclear titanium imido-nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$[8,9] (**1**). Nitrido complexes of the early transition metals (Groups 4 and 5) remain rare in the literature.[10,11] This is possibly, in part, because of their polynuclear structures, which make their characterization extremely hard, and the lack of a systematic method of syntheses. The structure of complex **1** reveals a cyclic $[Ti_3(\mu\text{-}NH)_3]$ system with three NH electron-donor imido groups and shows a strong resemblance to 1,4,7-triazacyclononane and, especially, 1,3,5-triazacyclohexane ligands. This similarity prompted us to explore its potential application as a tridentate, preorganized,[12] ligand toward different metal complexes and establish a rational strategy to prepare heterometallic nitrido complexes. This type of compound might be of interest as building blocks in the synthesis of ternary metal nitride materials.[13]

Our initial work with transition metal derivatives has shown that **1** is capable of acting as a neutral ligand through the basal NH groups, but later those imido groups can also be deprotonated to give monoanionic, dianionic, and even trianionic forms of **1** depending on the metal and the other ligands present in the coordination sphere.[11,14,15] In main-group chemistry, we have demonstrated the ability of **1** to coordinate metal cyclopentadienides and halides to yield stable adducts $[X_nM\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$.[16] However, the analogous treatment of **1** with alkyl and amido derivatives of the alkali and alkaline-earth metals immediately resulted in the elimination of alkane or amine. Thus, we have isolated Group 1 metal complexes with edge-linked $[\{M(\mu_4\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (M = Li, Na, K) or corner-shared $[M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_5Ti_6(\eta^5\text{-}C_5Me_5)_6\text{-}(\mu_3\text{-}N)_2\}]$ (M = Na, K, Rb, Cs) double-cube structures, depending on the reagents ratio (1:1 or 2:1) of **1** and $[MN(SiMe_3)_2]$.[17,18] Group 2 alkyl and amido $[MR_2]$ reagents react with **1** to give single-cube derivatives $[RM\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$, but only the magnesium bis(trimethylsilyl)amido complex $[\{(Me_3Si)_2N\}Mg\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ was stable in solution for long periods of time. In contrast, magnesium alkyls and derivatives bearing the heavier alkaline-earth elements undergo ligand redistribution reactions at room temperature to give corner-shared complexes $[M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (M = Mg, Ca, Sr, Ba).[18,19]

In view of these studies with s block metals and as a logical continuation of our endeavor in the synthesis of new heterometallic nitrido complexes, we report here the results obtained in the treatment of **1** with analogous zinc(II) and copper(I) derivatives. The synthesis, structures, and properties of the new compounds are discussed and compared with other zinc and cooper derivatives containing tridentate nitrogen-based ligands.[20]

Experimental Section

General Considerations. All manipulations were carried out under argon using Schlenk-line or glovebox techniques. Hexane was distilled from Na/K alloy just before use. Toluene was freshly distilled from sodium. Dichloromethane was distilled from P_2O_5. NMR solvents were dried with Na/K alloy (C_6D_6, $C_6D_5CD_3$) or calcium hydride ($CDCl_3$) and vacuum distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. Zinc(II) chloride (97%), copper(I) chloride (99.99%), copper(I) iodide (99.999%), $[ZnMe_2]$ (2.0 M in toluene), PPh_3, and $[LiN(SiMe_3)_2]$ were purchased from Aldrich and used as received. $[\{Ti(\eta^5\text{-}C_5Me_5)\text{-}(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**),[8,9] $[ZnR_2]$ (R = CH_2SiMe_3,[21] CH_2Ph,[22] $N(SiMe_3)_2$,[23,24] $C_5H_4SiMe_3$,[25] C_5H_5[26]), $[LiCH_2SiMe_3]$,[27] $[Li(C_5H_4\text{-}SiMe_3)]$,[28] $[Li(C_5H_5)]$,[29] $[Li(C_9H_7)]$,[30] and $[\{CuN(SiMe_3)_2\}_4]$[31,32] were prepared according to published procedures.

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(8) Roesky, H. W.; Bai, Y.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 754−755.

(9) Abarca, A.; Gómez-Sal, P.; Martín, A.; Mena, M.; Poblet, J. M.; Yélamos, C. *Inorg. Chem.* **2000**, *39*, 642−651.

(10) For general references of metal nitrido complexes, see: (a) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413−426. (b) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988. (c) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955−978. (d) Dehnicke, K.; Weller, F.; Strähle J. *Chem. Soc. Rev.* **2001**, *30*, 125−135.

(11) Abarca, A.; Galakhov, M. V.; Gracia, J.; Martín, A.; Mena, M.; Poblet, J. M.; Sarasa, J. P.; Yélamos, C. *Chem.−Eur. J.* **2003**, *9*, 2337−2346 and references therein concerning early transition metal nitrido complexes.

(12) Haack, K. J.; Goddard, R.; Pörschke, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 7992−7999.

(13) (a) Oyama, S. T., Ed. *The Chemistry of Transition Metal Carbides and Nitrides*; Blackie Academic & Professional: London, 1996. (b) Kniep, R. *Pure Appl. Chem.* **1997**, *69*, 185−191. (c) Niewa, R.; DiSalvo, F. J. *Chem. Mater.* **1998**, *10*, 2733−2752. (d) Gregory, D. H. *J. Chem. Soc., Dalton Trans.* **1999**, 259−270.

(14) (a) Abarca, A.; Galakhov, M.; Gómez-Sal, P.; Martín, A.; Mena, M.; Poblet, J. M.; Santamaría, C.; Sarasa, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 534−537. (b) Abarca, A.; Martín, A.; Mena, M.; Yélamos, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 3460−3463.

(15) Freitag, K.; Gracia, J.; Martín, A.; Mena, M.; Poblet, J. M.; Sarasa, J. P.; Yélamos, C. *Chem.−Eur. J.* **2001**, *7*, 3644−3651.

(16) (a) García-Castro, M.; Martín, A.; Mena, M.; Yélamos, C. *Organometallics* **2004**, *23*, 1496−1500. (b) García-Castro, M.; Gracia, J.; Martín, A.; Mena, M.; Poblet. J. M.; Sarasa, J. P.; Yélamos, C. *Chem.−Eur. J.* **2005**, *11*, 1030−1041.

(17) García-Castro, M.; Martín, A.; Mena, M.; Pérez-Redondo, A.; Yélamos, C. *Chem.−Eur. J.* **2001**, *7*, 647−651.

(18) Martín, A.; Mena, M.; Pérez-Redondo, A.; Yélamos, C. *Inorg. Chem.* **2004**, *43*, 2491−2498.

(19) Martín, A.; Mena, M.; Pérez-Redondo, A.; Yélamos, C. *Organometallics* **2002**, *21*, 3308−3310.

(20) (a) Reger, D. L. *Comments Inorg. Chem.* **1999**, *21*, 1−28. (b) Pettinari, C.; Cingolani, A.; Lobbia, G. G.; Marchetti, F.; Martini, D.; Pellei, M.; Pettinari, R.; Santini, C. *Polyhedron* **2004**, *23*, 451−469.

(21) Westerhausen, M.; Rademacher, B.; Poll, W. *J. Organomet. Chem.* **1991**, *421*, 175−188.

(22) Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209−225.

(23) Bürger, H.; Sawodny, W.; Wannagat, U. *J. Organomet. Chem.* **1965**, *3*, 113−120.

(24) Bochmann, M.; Bwembya, G.; Webb, K. J. *Inorg. Synth.* **1997**, *31*, 19−24.

(25) (a) Blom, A.; Boersma, J.; Budzelaar, P. H.; Fischer, B.; Haaland, A.; Volden, H. V.; Weidlein, J. *Acta Chem. Scand.* **1986**, *A40*, 113−120. (b) Fischer, B.; Boersma, J.; van Koten, G.; Spek, A. L. *New J. Chem.* **1988**, *12*, 613−620.

Samples for infrared spectroscopy were prepared as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-300, Unity-500 Plus, or both spectrometers. Chemical shifts (δ, ppm) are given relative to residual protons or to the carbon of the solvent. Electron impact mass spectra were obtained at 70 eV. Microanalyses (C, H, N) were performed in a Heraeus CHN-O-Rapid or a Leco CHNS-932 microanalyzer.

Synthesis of [$Cl_2Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (2). A 100 mL Schlenk flask was charged with **1** (0.50 g, 0.82 mmol), $ZnCl_2$ (0.11 g, 0.81 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 3 h to give a yellow solid and a brown solution. The solid was isolated by filtration onto a glass frit, washed with toluene (5 mL), and vacuum dried to give **2** as a yellow powder (0.41 g, 68%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3363 (w), 3291 (m), 2972 (w), 2908 (s), 2857 (m), 1618 (w), 1490 (w), 1429 (m), 1375 (m), 1260 (w), 1165 (w), 1025 (w), 743 (s), 719 (s), 704 (s), 653 (vs), 624 (m), 606 (s), 549 (w), 532 (m), 468 (m), 419 (m). ^{1}H NMR ($CDCl_3$, 20 °C): δ 11.51 (s broad, 3H, NH), 2.09 (s, 45H, C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 122.4 (*C*$_5$Me$_5$), 12.2 (C$_5$*Me*$_5$). MS (EI, 70 eV): *m/z* 709 (2) [M − Cl]$^+$, 608 (1) [M − $ZnCl_2$]$^+$. Anal. Calcd for $C_{30}H_{48}Cl_2N_4Ti_3Zn$ (M_w = 744.65): C, 48.39; H, 6.50; N, 7.52. Found: C, 48.22; H, 6.60; N, 7.26.

Reaction of 1 with [$Zn(CH_2SiMe_3)_2$] in a NMR Tube-Scale Experiment. A 5 mm valved NMR tube was charged with **1** (0.010 g, 0.016 mmol), [$Zn(CH_2SiMe_3)_2$] (0.004 g, 0.017 mmol), and benzene-d_6 (1.00 mL). The resultant brown solution was monitored by NMR spectroscopy. After 10 min at room temperature, the spectra showed a complete reaction, and the corresponding complex, [$(Me_3SiCH_2)_2Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**4**), was characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **4** decomposed completely within hours at room temperature to give a red solution containing **5** and $SiMe_4$ according to the NMR spectra.

NMR data for [$(Me_3SiCH_2)_2Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**4**). ^{1}H NMR ($C_6D_6$, 20 °C): δ 13.66 (s broad, 3H, NH), 1.99 (s, 45 H, C_5Me_5), 0.15 (s, 18H, CH$_2$Si*Me*$_3$), −0.67 (s, 4H, C*H*$_2$SiMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 117.5 (*C*$_5$Me$_5$), 11.8 (C$_5$*Me*$_5$), 3.2 (CH$_2$Si*Me*$_3$), 2.7 (*C*H$_2$SiMe$_3$).

Synthesis of [$(Me_3SiCH_2)Zn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (5). Method A. A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [$Zn(CH_2SiMe_3)_2$] (0.12 g, 0.50 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 20 h to give an orange solution. After filtration, the volatile components were removed under reduced pressure to give **5** as a red solid (0.34 g, 92%).

Method B. A 100 mL Schlenk flask was charged with **2** (0.15 g, 0.20 mmol), [$LiCH_2SiMe_3$] (0.040 g, 0.42 mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature for 20 h to give a red solution and a white precipitate. After filtration, the volatile components of the solution were removed under reduced pressure to give **5** as a red solid (0.11 g, 73%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3363 (w), 2911 (s), 2858 (s), 1491 (w), 1437 (m), 1376 (m), 1250 (w), 1239 (m), 1067 (w), 1024 (m), 937 (m), 857 (m), 819 (s), 787 (s), 722 (vs), 700 (s), 675 (s), 616 (s), 535 (w), 513 (w), 483 (w), 450 (w), 426 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 10.55 (s broad, 2H, NH), 2.08 (s, 30H, C_5Me_5), 1.88 (s, 15H, C_5Me_5), 0.22 (s, 9H, CH$_2$Si*Me*$_3$), −0.77 (s, 2H, C*H*$_2$SiMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 118.8, 117.8 (*C*$_5$Me$_5$), 11.9, 11.8 (C$_5$*Me*$_5$), 3.3 (CH$_2$Si*Me*$_3$), −13.3 (*C*H$_2$SiMe$_3$). MS (EI, 70 eV): *m/z* 760 (2) [M]$^+$, 607 (5) [M − $ZnCH_2SiMe_3$]$^+$, 472 (7) [M − $ZnCH_2SiMe_3$ − C_5Me_5]$^+$. Anal. Calcd for $C_{34}H_{58}N_4SiTi_3Zn$ (M_w = 759.96): C, 53.74; H, 7.69; N, 7.37. Found: C, 53.62; H, 7.54; N, 6.69.

Synthesis of [$(PhCH_2)Zn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (6). In a fashion similar to the preparation of **5** (method A), the treatment of **1** (0.50 g, 0.82 mmol) with [$Zn(CH_2Ph)_2$] (0.20 g, 0.81 mmol) in toluene (25 mL) produced **6** as a red solid (0.57 g, 92%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3361 (w), 2908 (s), 2856 (s), 1593 (m), 1486 (m), 1429 (m), 1374 (m), 1204 (w), 1178 (w), 1057 (w), 1025 (w), 997 (w), 889 (w), 798 (m), 749 (s), 723 (vs), 696 (vs), 664 (s), 613 (m), 539 (w), 483 (w), 451 (w), 427 (s). ^{1}H NMR (C_6D_6, 20 °C): δ 10.39 (s broad, 2H, NH), 7.20−6.89 (m, 5H, CH$_2$C$_6$*H*$_5$), 2.08 (s, 2H, C*H*$_2$C$_6$H$_5$), 2.04 (s, 30H, C_5Me_5), 1.81 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 151.5, 127.8, 126.9, 120.8 (*C*$_6$H$_5$), 119.1, 118.0 (*C*$_5$Me$_5$), 14.1 (*C*H$_2$C$_6$H$_5$), 11.8, 11.6 (C$_5$*Me*$_5$). MS (EI, 70 eV): *m/z* 764 (6) [M]$^+$, 673 (11) [M − CH_2Ph]$^+$, 607 (21) [M − $ZnCH_2Ph$]$^+$. Anal. Calcd for $C_{37}H_{54}N_4Ti_3Zn$ (M_w = 763.87): C, 58.18; H, 7.14; N, 7.33. Found: C, 57.87; H, 7.42; N, 7.05.

Synthesis of [$MeZn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (7). In a fashion similar to the preparation of **6**, the treatment of **1** (1.00 g, 1.64 mmol) with [$ZnMe_2$] (2.0 M in toluene, 0.82 mL, 1.64 mmol) in toluene (50 mL) produced **7** as a red solid (1.11 g, 98%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3365 (w), 2904 (s), 2856 (m), 2722 (w), 1489 (w), 1429 (m), 1375 (m), 1167 (w), 1066 (w), 1024 (w), 953 (w), 905 (w), 783 (m), 724 (vs), 699 (vs), 664 (s), 616 (s), 527 (m), 484 (w), 452 (w), 428 (s). ^{1}H NMR (C_6D_6, 20 °C): δ 10.66 (s broad, 2H, NH), 2.08 (s, 30H, C_5Me_5), 1.86 (s, 15H, C_5Me_5), −0.37 (s, 3H, ZnMe). ^{13}C NMR (C_6D_6, 20 °C): δ 118.8 (m, *C*$_5$Me$_5$), 117.8 (m, *C*$_5$Me$_5$), 11.8 (q, $^1J_{C-H}$ = 125 Hz, C$_5$*Me*$_5$), 11.7 (q, $^1J_{C-H}$ = 126 Hz, C$_5$*Me*$_5$), −20.8 (q, $^1J_{C-H}$ = 121 Hz, Zn*Me*). MS (EI, 70 eV): *m/z* 688 (35) [M]$^+$, 673 (4) [M − Me]$^+$, 607 (27) [M − ZnMe]$^+$, 472 (25) [M − ZnMe − C_5Me_5]$^+$, 337 (27) [M − ZnMe − 2C_5Me_5]$^+$. Anal. Calcd for $C_{31}H_{50}N_4Ti_3Zn$ (M_w = 687.77): C, 54.14; H, 7.33; N, 8.15. Found: C, 54.30; H, 7.37; N, 7.69.

Synthesis of [$\{(Me_3Si)H_4C_5\}Zn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (8). In a fashion similar to the preparation of **5** (method A), the treatment of **1** (0.30 g, 0.49 mmol) with [$Zn\{C_5H_4SiMe_3\}_2$] (0.17 g, 0.50 mmol) in toluene (20 mL) produced **8** as a red solid (0.39 g, 98%). Also with method B, the treatment of **2** (0.30 g, 0.40 mmol) with [$Li(C_5H_4SiMe_3)$] (0.12 g, 0.83 mmol) in toluene (25 mL) yielded **8** as a red solid (0.25 g, 78%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3361 (w), 3344 (w), 3070 (w), 2948 (m), 2909 (s), 2860 (m), 1491 (w), 1430 (m), 1375 (m), 1246 (m), 1145 (w), 1063 (w), 1043 (w), 1019 (m), 888 (m), 833 (s), 741 (vs), 720 (vs), 699 (vs), 613 (s), 532 (m), 483 (w), 426 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 9.61 (s broad, 2H, NH), 6.88 (m, 2H, C$_5$*H*$_2$H$_2$SiMe$_3$), 6.67 (m, 2H, C$_5$H$_2$*H*$_2$SiMe$_3$), 2.06 (s, 30H, C_5Me_5), 1.85 (s, 15H, C_5Me_5), 0.19 (s, 9H, C$_5$H$_4$Si*Me*$_3$). ^{13}C NMR (C_6D_6, 20 °C): 129.9 (m, $^1J_{C-H}$ = 163 Hz, *C*$_4$H$_4$CSiMe$_3$), 121.5 (m, $^1J_{C-H}$ = 158 Hz, *C*$_4$H$_4$CSiMe$_3$), 119.5 (m, *C*$_5$Me$_5$), 118.3 (m, *C*$_5$Me$_5$), 72.1 (m, C$_4$H$_4$*C*SiMe$_3$), 12.0 (q, $^1J_{C-H}$ = 125 Hz, C$_5$*Me*$_5$), 11.8 (q, $^1J_{C-H}$ = 126 Hz, C$_5$*Me*$_5$), 0.3 (q, $^1J_{C-H}$ = 117 Hz, C$_4$H$_4$CSi*Me*$_3$). MS (EI, 70 eV): *m/z* 810 (2) [M]$^+$, 673 (3) [M − $C_5H_4SiMe_3$]$^+$, 607 (4) [M − $ZnC_5H_4SiMe_3$]$^+$. Anal.

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(26) Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *J. Organomet. Chem.* **1985**, *281*, 123−130.

(27) Tessier-Youngs, C.; Beachley, O. T., Jr. *Inorg. Synth.* **1986**, *24*, 95−97.

(28) Jutzi, P.; Sauer, R. *J. Organomet. Chem.* **1973**, *50*, C29−C30.

(29) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855−3858.

(30) Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4038−4044.

(31) Bürger, H.; Wannagat, U. *Monatsh. Chem.* **1964**, *95*, 1099−1102.

(32) James, A. M.; Laxman, R. K.; Fronczek, F. R.; Maverick, A. W. *Inorg. Chem.* **1998**, *37*, 3785−3791.

Calcd for $C_{38}H_{60}N_4SiTi_3Zn$ ($M_w = 810.02$): C, 56.35; H, 7.46; N, 6.92. Found: C, 56.27; H, 7.32; N, 6.61.

Synthesis of [{(Me$_3$Si)$_2$N}Zn{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (9). In a manner similar to the preparation of **5** (method A), using amber-stained glassware, the treatment of **1** (1.00 g, 1.64 mmol) with [Zn{N(SiMe$_3$)$_2$}$_2$] (0.63 g, 1.63 mmol) in toluene (50 mL) produced **9** as a red solid (1.19 g, 88%). Also through method B with amber-stained glassware, the treatment of **2** (0.20 g, 0.27 mmol) with [LiN(SiMe$_3$)$_2$] (0.090 g, 0.54 mmol) in toluene (20 mL) yielded **9** as a red solid (0.15 g, 68%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3383 (w), 3351 (w), 2909 (s), 1491 (w), 1435 (m), 1377 (m), 1239 (s), 1066 (w), 992 (s), 885 (s), 830 (s), 720 (vs), 703 (vs), 665 (s), 615 (s), 530 (w), 480 (w), 445 (w), 425 (m). ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 10.24 (s broad, 2H, NH), 2.07 (s, 30H, C$_5$Me$_5$), 1.90 (s, 15H, C$_5$Me$_5$), 0.30 (s, 18H, N(SiMe$_3$)$_2$).^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): δ 119.6, 118.4 (*C*$_5$Me$_5$), 12.1, 12.0 (C$_5$*Me*$_5$), 6.7 (SiMe$_3$). MS (EI, 70 eV): *m/z* 833 (2) [M]$^+$, 607 (2) [M − ZnN(SiMe$_3$)$_2$]$^+$, 472 (2) [M − ZnN(SiMe$_3$)$_2$ − C$_5$Me$_5$]$^+$. Anal. Calcd for $C_{36}H_{65}N_5Si_2Ti_3Zn$ ($M_w = 833.13$): C, 51.90; H, 7.86; N, 8.41. Found: C, 52.16; H, 7.97; N, 7.98.

Synthesis of [{Me$_3$Si(H)N(Me)$_2$SiCH$_2$}Zn{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (10). A 150 mL ampule (Teflon stopcock) was charged with **9** (1.21 g, 1.45 mmol), toluene (50 mL), and a magnetic stir bar. The orange solution was stirred under irradiation with a sun lamp (Ultra-Vitalux E27/ES OSRAM, 300 W) for 20 h. The resultant brown solution was filtered, and the volatile components were removed under reduced pressure to give **10** as a brown solid (0.96 g, 79%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3365 (m), 2948 (s), 2910 (s), 1494 (w), 1436 (m), 1376 (s), 1243 (s), 1168 (m), 1066 (w), 1023 (w), 922 (s), 838 (s), 800 (s), 774 (s), 723 (vs), 702 (vs), 678 (s), 616 (s), 529 (w), 483 (w), 451 (w), 427 (m). ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 10.54 (s broad, 2H, NH), 2.08 (s, 30H, C$_5$Me$_5$), 1.86 (s, 15H, C$_5$Me$_5$), 0.30 (s, 6H, CH$_2$Si(*Me*)$_2$N(H)SiMe$_3$), 0.28 (s, 9H, CH$_2$Si(Me)$_2$N(H)Si*Me*$_3$), −0.69 (s, 2H, C*H*$_2$Si(Me)$_2$N(H)SiMe$_3$), not observed CH$_2$Si(Me)$_2$N(*H*)SiMe$_3$. ^{13}C NMR (C$_6$D$_6$, 20 °C): δ 118.9 (m, *C*$_5$Me$_5$), 117.9 (m, *C*$_5$Me$_5$), 12.0 (q, $^1J_{C-H} = 125$ Hz, C$_5$*Me*$_5$), 11.8 (q, $^1J_{C-H} = 126$ Hz, C$_5$*Me*$_5$), 5.6 (q, $^1J_{C-H} = 117$ Hz, CH$_2$Si(*Me*)$_2$N(H)SiMe$_3$), 3.2 (q, $^1J_{C-H} = 117$ Hz, CH$_2$Si(Me)$_2$N(H)Si*Me*$_3$), −11.0 (t, $^1J_{C-H} = 115$ Hz, Zn*C*H$_2$Si(Me)$_2$N(H)SiMe$_3$). MS (EI, 70 eV): *m/z* 833 (2) [M]$^+$, 607 (4) [M − ZnCH$_2$Si(Me)$_2$NHSiMe$_3$]$^+$. Anal. Calcd for $C_{36}H_{65}N_5Si_2Ti_3Zn$ ($M_w = 833.13$): C, 51.90; H, 7.86; N, 8.41. Found: C, 52.33; H, 7.96; N, 7.52.

Synthesis of [(H$_5$C$_5$)Zn{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (11). A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.40 mmol), [Li(C$_5$H$_5$)] (0.060 g, 0.83 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 5 h to give a red solution and a white precipitate. After filtration, the volatile components were removed under reduced pressure to give **11** as a red solid (0.22 g, 73%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3356 (w), 3334 (w), 2909 (s), 2857 (m), 1490 (w), 1431 (m), 1375 (m), 1261 (w), 1107 (w), 1067 (w), 1023 (w), 983 (w), 781 (s), 730 (s), 702 (vs), 665 (s), 613 (s), 533 (m), 481 (w), 448 (m), 427 (s). ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 9.56 (s broad, 2H, NH), 6.38 (s, 5H, C$_5$H$_5$), 2.04 (s, 30H, C$_5$Me$_5$), 1.85 (s, 15H, C$_5$Me$_5$). ^{13}C NMR (C$_6$D$_6$, 20 °C): δ 119.6 (m, *C*$_5$Me$_5$), 118.3 (m, *C*$_5$Me$_5$), 108.8 (m, $^1J_{C-H} = 160$ Hz, C$_5$H$_5$), 11.8 (q, $^1J_{C-H} = 125$ Hz, C$_5$*Me*$_5$), 11.7 (q, $^1J_{C-H} = 126$ Hz, C$_5$*Me*$_5$). MS (EI, 70 eV): *m/z* 738 (3) [M]$^+$, 673 (11) [M − C$_5$H$_5$]$^+$, 607 (18) [M − ZnC$_5$H$_5$]$^+$, 472 (11) [M − ZnC$_5$H$_5$ − C$_5$Me$_5$]$^+$. Anal. Calcd for $C_{35}H_{52}N_4Ti_3Zn$ ($M_w = 737.83$): C, 56.98; H, 7.10; N, 7.59. Found: C, 57.16; H, 6.86; N, 7.32.

Synthesis of [(H$_7$C$_9$)Zn{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (12). A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.40 mmol), [Li(C$_9$H$_7$)] (0.10 g, 0.82 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 3 h to give a red solution and a white precipitate. After filtration, the volatile components were removed under reduced pressure, and the resultant solid was washed with hexane (5 mL) to yield **12** as a red powder (0.23 g, 72%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3352 (w), 3055 (w), 2908 (m), 2856 (m), 1599 (w), 1491 (w), 1431 (m), 1375 (m), 1323 (w), 1261 (w), 1230 (w), 1198 (w), 1161 (w), 1143 (w), 1063 (w), 1024 (w), 992 (w), 924 (w), 887 (w), 865 (w), 809 (m), 774 (m), 735 (s), 721 (s), 699 (vs), 664 (s), 614 (m), 536 (w), 483 (w), 449 (w), 429 (m). ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 9.85 (s broad, 2H, NH), 7.67 (m, 2H, C$_9$H$_7$), 7.29 (m, 2H, C$_9$H$_7$), 7.05 (t, ^3J = 3 Hz, 1H, C$_9$H$_7$), 5.63 (d, ^3J = 3 Hz, 2H, C$_9$H$_7$), 2.03 (s, 30H, C$_5$Me$_5$), 1.68 (s, 15H, C$_5$Me$_5$). ^{13}C NMR (C$_6$D$_6$, 20 °C): δ 144.8 (s, *C*$_9$H$_7$), 137.2 (d, $^1J_{C-H} = 161$ Hz, *C*$_9$H$_7$), 121.5 (m, $^1J_{C-H} = 151$ Hz, *C*$_9$H$_7$), 121.3 (m, $^1J_{C-H} = 155$ Hz, *C*$_9$H$_7$), 119.6 (m, *C*$_5$Me$_5$), 118.3 (m, *C*$_5$Me$_5$), 82.2 (m, $^1J_{C-H} = 152$ Hz, *C*$_9$H$_7$), 11.8 (q, $^1J_{C-H} = 125$ Hz, C$_5$*Me*$_5$), 11.5 (q, $^1J_{C-H} = 125$ Hz, C$_5$*Me*$_5$). MS (EI, 70 eV): *m/z* 788 (2) [M]$^+$, 673 (24) [M − C$_9$H$_7$]$^+$, 607 (27) [M − ZnC$_9$H$_7$]$^+$, 472 (24) [M − ZnC$_9$H$_7$ − C$_5$Me$_5$]$^+$, 337 (41) [M − ZnC$_9$H$_7$ − 2C$_5$Me$_5$]$^+$. Anal. Calcd for $C_{39}H_{54}N_4Ti_3Zn$ ($M_w = 787.89$): C, 59.45; H, 6.91; N, 7.11. Found: C, 59.59; H, 6.72; N, 7.20.

Synthesis of [ClCu{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (13). A 100 mL Schlenk flask was charged with **1** (0.70 g, 1.15 mmol), CuCl (0.11 g, 1.11 mmol), and toluene (40 mL). The reaction mixture was stirred at room temperature for 18 h to give a red solution. After filtration, the volatile components were removed under reduced pressure to give a red solid. The solid was washed with hexane (15 mL) and vacuum dried to give **13** as a red powder (0.56 g, 72%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3362 (m), 3219 (broad, m), 2909 (s), 2857 (m), 2723 (w), 1489 (w), 1450 (m), 1428 (m), 1377 (s), 1067 (w), 1025 (m), 797 (m), 739 (s), 668 (s), 645 (vs), 639 (vs), 520 (w), 476 (w), 430 (m), 403 (m). ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 11.70 (s broad, 3H, NH), 1.87 (s, 45H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): δ 119.4 (*C*$_5$Me$_5$), 11.6 (C$_5$*Me*$_5$). MS (EI, 70 eV): *m/z* 706 (1) [M]$^+$, 671 (4) [M − Cl]$^+$. Anal. Calcd for $C_{30}H_{48}ClCuN_4Ti_3$ ($M_w = 707.34$): C, 50.94; H, 6.84; N, 7.92. Found: C, 50.89; H, 6.71; N, 7.66.

Synthesis of [ICu{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (14). In a fashion similar to the preparation of **13**, the treatment of **1** (0.50 g, 0.82 mmol) with CuI (0.16 g, 0.84 mmol) in toluene (30 mL) produced **14** as a red solid (0.43 g, 65%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3363 (m), 2906 (s), 2857 (m), 1488 (w), 1427 (m), 1377 (m), 1024 (m), 746 (s), 735 (s), 685 (s), 670 (s), 644 (vs), 628 (s), 522 (w), 479 (w), 435 (m), 407 (m). ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 11.68 (s broad, 3H, NH), 1.87 (s, 45H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): δ 119.5 (*C*$_5$Me$_5$), 11.7 (C$_5$*Me*$_5$). MS (EI, 70 eV): *m/z* 671 (23) [M − I]$^+$, 610 (5) [M − I − Cu]$^+$. Anal. Calcd for $C_{30}H_{48}CuIN_4Ti_3$ ($M_w = 798.78$): C, 45.11; H, 6.06; N, 7.01. Found: C, 45.41; H, 5.77; N, 6.63.

Synthesis of [{Cu(μ_4-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (15). Method A. A solution of [LiN(SiMe$_3$)$_2$] (0.047 g, 0.28 mmol) in toluene (5 mL) was carefully added to **13** (0.20 g, 0.28 mmol) in toluene (15 mL). The system was allowed to react without any stirring for 6 days to give the precipitation of huge red crystals of **15** and a fine white powder. After elimination of the solution by decantation, the crystals were rinsed with several portions of toluene (4 × 5 mL) to remove the powder and characterized as **15**·2C$_7$H$_8$ (0.11 g, 51%).

Method B. A 100 mL Carius tube was charged with **1** (0.30 g, 0.49 mmol), [{CuN(SiMe$_3$)$_2$}$_4$] (0.11 g, 0.12 mmol), and toluene (30 mL). The tube was flame sealed and heated at 150 °C for 6

Table 1. Experimental Data for the X-ray Diffraction Studies on **3**, **8**, **9**, and **15**

	3·CH_2Cl_2	**8**·C_7H_8	**9**	**15**·C_6D_6
formula	$C_{31}H_{53}Cl_4N_5Ti_3Zn$	$C_{45}H_{68}N_4SiTi_3Zn$	$C_{36}H_{65}N_5Si_2Ti_3Zn$	$C_{66}H_{100}Cu_2N_8Ti_6$
M_r	846.65	902.19	833.18	1420.02
T (K)	200(2)	200(2)	200(2)	200(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	11.595(2)	18.903(2)	11.645(3)	12.397(2)
b (Å)	23.461(2)	11.069(2)	11.906(3)	14.963(3)
c (Å)	14.608(2)	22.510(2)	17.621(4)	22.185(2)
α (deg)			81.76(2)	
β (deg)	100.69(1)	101.87(1)	87.73(2)	123.56(1)
γ (deg)			65.84(2)	
V (Å^3)	3904.7(8)	4609.2(9)	2205.6(9)	3429.3(9)
Z	4	4	2	2
ρ_{calcd} (g cm^{-3})	1.440	1.300	1.255	1.375
μ(Mo Kα) (mm^{-1})	1.500	1.075	1.144	1.312
F(000)	1752	1904	880	1484
cryst size (mm^3)	0.3 × 0.3 × 0.3	0.3 × 0.1 × 0.1	0.33 × 0.29 × 0.21	0.41 × 0.29 × 0.27
θ range (deg)	5.00−25.01	5.03−25.24	3.05−27.50	3.06−27.57
index ranges	−13 to 13, −27 to 27, −17 to 17	−22 to 22, −13 to 13, −27 to 27	−15 to 15, −15 to 15, −22 to 22	−13 to 16, 0 to 19, −26 to 28
reflns collected	23 861	29 828	18 592	134 861
unique data	6817 [R_{int} = 0.122]	8271 [R_{int} = 0.186]	9997 [R_{int} = 0.042]	7908 [R_{int} = 0.118]
obsd data [$I > 2\sigma(I)$]	4213	3773	7640	5418
GOF on F^2	1.042	1.092	1.065	1.087
final R^a indices [$I > 2\sigma(I)$]	R1 = 0.062 wR2 = 0.114	R1 = 0.087 wR2 = 0.172	R1 = 0.047 wR2 = 0.127	R1 = 0.096 wR2 = 0.282
R^a indices (all data)	R1 = 0.127 wR2 = 0.135	R1 = 0.231 wR2 = 0.231	R1 = 0.067 wR2 = 0.137	R1 = 0.138 wR2 = 0.307
largest diff. peak/hole (e·Å^{-3})	0.449/−0.541	0.966/−1.113	0.763/−0.674	1.58/−3.461

[a] $R1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

days. The reaction mixture was allowed to cool to room temperature overnight to produce red crystals of **15**·$2C_7H_8$ (0.27 g, 73%).

IR (KBr, cm^{-1}): $\tilde{\nu}$ 3357 (m), 2902 (s), 1604 (w), 1494 (m), 1431 (s), 1373 (s), 1080 (w), 1023 (m), 729 (vs), 671 (vs), 629 (vs), 617 (vs), 509 (s), 478 (w), 464 (m). Anal. Calcd for $C_{74}H_{110}Cu_2N_8Ti_6$ (M_w = 1526.03): C, 58.24; H, 7.26; N, 7.34. Found: C, 58.19; H, 7.13; N, 7.12.

Synthesis of [$(Ph_3P)Cu\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (16). A 100 mL Schlenk flask was charged with **13** (0.30 g, 0.42 mmol), PPh_3 (0.11 g, 0.42 mmol), and toluene (15 mL). After the mixture was stirred at room temperature for 10 min, a solution of [$Li\{N(SiMe_3)_2\}$] (0.070 g, 0.42 mmol) in toluene (5 mL) was added. The reaction mixture was stirred at room temperature for 18 h to give an orange solution and a fine solid. After filtration, the volatile components were removed under reduced pressure to give **16** as an orange solid (0.34 g, 87%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3362 (m), 3050 (m), 2907 (s), 2855 (s), 1587 (w), 1573 (w), 1481 (m), 1434 (s), 1374 (m), 1185 (w), 1096 (m), 1026 (m), 997 (w), 744 (m), 707 (vs), 667 (vs), 613 (vs), 518 (s), 492 (m), 423 (m), 387 (m). ^1H NMR (C_6D_6, 20 °C): δ 11.08 (s broad, 2H, NH), 7.59 (m, 6H, *o*-C_6H_5), 7.15−7.10 (m, 9H, *m*- and *p*-C_6H_5), 2.16 (s, 30H, C_5Me_5), 1.99 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 135.5 (d, $^1J_{C-P}$ = 33.7 Hz, *ipso*-C_6H_5), 134.3 (d, $^2J_{C-P}$ = 15.4 Hz, *o*-C_6H_5), 129.8 (d, $^4J_{C-P}$ = 1.4 Hz, *p*-C_6H_5), 128.5 (d, $^3J_{C-P}$ = 9.5 Hz, *m*-C_6H_5), 116.6 (C_5Me_5), 115.8 (C_5Me_5), 11.9 (C_5Me_5), 11.8 (C_5Me_5). MS (EI, 70 eV): *m/z* 671 (3) [M − PPh_3]$^+$, 608 (1) [M − PPh_3 − Cu]$^+$, 536 (2) [M − PPh_3 − C_5Me_5]$^+$, 400 (3) [M − PPh_3 − $2C_5Me_5$]$^+$, 262 (89) [PPh_3]$^+$, 183 (100) [PPh_2]$^+$, 108 (40) [PPh]$^+$. Anal. Calcd for $C_{48}H_{62}CuN_4PTi_3$ (M_w = 933.17): C, 61.78; H, 6.70; N, 6.00. Found: C, 61.62; H, 6.54; N, 5.36.

X-ray Structure Determination of 3, 8, 9, and 15. Crystals of complexes **3**, **8**, **9**, and **15** were grown as described in the Results and Discussion section, removed from the Schlenk flasks, and covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker−Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table 1.

The structures were solved, using the WINGX package,[33] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[34] All non-hydrogen atoms were anisotropically refined, while the hydrogen atoms were positioned geometrically and refined using a riding model. Crystals of compound **15** were of poor quality and also presented disorder for the carbon atoms C(16)−C(20) of the pentamethylcyclopentadienyl group linked to Ti(1), the PART tool and a free variable in the FVAR command of the SHELXL-97 program allowed two positions for each carbon atom to be refined with 54.8 and 45.2% of occupancy, respectively. The highest peak and hole found in the difference Fourier map of 1.58/−3.46 e·Å^{-3} are located close to Cu(1) (1.03 and 0.75 Å, respectively).

Results and Discussion

Azaheterometallocubanes of Zinc. Treatment of [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$] (**1**) with anhydrous zinc dichloride (1 equiv) in toluene at room temperature produces the adduct [$Cl_2Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**2**) as a yellow solid

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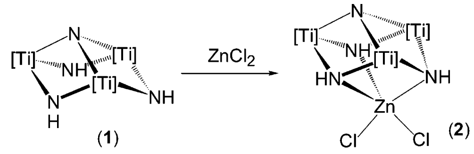
(33) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
(34) Sheldrick, G. M. *SHELX97, Program for Crystal Structure Analysis*, release 97-2; Universität Göttingen: Göttingen, Germany, 1998.

Scheme 1. Reaction of **1** with $ZnCl_2$[a]



[a] [Ti] = Ti(η^5-C_5Me_5).

in a 68% yield (Scheme 1). Complex **2** is not soluble in aromatic solvents but exhibits good solubility in chloroform or dichloromethane. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** in chloroform-d_1 at room temperature show resonances for equivalent NH and η^5-C_5Me_5 groups. The NH resonance signal (δ = 11.51) in the ^1H NMR spectrum is shifted to higher field with respect to that found for **1** (δ = 13.40), whereas the resonance signal for the ipso carbon of the pentamethylcyclopentadienyl groups (δ = 122.4) in the $^{13}C\{^1H\}$ NMR spectrum is shifted downfield with respect to that found for **1** (δ = 117.1). These data are similar to those recently reported for several main-group metal adducts $[X_nM\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$[16] and are consistent with a tridentate coordination of **1** to the zinc center or very fast exchange processes in solution.

Moreover, while the NMR data suggest a single-cube structure in solution, the insolubility of **2** in aromatic solvents might agree with a halide-bridged double-cube structure in the solid state like that recently determined for the tin derivative $[\{ISn(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}_2(\mu\text{-}I)_2]$.[16b] The mass spectrum (EI, 70 eV) shows the ion $[M - Cl]^+$ as that of the higher relation mass/charge, suggesting a single-cube structure in the gas phase, but higher aggregates cannot be ruled out. Attempts to grow suitable single crystals for a solid-state determination of **2** failed, but a solution of **2** in dichloromethane at −40 °C rendered a very small fraction of yellow crystals of the ammonia adduct $[(H_3N)Cl_2Zn\{(\mu_3\text{-NH})Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ (**3**). Complex **3** could not be obtained in a preparative scale experiment since reactions of **2** with an excess of ammonia in dichloromethane gave immediately **1** and a fine white precipitate of $[ZnCl_2(NH_3)_2]$.[35,36] Furthermore, we did not observe any reaction between complex **1** and $[ZnCl_2(NH_3)_2]$ in dichloromethane or toluene even at high temperatures.

The X-ray crystal structure of $[(H_3N)Cl_2Zn\{(\mu_3\text{-NH})Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ (**3**) is presented in Figure 1, and selected bond lengths and angles are given in Table 2. The solid-state structure reveals a distorted tetrahedral geometry for the zinc center, comprising two chloride, one ammonia ligand, and one NH imido group with angles spanning 123.3(1)−100.8(2)°. The Zn−Cl, average 2.283(2) Å, and Zn−N(ammonia), 2.044(5) Å, bond lengths compare well with those reported for $[ZnCl_2(NH_3)_2]$[36] and other $[ZnCl_2(\text{diamine})]$[37] complexes. The triaza ligand is bound to zinc by one NH group with a zinc−nitrogen bond length, Zn−N(13) 2.046(5) Å, very similar to that found for the ammonia ligand. Within the organometallic ligand, the average bond lengths and angles are similar to those determined in the free ligand **1**.[8]

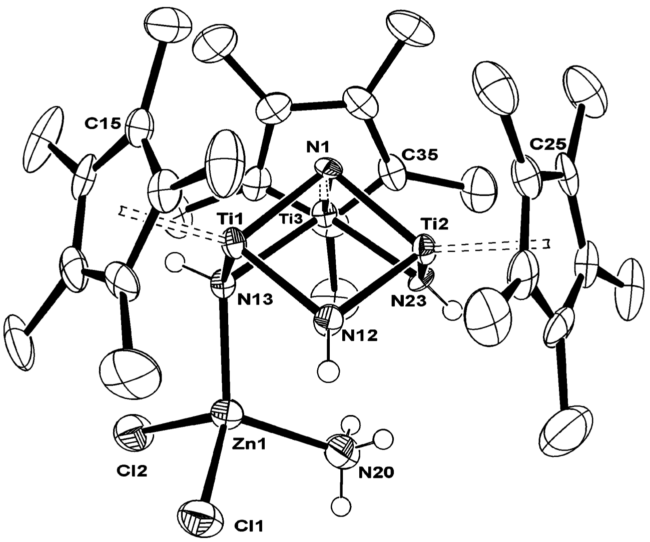


Figure 1. Perspective view of $[(H_3N)Cl_2Zn\{(\mu_3\text{-NH})Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ (**3**) with thermal ellipsoids at the 50% probability level. The dichloromethane solvent molecule is omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

Zn(1)−N(13)	2.046(5)	Zn(1)−N(20)	2.044(5)
Zn(1)−Cl(1)	2.274(2)	Zn(1)−Cl(2)	2.292(2)
Ti(1)−N(13)	2.009(4)	Ti(1)−N(12)	1.891(5)
Ti(1)−N(1)	1.908(4)	Ti(2)−N(12)	1.923(4)
Ti(2)−N(23)	1.927(4)	Ti(2)−N(1)	1.934(4)
Ti(3)−N(13)	2.009(4)	Ti(3)−N(23)	1.879(4)
Ti(3)−N(1)	1.922(4)	Ti···Ti (av)	2.815(1)
N(13)−Zn(1)−N(20)	111.9(2)	N(13)−Zn(1)−Cl(1)	123.3(1)
N(13)−Zn(1)−Cl(2)	103.4(1)	N(20)−Zn(1)−Cl(1)	100.8(2)
N(20)−Zn(1)−Cl(2)	108.3(2)	Cl(1)−Zn(1)−Cl(2)	108.7(1)
Ti(1)−N(1)−Ti(3)	95.9(2)	Ti(1)−N(1)−Ti(2)	93.9(2)
Ti(3)−N(1)−Ti(2)	93.0(2)	Ti(1)−N(12)−Ti(2)	94.8(2)
Ti(3)−N(13)−Ti(1)	90.1(2)	Ti(3)−N(13)−Zn(1)	120.0(2)
Ti(1)−N(13)−Zn(1)	113.0(2)	Ti(3)−N(23)−Ti(2)	94.6(2)
N(12)−Ti(1)−N(1)	86.2(2)	N(12)−Ti(1)−N(13)	103.6(2)
N(1)−Ti(1)−N(13)	87.0(2)	N(12)−Ti(2)−N(23)	107.3(2)
N(12)−Ti(2)−N(1)	84.6(2)	N(23)−Ti(2)−N(1)	85.0(2)
N(23)−Ti(3)−N(1)	86.7(2)	N(23)−Ti(3)−N(13)	105.3(2)
N(1)−Ti(3)−N(13)	86.7(2)		

Treatment of **1** with 1 equiv of the zinc alkyl, trimethylsilylcyclopentadienyl, or amido complexes $[ZnR_2]$ in toluene at room temperature leads to the cube-type derivatives $[RZn\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$ [R = CH_2SiMe_3 (**5**), CH_2Ph (**6**), Me (**7**), $C_5H_4SiMe_3$ (**8**), $N(SiMe_3)_2$ (**9**)] via alkane/trimethylsilylcyclopentadiene/amine elimination (Scheme 2). However, the analogous treatment of **1** with dicyclopentadienylzinc $[Zn(C_5H_5)_2]$[26] gave unaltered initial products, probably because of the insolubility of the zinc reagent in the reaction solvent.

The reactions most likely proceed via adducts similar to **2**, but only the bis(trimethylsilylmethyl)zinc derivative $[(Me_3SiCH_2)_2Zn\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$ (**4**) was

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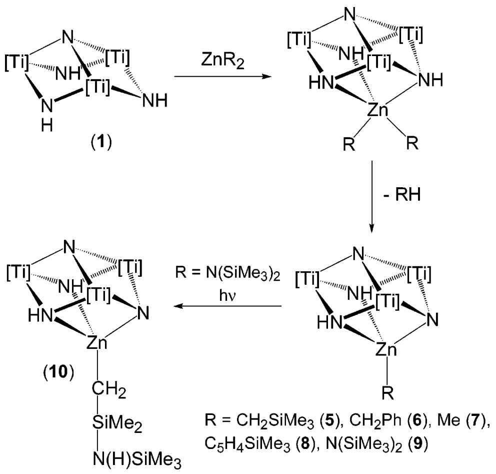
(35) Block, B. P.; Florentine, R. A.; Simkin, J.; Barth-Wehrenalp, G. *J. Inorg. Nucl. Chem.* **1962**, *24*, 371−380.

(36) Yamaguchi, T.; Lindqvist, O. *Acta Chem. Scand.* **1981**, *A35*, 727−728.

(37) (a) Steffen, W. L.; Palenik, G. J. *Acta Crystallogr. B* **1976**, *32*, 298−300. (b) Qin, J.; Su, N.; Dai, C.; Yang, C.; Liu, D.; Day, M. W.; Wu, B.; Chen, C. *Polyhedron* **1999**, *18*, 3461−3464. (c) Roh, S.-G.; Park, Y.-C.; Park, D.-K.; Kim, T.-J.; Jeong, J. H. *Polyhedron* **2001**, *20*, 1961−1965 and references therein.

Scheme 2. Reactions of **1** with ZnR_2[a]



[a] [Ti] = Ti(η^5-C_5Me_5).

stable for some minutes and clearly identified following the reaction course by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The spectra at room temperature of the reaction mixture in benzene-d_6 show, after 10 min, shifted resonances with respect to those of the starting materials for equivalent NH, η^5-C_5Me_5, and CH_2SiMe_3 groups. After some hours at room temperature, the spectra revealed complete consumption of **4** to give complex **5** and the corresponding equivalent of tetramethylsilane.

Complexes **5**−**9** were obtained in good yields (88−98%) as red solids, which are very soluble in hexane or toluene. These compounds were characterized by spectral and analytical methods, as well as by X-ray crystal structure determinations for **8** and **9**. Mass spectra (EI, 70 eV) show the expected molecular peaks suggesting a single-cube aggregation in the gas phase. ^1H and ^{13}C NMR spectra in benzene-d_6 at room temperature show resonance signals for two η^5-C_5Me_5 groups in a 2:1 ratio, one Zn−R fragment, and a broad signal for the NH groups. These NMR data are consistent with a C_s symmetry in solution and tetrahedral geometries for the zinc centers, in a manner similar to those recently reported for the analogous magnesium complexes $[RMg\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$[19] and several tris(pyrazolyl)hydroboratozinc derivatives.[38]

To confirm the proposed structures in the Scheme 2 and establish unambiguously the coordination mode of the trimethylsilylcyclopentadienyl ligand in **8**, X-ray crystallographic studies were undertaken for crystals of $\mathbf{8}\cdot C_7H_8$ and **9** grown in saturated toluene solutions. The X-ray structures are presented in Figures 2 and 3, while selected bond and angles are shown in Tables 3 and 4.

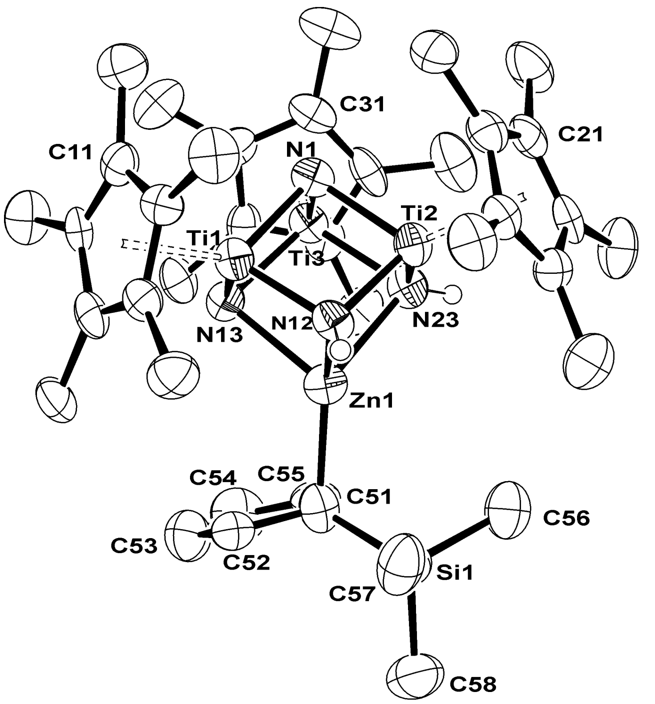


Figure 2. Perspective view of $[\{(Me_3Si)H_4C_5\}Zn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**8**) with thermal ellipsoids at the 50% probability level. The toluene solvent molecule is omitted for clarity.

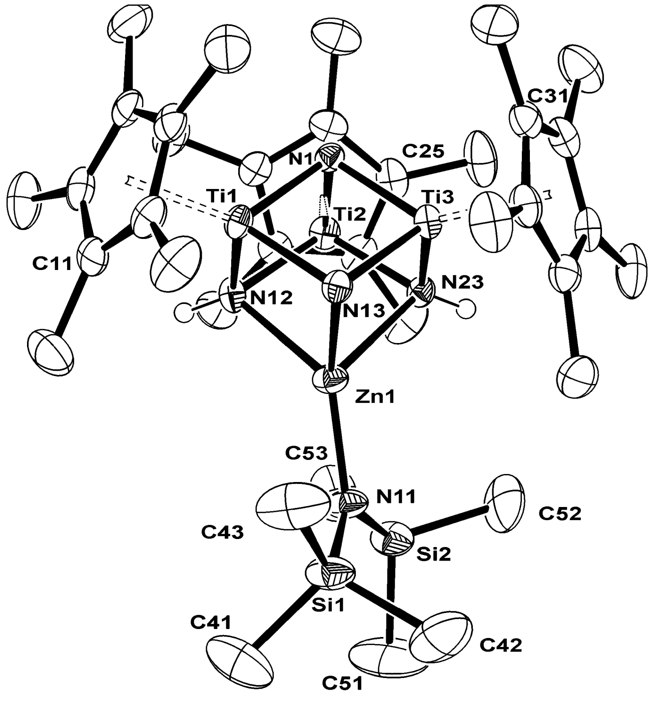


Figure 3. Perspective view of $[\{(Me_3Si)_2N\}Zn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**9**) with thermal ellipsoids at the 50% probability level.

Compound **8** crystallizes with one toluene solvent molecule per cube-type complex. The structure shows a cube-type $[ZnTi_3N_4]$ core with angles M−N−M and N−M−N spanning 85.2(3)−99.7(3)°. The coordination sphere about the zinc atom is best described as distorted tetrahedral, with three nitrogen atoms of the tridentate organometallic ligand $\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}^-$ and one carbon atom of the $C_5H_4SiMe_3$ group and angles of N−Zn−N = 86.0(3)° (av) and C(51)−Zn−N 128.0(4)° (av). The zinc−nitrogen bond lengths, average 2.140(8) Å, are slightly longer than that found for complex **3** but closer to those reported for several tris(pyrazolyl)hydroborates[38a,39] where the zinc

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[38] (a) Gorrell, I. B.; Looney, A.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1990**, 220−222. (b) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274−288. (c) Kisko, J. L.; Fillebeen, T.; Hascall, T.; Parkin, G. *J. Organomet. Chem.* **2000**, *596*, 22−26. (d) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **2003**, *42*, 5034−5036.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **8**[a]

Zn(1)−N(12)	2.148(8)	Zn(1)−N(13)	2.126(8)
Zn(1)−N(23)	2.147(8)	Zn(1)−C(51)	2.031(11)
Zn(1)···C(52)	2.753(11)	Zn(1)···C(53)	3.532(14)
Zn(1)···C(54)	3.482(15)	Zn(1)···C(55)	2.686(12)
C(51)−C(52)	1.461(14)	C(51)−C(55)	1.457(14)
C(52)−C(53)	1.372(16)	C(53)−C(54)	1.391(18)
C(54)−C(55)	1.376(16)	C(51)−Si(1)	1.855(11)
N(1)−Ti(3)	1.895(8)	N(1)−Ti(1)	1.922(8)
N(1)−Ti(2)	1.949(8)	N(12)−Ti(2)	1.857(7)
N(12)−Ti(1)	1.853(8)	N(13)−Ti(3)	1.961(8)
N(13)−Ti(1)	1.968(8)	N(23)−Ti(2)	1.946(8)
N(23)−Ti(3)	1.958(8)	Ti···Ti (av)	2.817(2)

N(12)−Zn(1)−N(13)	86.2(3)	N(12)−Zn(1)−N(23)	84.7(3)
N(13)−Zn(1)−N(23)	87.1(3)	N(12)−Zn(1)−C(51)	129.0(4)
N(13)−Zn(1)−C(51)	122.1(4)	N(23)−Zn(1)−C(51)	132.8(4)
Zn(1)−C(51)−Si(1)	107.9(5)	Zn(1)−C(51)−Cp	108.8(6)
Si(1)−C(51)−Cp	143.5(7)	Ti(3)−N(1)−Ti(1)	96.3(4)
Ti(3)−N(1)−Ti(2)	95.1(3)	Ti(1)−N(1)−Ti(2)	91.4(3)
Ti(2)−N(12)−Ti(1)	96.7(3)	Ti(2)−N(12)−Zn(1)	89.1(3)
Ti(1)−N(12)−Zn(1)	87.9(3)	Ti(3)−N(13)−Ti(1)	92.7(3)
Ti(3)−N(13)−Zn(1)	87.9(3)	Ti(1)−N(13)−Zn(1)	85.6(3)
Ti(2)−N(23)−Ti(3)	93.2(3)	Ti(2)−N(23)−Zn(1)	86.8(3)
Ti(3)−N(23)−Zn(1)	87.4(3)	N(12)−Ti(1)−N(1)	86.4(3)
N(12)−Ti(1)−N(13)	99.7(3)	N(1)−Ti(1)−N(13)	84.9(3)
N(12)−Ti(2)−N(1)	85.5(3)	N(12)−Ti(2)−N(23)	99.0(3)
N(1)−Ti(2)−N(23)	85.2(3)	N(1)−Ti(3)−N(23)	86.4(3)
N(1)−Ti(3)−N(13)	85.8(3)	N(23)−Ti(3)−N(13)	97.4(3)

[a] Cp = centroid of the C(51)−C(55) ring.

Table 4. Selected Lengths (Å) and Angles (deg) for **9**

Zn(1)−N(12)	2.174(2)	Zn(1)−N(13)	2.132(2)
Zn(1)−N(23)	2.209(2)	Zn(1)−N(11)	1.916(2)
N(1)−Ti(1)	1.936(2)	N(1)−Ti(3)	1.939(2)
N(1)−Ti(2)	1.950(2)	N(11)−Si(2)	1.721(3)
N(11)−Si(1)	1.722(3)	N(12)−Ti(1)	1.961(2)
N(12)−Ti(2)	1.966(2)	N(13)−Ti(1)	1.957(2)
N(13)−Ti(3)	1.972(2)	N(23)−Ti(2)	1.923(2)
N(23)−Ti(3)	1.930(2)	Ti···Ti (av)	2.836(1)

N(12)−Zn(1)−N(13)	87.1(1)	N(12)−Zn(1)−N(23)	84.6(1)
N(13)−Zn(1)−N(23)	86.2(1)	N(12)−Zn(1)−N(11)	134.1(1)
N(13)−Zn(1)−N(11)	126.8(1)	N(23)−Zn(1)−N(11)	122.8(1)
Ti(1)−N(1)−Ti(3)	94.3(1)	Ti(1)−N(1)−Ti(2)	94.0(1)
Ti(3)−N(1)−Ti(2)	93.2(1)	Si(2)−N(11)−Si(1)	123.8(1)
Si(2)−N(11)−Zn(1)	112.9(1)	Si(1)−N(11)−Zn(1)	122.6(1)
Ti(1)−N(12)−Ti(2)	92.7(1)	Ti(1)−N(12)−Zn(1)	86.4(1)
Ti(2)−N(12)−Zn(1)	88.3(1)	Ti(1)−N(13)−Ti(3)	92.6(1)
Ti(1)−N(13)−Zn(1)	87.7(1)	Ti(3)−N(13)−Zn(1)	87.8(1)
Ti(2)−N(23)−Ti(3)	94.4(1)	Ti(2)−N(23)−Zn(1)	88.4(1)
Ti(3)−N(23)−Zn(1)	86.7(1)	N(1)−Ti(1)−N(13)	86.8(1)
N(1)−Ti(1)−N(12)	86.9(1)	N(13)−Ti(1)−N(12)	98.5(1)
N(23)−Ti(2)−N(1)	86.1(1)	N(23)−Ti(2)−N(12)	98.6(1)
N(1)−Ti(2)−N(12)	86.3(1)	N(23)−Ti(3)−N(1)	86.2(1)
N(23)−Ti(3)−N(13)	98.9(1)	N(1)−Ti(3)−N(13)	86.2(1)

atom is also coordinated to three nitrogen atoms. The distance from the silyl-bearing carbon atom C(51) to the zinc atom [2.031(11) Å], typical for zinc−carbon covalent bonds,[40] is clearly shorter than those to the other carbon atoms of the trimethylsilylcyclopentadienyl ring, as can be seen in Table 3, in a manner similar to those found in $[Zn(C_5Me_4SiMe_3)_2]$[41] and $[Zn(C_5H_4SiMe_3)_2]$,[25a] confirming an $\eta^1(\sigma)$ coordination mode. Moreover, the Zn−C(51)−Si and Zn−C(51)−ring angles [107.9(5) and 108.8(6)°, respectively] are very close to the ideal 109.5° value for a tetrahedral geometry, suggesting an sp^3 hybridization for C(51).

The molecular structure of **9** confirms the azaheterometallocubane core $[ZnTi_3N_4]$ of the complex and the tridentate coordination of the $\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}^-$ ligand to zinc. The geometry about the zinc center is best described as distorted tetrahedral, with intraligand N−Zn−N angles spanning 84.6(1)−87.1(1)° and interligand N−Zn−N(11) angles in the range of 122.8(1)−134.1(1)°. The trimethylsilyl groups of the amido ligand are oriented in an alternate disposition with respect to the pentamethylcyclopentadienyl rings of the preorganized triaza ligand to decrease the steric repulsion. The zinc−nitrogen bond lengths within the cube core are in the range of 2.132(2)−2.209(2) Å and are longer than that found for the amido ligand [Zn−N(11) = 1.916(2) Å], in a manner similar to that of the (guanidinato)(amido) complex $[Zn(hpp)\{N(SiMe_3)_2\}]_2$ reported by Coles et al.[42] The overall structure of **9** is very similar to that determined for the magnesium amido analogue $[\{(Me_3Si)_2N\}Mg\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$,[19] but it shows slightly shorter Zn−N bond lengths and wider N−Zn−N intraligand angles because of the smaller size of the zinc atom.

Alkyl complexes **5**−**8** are stable in benzene-d_6 solutions at ambient light or temperatures of about 100 °C. In contrast, the magnesium analogues $[RMg\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$ undergo Schlenk-type redistribution reactions at room temperature to give the corner-shared nitrido complex $[Mg\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}_2]$.[19] Furthermore, compounds **5**−**8** did not react with 1 equiv of **1**, even at high temperatures. On the other hand, the bis(trimethylsilyl)amido derivative **9** is light sensitive in solution and decomposes slowly at room temperature and rapidly at higher temperatures, to give the alkyl derivative $[\{Me_3Si(H)N(Me)_2SiCH_2\}Zn\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$ (**10**) (Scheme 2). No intermediates or secondary products were identified in the NMR spectra by monitoring the reaction course of a benzene-d_6 solution of **9** exposed to ambient light. Complex **10** was obtained as a brown solid in a 79% yield by irradiation of toluene solutions of **9** with the light emitted by a sun lamp for 20 h. ^1H and ^{13}C NMR spectra of **10** reveal resonances for two different $\eta^5\text{-}C_5Me_5$ ligands in a 2:1 ratio and are consistent with a C_s symmetry in solution. The methylene CH_2 group of **10** shows a singlet resonance at −0.69 ppm in the ^1H NMR spectrum and a triplet resonance ($^1J_{C-H} = 115$ Hz) at −11.0 ppm in the ^{13}C NMR spectrum. These chemical shifts are similar to those found for the methylene group in the spectra of $[(Me_3SiCH_2)Zn\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$ (**5**), −0.77 (CH_2) and −13.3 (CH_2) ppm, respectively. However, the ^1H NMR spectrum of **10** did not allow the unambiguous identification of the N*H* resonance for the $CH_2Si(Me)_2N(H)SiMe_3$ group.

To test other methods to prepare the azaheterometallocubane complexes of zinc, we tried reactions of the dichloride

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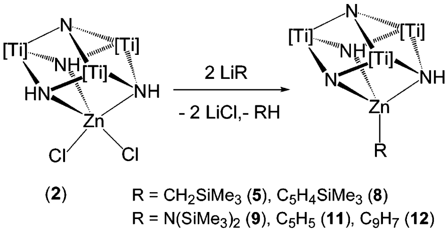
(39) (a) Alsfasser, R.; Powell, A. K.; Trofimenko, S.; Vahrenkamp, H. *Chem. Ber.* **1993**, *126*, 685−694. (b) Yoon, K.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 8414−8418.

(40) (a) Walker, D. A.; Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 797−803. (b) Ly, H. V.; Forster, T. D.; Maley, D.; Parvez, M.; Roesler, R. *Chem. Commun.* **2005**, 4468−4470 and references therein.

(41) Fernández, R.; Resa, I.; del Río, D.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, A. *Organometallics* **2003**, *22*, 381−383.

(42) Coles, M. P.; Hitchcock, P. B. *Eur. J. Inorg. Chem.* **2004**, 2662−2672.

Scheme 3. Reactions of **2** with LiR[a]

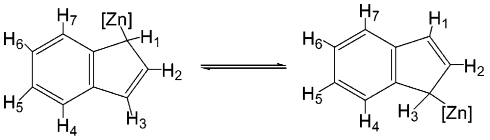


[a] [Ti] = Ti(η^5-C_5Me_5).

complex [$Cl_2Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**2**) with several organolithium reagents (Scheme 3). Thus, treatment of **2** with 2 equiv of lithium (trimethylsilyl)methyl, (trimethylsilyl)cyclopentadienyl or bis(trimethylsilyl)amido derivatives in toluene at room temperature afforded the alkyl or amido zinc complexes [$RZn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] [R = CH_2SiMe_3 (**5**), $C_5H_4SiMe_3$ (**8**), $N(SiMe_3)_2$ (**9**)] in good yields (68−78%). Analogous reactions of **2** with 2 equiv of lithium cyclopentadienyl [$Li(C_5H_5)$] or lithium indenyl [$Li(C_9H_7)$] reagents at room temperature gave the new cyclopentadienyl or indenyl zinc derivatives [$RZn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] [R = C_5H_5 (**11**), C_9H_7 (**12**)] as red solids in good yields (72−73%).

Complexes **11** and **12** exhibit a poor solubility in hexane but are very soluble in toluene or benzene, and the solutions are stable under an argon atmosphere at ambient light and temperature conditions. Compounds **11** and **12** were characterized by spectral and analytical methods. The mass spectra (EI, 70 eV) show the expected molecular peaks suggesting a single-cube aggregation for the complexes in the gas phase. ^1H and $^{13}C\{^1H\}$ NMR spectra in benzene-d_6 at room temperature show resonance signals for two η^5-C_5Me_5 groups in a 2:1 ratio, one cyclopentadienyl or indenyl ligand, and a broad signal for the NH groups. To investigate the coordination mode of the cyclopentadienyl or indenyl ligands to the zinc center, we studied a toluene-d_8 solution of complex **12** by low-temperature ^1H NMR spectroscopy in a 500 MHz spectrometer. The room temperature ^1H NMR spectrum of **12** showed the following resonances for the indenyl group: one doublet (^3J = 3.0 Hz) at δ = 5.53 for the H_1 and H_3, one triplet at δ = 6.98 for the H_2, and a sharp AA′BB′ pattern at δ = 7.59−7.23 for the H_4, H_5, H_6 and H_7. When cooled to −20 °C, the resonance signal at δ = 5.53 began to broaden and, at −94 °C, gave two very broad resonances centered at approximately δ = 4.6 and 7.0 which coalesced at about −89 °C. This nonequivalence of the protons of the indenyl ligand at low temperature is consistent with a $\eta^1(\sigma)$ coordination of the indenyl ligand by the C_1 or C_3 to the zinc center. The fluxional process observed can be explained by an intramolecular 1,3 migration of the zinc on the indenyl ligand that is very fast on the NMR time scale at room temperature and slower at −94 °C (Scheme 4).

Scheme 4. 1,3 Migration of the [Zn] Fragment on the Indenyl Ligand in **12**

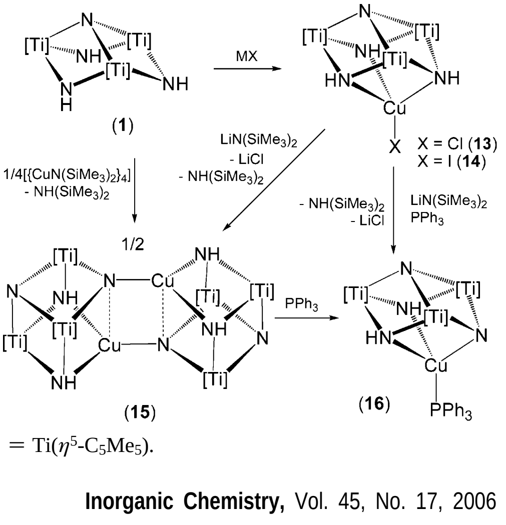


An analogous 1,3 migration has been investigated in detail by Casey on several indenylrhenium derivatives.[43] In those studies on the fluxional processes and in many others previously,[44] the authors observed a smaller barrier for η^1-cyclopentadienyl systems compared with the η^1-indenyl systems. Therefore, we did not study the fluxional process occurring on complex **11**, but the NMR spectra are consistent with $\eta^1(\sigma)$ coordination of the cyclopentadienyl ligand bound to zinc and a more rapid 1,2 migration of the zinc on the cyclopentadienyl ring.

Azaheterometallocubanes of Copper(I). The treatment of [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$] (**1**) with anhydrous copper(I) halides (1 equiv) in toluene at room temperature produces the adducts [$XCu\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (X = Cl (**13**), I (**14**)) in good yields (72 and 65%, respectively) (Scheme 5). Complexes **13** and **14** were obtained as red solids, which are very soluble in toluene and scarcely soluble in hexane. The mass spectrum (EI, 70 eV) of **13** shows the molecular peak for a single-cube structure, whereas the spectrum of **14** reveals the $[M - I]^+$ ion, as that of the higher relation mass/charge. ^1H and $^{13}C\{^1H\}$ NMR spectra of **13** and **14** in benzene-d_6 reveal resonances for equivalent NH and η^5-C_5Me_5 groups. The NH resonance signals (δ = 11.70 and 11.68) are shifted toward higher field than that found for **1** (δ = 13.40), whereas the resonance signal for the C_5Me$_5$ groups (δ = 119.4 and 119.5) are shifted downfield with respect to that found for **1** (δ = 117.1). These NMR data are similar to those described above for **2** and are consistent with a tridentate coordination of **1** to the copper center and a C_{3v} symmetry in solution.

Treatment of the chloride derivative **13** with lithium bis(trimethylsilyl)amido in toluene at room temperature leads to bis(trimethylsilyl)amine and the precipitation of huge red crystals of the dicubane complex [$\{Cu(\mu_4\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2$] (**15**), together with a fine powder of LiCl. Lithium chloride can be removed from the mixture after rinsing with toluene several times to give **15** in a 51% yield.

Scheme 5. Synthesis of Copper(I) Azaheterometallocubane Complexes[a]



[a] [Ti] = Ti(η^5-C_5Me_5).

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(43) Casey, C. P.; O’Connor, J. M. *Organometallics* **1985**, *4*, 384−388.

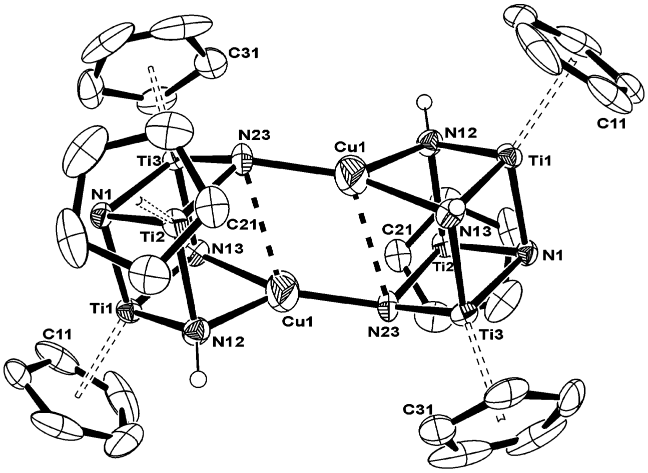

Figure 4. Perspective view of $[\{Cu(\mu_4\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}_2]$ (**15**) with thermal ellipsoids at the 50% probability level. The benzene solvent molecule and methyl groups of the pentamethylcyclopentadienyl rings are omitted for clarity.

Table 5. Selected Lengths (Å) and Angles (deg) for **15**

Cu(1)−N(12)	2.218(5)	Cu(1)−N(13)	2.101(5)
Cu(1)−N(23)[a]	1.912(5)	Cu(1)···N(23)	2.690(5)
Cu(1)···Cu(1)	2.614(2)	N(1)−Ti(1)	1.916(4)
N(1)−Ti(3)	1.947(4)	N(1)−Ti(2)	1.952(4)
N(12)−Ti(1)	1.968(5)	N(12)−Ti(2)	2.007(5)
N(13)−Ti(1)	1.975(5)	N(13)−Ti(3)	1.987(5)
N(23)−Ti(2)	1.882(5)	N(23)−Ti(3)	1.891(5)
N(13)−Cu(1)−N(12)	89.4(2)	N(23)[a]−Cu(1)−N(13)	140.2(2)
N(23)[a]−Cu(1)−N(12)	130.0(2)	N(23)[a]−Cu(1)−N(23)	113.2(2)
Ti(1)−N(1)−Ti(2)	95.4(2)	Ti(1)−N(1)−Ti(3)	95.2(2)
Ti(2)−N(1)−Ti(3)	90.8(2)	Ti(1)−N(12)−Ti(2)	92.0(2)
Ti(1)−N(12)−Cu(1)	81.8(2)	Ti(2)−N(12)−Cu(1)	95.5(2)
Ti(1)−N(13)−Ti(3)	92.1(2)	Ti(1)−N(13)−Cu(1)	84.7(2)
Ti(3)−N(13)−Cu(1)	97.1(2)	Ti(2)−N(23)−Ti(3)	94.8(2)
Ti(2)−N(23)−Cu(1)[a]	121.0(3)	Ti(3)−N(23)−Cu(1)[a]	127.8(3)
N(1)−Ti(1)−N(12)	87.1(2)	N(1)−Ti(1)−N(13)	86.8(2)
N(12)−Ti(1)−N(13)	100.8(2)	N(1)−Ti(2)−N(23)	87.1(2)
N(1)−Ti(2)−N(12)	85.0(2)	N(23)−Ti(2)−N(12)	103.6(2)
N(1)−Ti(3)−N(23)	87.0(2)	N(1)−Ti(3)−N(13)	85.6(2)
N(23)−Ti(3)−N(13)	103.1(2)		

[a] Intercube atoms.

Complex **15** can be obtained in higher yield (73%) through the reaction of **1** with $[\{CuN(SiMe_3)_2\}_4]$[31,32] (0.25 equiv) in toluene at 150 °C for 6 days. A mixture of **1** with $[\{CuN(SiMe_3)_2\}_4]$ in benzene-d_6 was monitored by NMR spectroscopy at different temperatures. After it was heated at 40 °C, red crystals precipitated at the bottom of the tube and resonances resulting from bis(trimethylsilyl)amine were detected in the spectra. However, the reaction rate was very slow at temperatures below 120 °C, probably because of the high stability of the tetranuclear structure determined for the copper amido reagent.[32,45] Complex **15** was characterized by IR spectroscopy and C,H,N microanalysis, as well as by an X-ray crystal structure determination for suitable crystals of **15**·C_6D_6 grown in the treatment of **13** with $LiN(SiMe_3)_2$ in benzene-d_6 without any stirring.

The X-ray structure of **15** is presented in Figure 4, while selected bond and angles are given in Table 5. The crystals of **15** bear one benzene solvent molecule per double-cube complex. The molecule lies on an inversion center and shows an edge-linked double-cube arrangement with two cube-type $[CuTi_3N_4]$ units, resembling the molybdenum−copper sulfido complex published by Shibahara and co-workers.[46] The two $\{Cu(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$ moieties adopt a mutually staggered disposition which minimizes the steric repulsion between the bulky pentamethylcyclopentadienyl ligands, in a manner similar to that of the previously reported edge-linked Group 1 azaheterometallocubane complexes.[17]

Each copper atom in **15** presents an almost trigonal environment (sum of angles = 359.6°) with Cu−N bond distances from 1.912(5) to 2.218(5) Å. These lengths are in the same range than those found for other nitrogen polydentate ligands joined to copper[47] and slightly longer than those reported for several tris(pyrazolyl)hydroboratecopper(I) $[\{(Tp^x)Cu\}_2]$ derivatives.[48] On the other hand, a triangular pyramidal environment could be proposed if the long-range interaction of copper with the intracube N(23) atom (2.690(5) Å) is taken into consideration. Bond distances and angles involving the titanium and nitrogen atoms of the same cube do not differ significantly with respect to the preorganized organometallic ligand **1**,[8] with Ti−N = 1.947(5) Å av [1.924(6) Å in **1**], Ti−N−Ti = 93.4(2)° av [93.7(3)° in **1**], N1−Ti−N = 87.0(2)° av [85.9(3)° in **1**] and only 5° narrower N−Ti−N angles, 102.5(2)° av in **15** and 107.5(3)° in **1**. This latter deviation can be attributed to the coordination of the nitrogen atoms to copper.

Crystals of **15** are not soluble in common organic solvents (benzene-d_6, chloroform-d_1, pyridine-d_5, etc.), precluding its characterization by NMR spectroscopy. However, treatment of **15** with triphenylphosphane (2 equiv) in benzene-d_6 at 80 °C gave an orange solution where the single-cube complex $[(Ph_3P)Cu\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$ (**16**) was characterized by NMR spectroscopy. Complex **16** was prepared in good yield (87%) by the direct reaction of a toluene solution of **13** and triphenylphosphane with $[LiN(SiMe_3)_2]$.

Compound **16** was obtained as an orange solid, which is very soluble in toluene and hexane, and was characterized by spectral and analytical techniques. The ^1H and $^{13}C\{^1H\}$ NMR spectra in benzene-d_6 at room temperature show resonance signals for two η^5-C_5Me_5 groups in a 2:1 ratio,

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(44) Mann, B. E. In *Comprehensive Organometallic Chemistry, Vol. 3*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Elmsford, NY, 1982; pp 89−171 and references therein.

(45) Miele, P.; Foulon, J. D.; Hovnanian, N.; Durand, J.; Cot, L. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 573−583.

(46) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988**, *110*, 3313−3314.

(47) For example, see: (a) Solanki, N. K.; McInnes, E. J. L.; Collison, D.; Kilner, C. A.; Davies, J. E.; Halcrow, M. A. *J. Chem. Soc., Dalton Trans.* **2002**, 1625−1630. (b) Shimazaki, Y.; Yokoyama, H.; Yamauchi, O. *Angew. Chem., Int. Ed.* **1999**, *38*, 2401−2403. (c) Marlin, D. S.; Olmstead, M. M.; Mascharak, P. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4752−4754.

(48) (a) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711−718. (b) Carrier, S. M.; Ruggiero, C. E.; Houser, R. P.; Tolman, W. B. *Inorg. Chem.* **1993**, *32*, 4889−4899. (c) Yoon, K.; Parkin, G. *Polyhedron* **1995**, *14*, 811−821. (d) Kiani, S.; Long, J. R.; Stavropoulos, P. *Inorg. Chim. Acta* **1997**, *263*, 357−366.

one triphenylphosphane ligand, and a broad signal for the NH groups. These data are consistent with a C_s symmetry and a single-cube structure in solution. The tetrahedral environment around the copper center in **16** would be similar to those reported for several [$Tp^xCu(PPh_3)$] derivatives.[49]

Conclusion

In summary, the imido-nitrido titanium complex [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$] (**1**) is capable of acting as a neutral ligand to give stable adducts with zinc(II) and copper(I) halides, while analogous derivatives with zinc and copper alkyl or amido groups undergo alkane or amine elimination to give complexes bearing the monoanionic [$\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$]$^-$ ligand. The coordination modes of **1** and its monoanionic form in those complexes resemble other well-established "nonorganometallic" nitrogen-based ligands. The new heterometallic nitrido compounds reported here exhibit single-cube structures with [MTi_3N_4] central cores, except the copper derivative [$\{Cu(\mu_4\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2$] which shows a double-cube structure with a [$Cu_2Ti_6N_8$] core.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **3**, **8**, **9**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0603407

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(49) (a) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5664−5671. (b) Dias, H. V. R.; Jin, W.; Kim, H.-J.; Lu, H.-L. *Inorg. Chem.* **1996**, *35*, 2317−2328. (c) Gioia Lobbia, G.; Pettinari, C.; Marchetti, F.; Bovio, B.; Cecchi, P. *Polyhedron* **1996**, *15*, 881−890. (d) Gioia Lobbia, G.; Hanna, J. V.; Pellei, M.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2004**, 951−958.