

Formation of a Titanium Complex with a Ti=CHAl₂ Structural Unit from LTiMe₃ and Trimethylaluminum[§]

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The reaction of LTiCl₃ (**1**) (L = HC(CMeN(2,6-*i*Pr₂C₆H₃))₂, nacnac) with MeLi·(Et₂O)_{0.14} in toluene afforded the stable Ti(IV) alkyl complex LTiMe₃ (**1**). Reaction of **1** with 2 equiv of AlMe₃ in toluene resulted in the formation of LTi(Me)=CH(Al₂Me₃) (**2**) in high yield. Compounds **1** and **2** were characterized by X-ray structural analysis, NMR, IR, mass spectrometry, and elemental analysis. The Ti–CH bond length (1.880(2) Å) of **2** is in the range of a short Ti–C bond. This was additionally supported by NMR and DFT calculations. Compound **2** polymerized ethylene without adding any cocatalyst, although activity is low; the best TOF value was 2.4 × 10⁴ g(polymer)/mol catalyst · h · bar.

Introduction

Organometallic reagents bearing titanium and aluminum at the same carbon atom, such as Tebbe's reagent,¹ have attracted great interest in both academia and industry over the last decades. They have found wide application in organic synthesis for conversion of ketones to terminal olefins,² in olefin metathesis,³ in carbonyl alkylation,⁴ and for the synthesis of metallacyclobutanes.⁵ Tebbe-type complexes have been obtained from Ti(IV) chloride or Ti(IV) alkyl complexes and AlMe₃. These complexes consist

of a Ti(IV) center with single bonds to one or two bridging CH₂ groups.^{1,6} To date, Cp₂Ti(μ-Cl)(μ-CH₂)Al(CH₂CMe₃)₂ remains the only Tebbe complex to have been structurally characterized by X-ray diffraction.⁷ When treated with Lewis base, Tebbe's compound can be transformed into the transient methyldiyne titanocene Cp₂Ti=CH₂,¹ which is the reactive intermediate in organic transformations.^{2b} The recently reported Tebbe derivative (PNP)Ti=CtBu(μ-Me)AlMe₂ (PNP = [2-{P(CHMe₂)₂}-4-methylphenyl]₂N[−]) was prepared from (PNP)Ti=CtBu(CtBu₂) and AlMe₃.⁸ A number of complexes with bridging carbon atom, CH₂, or Me groups have been obtained by reaction of Cp*(R₃PN)TiMe₂ (Cp* = Cp, indenyl; R = *i*Pr, Cy, Ph) or (tBu₃PN)₂TiMe₂ with an excess of AlMe₃, affording for example Cp*(μ-Me)(μ-NPr₃)(μ₄-C)(AlMe₂)₃ and CpTi(μ-Me)(μ-NPr₃)(μ₅-C)(AlMe₂)·(AlMe₃), respectively.⁹ To the best of our knowledge only Cp*(Ti(μ-Me)(μ-NP*i*Pr₃)(μ₃-CH)(AlMe₂)₂) contains a bridging CH group between the titanium and aluminum centers.^{9c,10}

[§] Dedicated to Professor Bernt Krebs on the occasion of his 70th birthday.

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(1) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.

(2) (a) Takeda, T.; Tsubouchi, A. *Modern Carbonyl Olefination*; Wiley-VCH: Weinheim, Germany, 2004; pp 151–159. (b) Kulinkovich, O. G.; de Meijere, A. *Chem. Rev.* **2000**, *100*, 2789–2834. (c) Taillefumier, C.; Chapleur, Y. *Chem. Rev.* **2004**, *104*, 263–292. (d) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835–2886. (e) Uttaro, J.-P.; Audran, G.; Monti, H. *J. Org. Chem.* **2005**, *70*, 3484–3489. (f) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270–3272. (g) Nicolaou, K. C.; Postema, M. H. D.; Claiborne, C. F. *J. Am. Chem. Soc.* **1996**, *118*, 1565–1566. (h) Kocovsky, P.; Dunn, V.; Gogoll, A.; Langer, V. *J. Org. Chem.* **1999**, *64*, 101–119. (i) Notz, W.; Hartel, C.; Walds, B.; Schmidt, R. R. *J. Org. Chem.* **2001**, *66*, 4250–4260. (j) Paquette, L. A.; Sun, L.-Q.; Friedrich, D.; Savage, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 8438–8450. (k) Negishi, E.-I.; Kondakov, D. Y.; Van Horn, D. E. *Organometallics* **1997**, *16*, 951–957. (l) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733–1744. (m) Lu, X.; Arthur, G.; Bittman, R. *Org. Lett.* **2005**, *7*, 1645–1648. (n) Chambers, D. J.; Evans, G. R.; Fairbanks, A. *J. Tetrahedron Asymmetry* **2005**, *16*, 45–55.

(3) (a) Ivin, K. J. *J. Mol. Catal. A* **1998**, *133*, 1–16. (b) Halterman, R. L.; Ramsey, T. M. *J. Organomet. Chem.* **1997**, *547*, 41–48. (c) Grubbs, R. H. *Prog. Inorg. Chem.* **1977**, *24*, 1–50.

(4) Hartley, R. C.; McKiernan, G. J. *J. Chem. Soc., Perkin Trans. 1* **2002**, *24*, 2763–2793.

(5) (a) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721–724. (b) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733–742. (c) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658–1661. (d) Eisch, J. J.; Piotrowski, A. *Tetrahedron Lett.* **1983**, *24*, 2043–2046. (e) Bruin, J. W.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1983**, *24*, 3935–3936. (f) Straus, D. A.; Grubbs, R. H. *J. Mol. Catal.* **1985**, *28*, 9–25. (g) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876–6878.

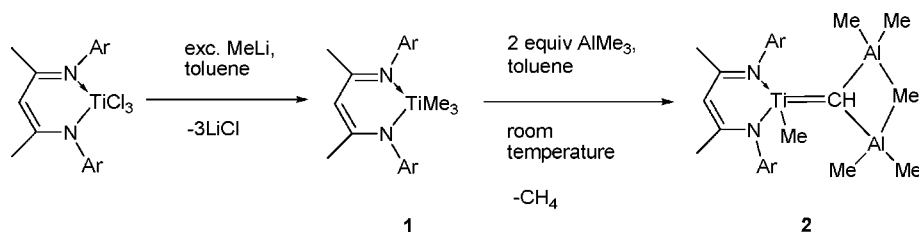
(6) (a) Meurer, E. C.; da Rocha, L. L.; Pilli, R. A.; Eberlin, M. N.; Santos, L. S. *Rapid Commun. Mass Spectrom.* **2006**, *20*, 2626–2629. (b) van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1987**, *28*, 6493–6496. (c) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2386–2387. (d) Chou, T. S.; Huang, S. B.; Hsu, W. H. *J. Chin. Chem. Soc.* **1982**, *30*, 277–279.

(7) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37–51.

(8) Bailey, B. C.; Fout, A. R.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 8246–8249; *Angew. Chem.* **2007**, *119*, 8394–8397.

(9) (a) Kickham, J. E.; Guérin, F.; Stewart, J. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3263–3266; *Angew. Chem.* **2000**, *112*, 3406–3409. (b) Kickham, J. E.; Guérin, F.; Stephan, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 11486–11494. (c) Kickham, J. E.; Guérin, F.; Stewart, J. C.; Urbanska, E.; Stephan, D. W. *Organometallics* **2001**, *20*, 1175–1182. (d) Guérin, F.; Stephan, D. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3698–3700; *Angew. Chem.* **1999**, *111*, 3910–3913. (e) Ong, C.; Kickham, J.; Clemens, S.; Guérin, F.; Stephan, D. W. *Organometallics* **2002**, *21*, 1646–1653. (f) Bolton, P. D.; Clot, E.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2005**, 3313–3315. (g) Graham, T. W.; Ong, C.; Wei, P.; Stephan, D. W. *J. Organomet. Chem.* **2007**, *692*, 4481–4485.

(10) Complex bis(μ₃-bicyclohexyl-1,1'-diol-O,O')-(μ-ethano-C,C)-bis-(diethylaluminum)titanium(IV) contained a bridging CHMe group between the Ti(IV) and Al(III) centers. Krüger, C.; Mynott, R.; Siedenbiedel, C.; Stehling, L.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1668–1670; *Angew. Chem.* **1991**, *103*, 1714–1715. Complex Cp*(Ti(μ-Me)(μ-NP*i*Pr₃)(μ₃-CH)(AlMe₂)₂) contained a bridging CH group in the Ti(IV)–Al(III) {TiAlCAIN} framework (see ref 9c, compound 16)

Scheme 1^a^a Ar = 2,6-*i*Pr₂C₆H₃.

The synthesis and investigation of catalytically active heterometallic complexes containing the group 4 elements (Ti, Zr, Hf) and aluminum are the focus of our interest.¹¹ Herein we report the preparation and characterization of the room-temperature-stable LTiMe₃ (**1**) (L = HC(CMeN(2,6-*i*Pr₂C₆H₃))₂) and the first heterometallic Ti(IV)–Al(III) complex LTi(Me)=CH(Al₂Me₅) (**2**) containing the Ti=CH[Al₂Me₄(μ-Me)] moiety with a formal Ti=C bond.

Results and Discussion

Synthesis and Characterization of 1 and 2. The reaction of TiCl₄ with LLi in a ratio of 1:1 resulted in the formation of LTiCl₃ (L = HC(CMeN(2,6-*i*Pr₂C₆H₃))₂). We observed reduction of LTiCl₃ to LTiCl₂ (EPR, EI-MS),¹² when LTiCl₃ interacted with 2, 3, or 4 equiv of AlMe₃. The mechanism of this reduction is presently not understood. However the reaction of LTiCl₃ and excess solid MeLi·(Et₂O)_x (*x* = 0.12–0.14) in toluene produced LTiMe₃ (**1**) in high yield (Scheme 1). Solid **1** is stable at room temperature for at least 3 days in the absence of light, and for extended times at 0 °C. This shows that **1** is a rare example of a room-temperature-stable Ti(IV) trialkyl complex.¹³

Reaction of **1** with 2 equiv of AlMe₃ at room temperature resulted in the formation of LTi(Me)=CH(Al₂Me₅) (**2**) (Scheme 1). The *in situ* ¹H NMR spectrum of **1** and AlMe₃ in C₆D₆ (after 15 h) showed the resonances of CH₄ (0.19 ppm¹⁴) and complex **2** as the major product even when an excess of AlMe₃ was used.

The single-crystal X-ray structure of **1** (Figure 1) exhibits the discrete LTiMe₃ molecule with the Ti(IV) center in a

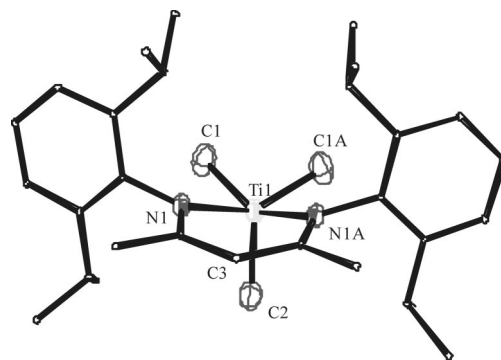


Figure 1. Molecular structure of **1** with labeled selected atoms. Selected bond lengths (Å) and angles (deg): Ti–N(1) 2.161(2), Ti–C(1) 2.185(3), Ti–C(2) 2.102(4); N(1)–Ti–N(1A) 86.14(11), N(1)–Ti–C(2) 105.12(11), N(1)–Ti–C(1) 88.50(10), C(1)–Ti–C(1A) 80.48(16), C(1)–Ti–C(2) 105.87(14). Symmetry transformation used to generate equivalent atoms A of **1**: *x*, *−y*+3/2, *z*.

distorted square-pyramidal environment. The asymmetric unit contains only half a molecule; the other half is generated by a crystallographic mirror plane passing through Ti(1), C(2), and C(3). The Ti atom is 0.580(2) Å out of the (N1 N1A C1 C1A) plane (mean deviation from this plane is zero by symmetry). The inequivalent Ti(1)–C(1) (2.185(3) Å) and Ti(1)–C(2) bond lengths (2.102(4) Å) might be due to the different geometrical sites of C1 and C2 at the base and the apex of a distorted square pyramid. The range of the Ti–C bond lengths is similar to those of tetramethyltitanium adducts TiMe₄L₂ (L = OEt₂ 2.074(4) to 2.100(5) Å,^{13a} dmpe 2.122(7) to 2.201(7) Å,¹⁵ and THF 2.093(2) to 2.107(3) Å¹⁶) and is similar to the Ti–Me bond distance of 2.155(2) Å in the β-diketiminato complex (nacnac)Ti=P[Trip](Me) (Trip = 2,4,6-*i*Pr₃C₆H₂).¹⁷ The bond lengths between titanium and nitrogen atoms in **1** are in the normal range (1.95–2.21 Å) found for Ti(IV) β-diketiminato complexes^{18,21} and Ti(IV) compounds supported by monoanionic nitrogen donor ligands.¹⁹ For instance, the Ti–N bond length in (L₂)Ti=NAr(OTf) is 2.187(9) Å (L₂ = ArNC(Me)CHC(O)=CPh₂C(Me)NAr) and

(11) (a) Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449–3455. (b) Singh, S.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Inorg. Chem.* **2006**, *45*, 949–951. (c) Gurubasavaraj, P. M.; Mandal, S. K.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Noltemeyer, M. *Inorg. Chem.* **2007**, *46*, 1056–1061. (d) Jancik, V.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2005**, *44*, 6016–6018; *Angew. Chem.* **2005**, *117*, 6170–6172. (e) Singh, S.; Roesky, H. W. *Dalton Trans.* **2007**, 1360–1370. (f) Mandal, S. K.; Gurubasavaraj, M.; Roesky, H. W.; Oswald, R. B.; Magull, J.; Ringe, A. *Inorg. Chem.* **2007**, *46*, 4599–4604.

(12) 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.

(13) (a) Kleinhenz, S.; Seppelt, K. *Chem.–Eur. J.* **1999**, *5*, 3573–3580. (b) Milione, S.; Bertolasi, V.; Cuenca, T.; Grassi, A. *Organometallics* **2005**, *24*, 4915–4925. (c) Buil, M. L.; Esteruelas, M. A.; Lopez, A. M.; Mateo, A. C. *Organometallics* **2006**, *25*, 4079–4089. (d) Esteruelas, M. A.; Lopez, A. M.; Mateo, A. C.; Onate, E. *Organometallics* **2006**, *25*, 1448–1460. (e) Esteruelas, M. A.; Lopez, A. M.; Mateo, A. C.; Onate, E. *Organometallics* **2005**, *24*, 5084–5094. (f) Vazquez, A. B.; Royo, P.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *683*, 155–164. (g) Mena, M.; Royo, P.; Serrano, R. *Organometallics* **1989**, *8*, 476–482. Only two non-metallocene trialkyls ((TiMe₃Cl)₄ and TiMe₃Cl·OEt₂), which are stable below −30 °C, were structurally characterized. Only complex (bpzmp)TiMe₃ (bpzmp = (3,5-*t*Bu₂-2-phenoxo)bis(3,5-Me₂-pyrazol-1-yl)methane) was isolated and characterized by NMR; none of metallocene trialkyls were structurally characterized (c–g).

(14) Abraham, R. J.; Edgar, M.; Glover, R. P.; Warne, M. A.; Griffiths, L. J. *Chem. Soc., Perkin Trans. 2* **1996**, 333–341.

(15) Thiele, K. H.; Windisch, H.; Schumann, H.; Kociok-Köhn, G. Z. *Anorg. Allg. Chem.* **1994**, *620*, 523–526.

(16) Windisch, H.; Thiele, K. H.; Kociok-Köhn, G.; Schumann, H. Z. *Anorg. Allg. Chem.* **1995**, *621*, 861–864.

(17) Zhao, G.; Basuli, F.; Kilgore, U. J.; Fan, H.; Aneetha, H.; Huffman, J. C.; Wu, G.; Mindiola, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 13575–13585.

(18) Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2003**, *42*, 8003–8010.

(19) (a) Fenske, D.; Hartmann, E.; Dehnicke, K. Z. *Naturforsch.* **1988**, *B43*, 1611–1615. (b) Steinhuebel, D. P.; Lippard, S. J. *Inorg. Chem.* **1999**, *38*, 6225–6233. See bond distances in [LTiCl₂(μ-Cl)]₂ (Ti–N 2.072, 1.986 Å, L = benzamidinato ligand (NSiMe₃)₂CPh), L₂Ti(NCMe₃) (Ti–N 2.152(2) and 2.156(3) Å, L = PhC(NSiMe₃)₂), L₂Ti(CH₂SiMe₃)₂ (Ti–N 2.006(2), 2.045(3) Å), L₂TiCl(CH₂SiMe₃) (Ti–N 2.087(2), 2.091(2) Å, L = aminotroponimate ligand).

(20) Bailey, B. C.; Fout, A. R.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Gary, J. B.; Johnson, M. J. A.; Mindiola, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 2234–2235.

in (*t*Bu-nacnac)Ti=PH[Trip](CH*t*Bu), 2.114(3) Å.¹⁷ The Ti–Me as well as the Ti–N bond distances in **2** are longer than those in (nacnac)Ti(OTf)(Me)₂ (Ti–C 2.079(9) and 2.097(7) Å and Ti–N 2.039(3) and 2.0409(13) Å).^{21a} The elongation of bond distances in **2** is attributed to the mutual influence of the ligands; (nacnac)Ti(OTf)(Me)₂ contains the electron-withdrawing triflate group attached to the titanium center.

Complex **2** contains a Ti(IV) center in a distorted tetrahedral environment formed by two nitrogen atoms, a methyl, and the CH group connected to two aluminum atoms of the Al₂Me₄-(μ -Me) moiety. The hydrogen atom of the CH group was found in the difference Fourier map. Compound **2** contains a Ti=CH[Al₂Me₄(μ -Me)] unit, which is close in geometry and isoelectronic to the Ti=N[Al₂Me₄(μ -Me)] moiety of (PNP)Ti=N[Al₂Me₄(μ -Me)](Me) (PNP = [2-{P(CHMe₂)₂}-4-methylphenyl]₂N[–]).²⁰ The Al(3)–C(35)–Al(2) bond angle of **2** (81.70(9)°) is smaller than the Al–N–Al angles (90.55(9)° and 91.93°) in the latter complex, while the Al(3)–C(36)–Al(2) angle of **2** (75.64(10)°) is close to the corresponding Al–C–Al (77.28(11)° and 76.28(10)°) angles. The Al(2)–Al(3) distance in **2** (2.6693(12) Å) is also close to the Al–Al distances (2.687(1) and 2.711(1) Å) in the reported imido complex.²⁰

Compound **2** can also be considered to contain a Ti(μ -CH)Al₂ bond. To the best of our knowledge only the reported Cp*Ti(μ -Me)(μ -NPiPr₃)(μ -CH)(AlMe₂)₂ (**1**)^{9c} contains a similar Ti(μ -CH)Al₂ arrangement. The Ti–C(35) bond length of **2** (1.880(2) Å) is only slightly shorter than the Ti(μ -CH) distance given in ref 9c for **1** (1.900(2) Å). However according to DFT calculations (see the Supporting Information) the nature of the titanium carbon bonds in both complexes is different; complex **2** contains a multiple Ti–C bond, while that of **1** can be better described as a single bond.

The Ti(1)–C(18) bond length in **2** is in the normal range for Ti–C single bonds (see discussion above). The Ti(1)–C(35) distance (1.880(2) Å) is close to a formal Ti=C double bond. Ti=C bond lengths range from 1.826(2) to 1.86(1) Å²¹ in complexes supported by the nacnac ligand and 1.883(7) Å in (PNP)Ti=CH*t*Bu(SO₃CF₃)²² and 1.896(5) Å for [(*t*BuN)–(*t*BuNP)]₂Ti(CHPh)(THF).²³ The determined Ti(1)–C(35) distance in **2** is longer than the Ti–C bond length (1.825(2) Å) of the recently reported (PNP)Ti=C*t*Bu(μ -Me)AlMe₂ (PNP = [2-{P(CHMe₂)₂}-4-methylphenyl]₂N[–]); however the latter complex has stronger Ti–C interactions than a generic Ti=C bond according to the DFT calculations.⁸

The Al(2)–C(35) and Al(3)–C(35) bond lengths (2.042(3), 2.039(3) Å) are slightly longer than the corresponding terminal ones (1.967(3) to 1.982(3) Å) in **2**, however shorter than the aluminum-bridging methyl bond lengths (2.180(3) and 2.174(3) Å).

It can be concluded on the basis of the discussed bond lengths in **2** that the Ti(IV) atom forms a formal double bond to the CH group, and a similar degree of interaction can be described between the two aluminum centers with the carbon of the CH group.

The ¹H and ¹³C NMR data of **1** and **2** are consistent with the proposed structures. The resonance of the methyl groups attached to the Ti(IV) center appeared at 1.79 ppm for **1** and at 1.43 ppm for **2**, thus being close to that of (*b*p*z*m*p*)TiMe₃ (1.55 ppm) (*b*p*z*m*p* = (3,5-*t*Bu₂-2-phenoxo)bis(3,5-Me₂-pyrazol-1-

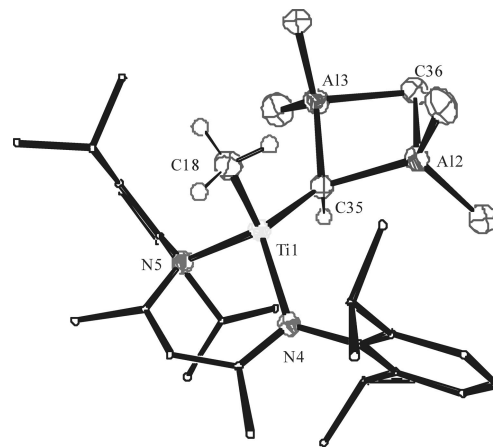


Figure 2. Molecular structure of **2** with the labeled selected atoms. Selected bond lengths (Å) and angles (deg): Ti(1)–C(35) 1.880(2), Ti(1)–N(5) 2.011(2), Ti(1)–N(4) 2.030(2), Ti(1)–C(18) 2.088(2), Al(2)–C(35) 2.042(3), Al(2)–C(36) 2.180(3), Al(2)–Al(3) 2.6693(12), Al(3)–C(35) 2.039(3), Al(3)–C(36) 2.174(3), C(35)–Ti(1)–N(5) 114.09(10), N(5)–Ti(1)–N(4) 95.41(8), C(35)–Ti(1)–C(18) 109.90(11), N(5)–Ti(1)–C(18) 110.59(10), Ti(1)–C(35)–Al(3) 130.29(13), Ti(1)–C(35)–Al(2) 134.66(13), Al(3)–C(35)–Al(2) 81.70(9), Al(3)–C(36)–Al(2) 75.64(10), C(35)–Al(2)–C(36) 97.93(11).

yl)methane)²⁴ however shifted to higher frequency relative to that of Cp*TiMe₃ (0.99 ppm).²⁵ Resonances for the α -H and α -C in **2** are 9.71 and 290.5 ppm, which is in the range of those reported for other titanium alkylidyne. For example, the resonances for the CH protons and carbon of (PMe₃– η -Ph)₂Cp₂Ti=CHCMe₂CHCH₂ (*n* = 0–3) are observed from 12.06 to 12.32 ppm and from 306.4 to 312.2 ppm, respectively.^{5a,26} The resonances of the α -H and α -C of the Tebbe-type complexes (Cp₂Ti(CH₂)(AlMe₃) and Cp₂Ti(CH₂)(AlMe₂Cl) appear in the same range (9.1 and 204 ppm and 8.48 and 188 ppm^{1,27}). The *J*_{C–H} coupling constant (87.7 Hz) in **2** is similar to those of LTi=CH*i*Pr(OTf) (L = HC(CMeN(2,6-*i*Pr₂-C₆H₃))₂) (*J*_{C–H} = 86 Hz)²⁸ and LTi=CH*t*Bu(L) (L = Hal, [BH₄][–]) (*J*_{C–H} = 85–95 Hz).^{21a} Thus, the *J*_{C–H} confirms the presence of the alkylidyne functionality in **2**,^{28,21a,29} and additionally the value of the *J*_{C–H} constant suggests significant α -hydrogen agostic interaction with the electron-deficient titanium center similarly to those of LTi=CH*i*Pr(OTf)²⁸ and LTi=CH*t*Bu(L).^{21a}

In order to explore the bonding situation in **2**, the NMR shifts were calculated and a bond analysis was accomplished for the methylidyne carbon atom of the Ti=CH[Al₂Me₄(μ -Me)] moiety (C(35) atom in Figure 2). The bond analysis in terms of natural atomic orbitals, performed with the NBO module of the

(24) Milione, S.; Bertolasi, V.; Cuenca, T.; Grassi, A. *Organometallics* **2005**, *24*, 4915–4925.

(25) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476–482.

(26) van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. J. *Organomet. Chem.* **1986**, *310*, C25–C28.

(27) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577–6578.

(28) Bailey, B. C.; Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2006**, *25*, 3963–3968.

(29) (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145–179. (b) Beckhaus, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686–713; *Angew. Chem.* **1997**, *109*, 694–722. (c) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822–7836. (d) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1–74. (e) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158–165. (f) Basuli, F.; Bailey, B. C.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6052–6053.

(21) (a) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 1886–1906. (b) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 3321–3334.

(22) Bailey, B. C.; Huffman, J. C.; Mindiola, D. J.; Weng, W.; Ozerov, O. V. *Organometallics* **2005**, *24*, 1390–1393.

(23) Axenov, K. V.; Kilpeläinen, I.; Klinga, M.; Leskelä, M.; Repo, T. *Organometallics* **2006**, *25*, 463–471.

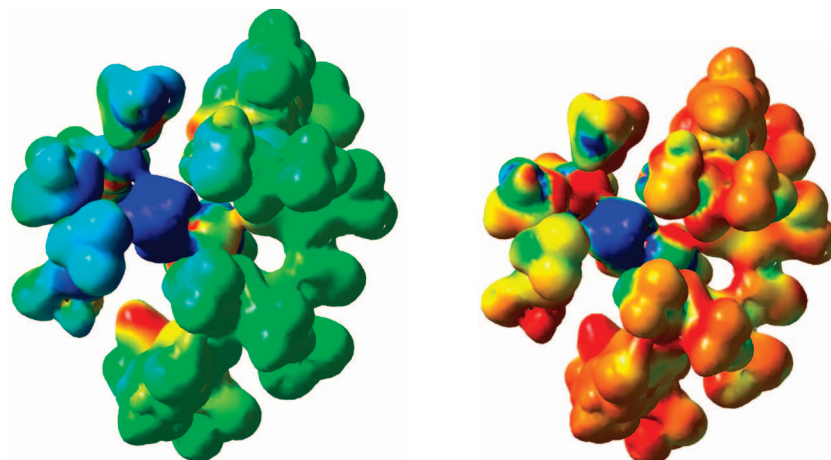


Figure 3. Shielding density as seen by C(35) in the XX direction mapped on the current density (X) isosurface (left), and shielding density as seen by C(35) in the YY direction mapped on the current density (Y) isosurface.

Gaussian program,³⁰ reveals that the bonds to the aluminum atoms are leading to a three-center two-electron ($3c2e$) bond ($\text{Al}-\text{C}-\text{Al}$) in which an $\text{sp}^{0.89}$ hybrid orbital on carbon overlaps with p-rich sp -hybrid orbitals located on the aluminum centers and therefore leaving the carbon atom with enough electron density to form two bonds with Ti. One of these bonds can be characterized as the overlap of one titanium d-orbital with a carbon $\text{sp}^{3.2}$ hybrid orbital and the other as a π -bond resulting from the overlap of pure p-orbitals. The bond between carbon and the hydrogen consists of a $\text{sp}^{3.3}$ hybrid on carbon and a s-orbital on hydrogen.

A common feature of all the bonds involving this carbon atom is that most of the electronic density remains on the carbon. The calculated (1.879 Å) and the experimental (1.886(4) Å) $\text{Ti}(1)-\text{C}(35)$ bond lengths are in good agreement. The calculated NMR chemical shift for C(35) (relative to TMS 290.7 ppm, Figure 14, Supporting Information) agrees well with the experimental one, and as already expected from the NBO analysis, the carbon atom is strongly shielded, leading to the large high-frequency shift. The shielding tensors are shown in Figure 3 with negative (red/green) values representing deshielding and positive values representing shielding (blue).

Conclusion

In summary, we have reported on the protocol for preparing LTiMe_3 and its reaction with AlMe_3 that results in the formation of $\text{LTi}(\text{Me})=\text{CH}(\text{Al}_2\text{Me}_5)$ (**2**), containing the $\text{Ti}=\text{CH}[\text{Al}_2\text{Me}_4(\mu\text{-Me})]$ moiety, where the titanium atom has formed a double bond to the carbon atom. Compound **2** gives a mixture of species upon heating, which polymerize ethylene without adding any cocatalyst. Obviously these experimental observations demonstrate the potential importance of the heterometallic complex **2** containing the $\text{Ti}=\text{CH}[\text{Al}_2\text{Me}_4(\mu\text{-Me})]$ unit.

Experimental Section

All operations were performed under an atmosphere of dry, O_2 -free N_2 employing both Schlenk line techniques and a MBrown MB-150B inert atmosphere glovebox. Solvents toluene and hexane were dried over Na/benzophenone and distilled under nitrogen prior to use. C_6D_6 was dried over K and degassed. The compounds LH

(with the ligand $\text{L} = (2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{NC}(\text{Me}))_2\text{CH}$, *nacnac*)^{31,32} and LTiCl_3 ³³ were prepared by the known literature methods. The purity of all compounds was checked by ^1H and ^{13}C NMR spectra. TiCl_4 (Aldrich 95%) was distilled prior to use in a dry and O_2 -free N_2 atmosphere. Solutions of MeLi (1.6 M) in Et_2O , AlMe_3 (2 M) in toluene, and ethylene (Air–Liquide, ethylene 3.5, <50 ppm N_2 , <10 ppm O_2 , <10 ppm H_2O) were used as received. $\text{MeLi} \cdot (\text{Et}_2\text{O})_{0.137}$ was prepared from the known amount (60 mL) of MeLi solution in Et_2O (1.6 M) by evaporation of Et_2O in a dynamic vacuum to constant weight. The amount of Et_2O was determined by the weight of the resulting solid and confirmed by ^1H NMR. ^1H and ^{13}C NMR spectra were recorded using Bruker Avance DPX 200, Bruker Avance DRX 500, and Varian INOVA-600 instruments. Chemical shifts are reported in δ ppm to high frequency of Me_4Si with the solvent as the reference signal. EPR spectra were recorded on a Bruker ELEXSYS CW-EPR spectrometer equipped with an electromagnet capable of providing a magnetic field up to 14 000 G and a microwave counter. Typical measurement conditions were microwave power 10–20 mW, microwave frequency 9.45 GHz, modulation amplitude 1–5 G, temperature 250 K, and about 2K data points covering a sweep range of 2000 G. Mass spectra were recorded using a Finnigan MAT 8230 mass spectrometer, and elemental analyses were carried out at the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were measured in sealed capillary tubes under nitrogen and are not corrected. Melting points of polymers were measured on a Netzsch STA 409 PC instrument.

Synthesis of 1. Toluene (300 mL) was added to the mixture of LTiCl_3 (6.34 g, 11.1 mmol) and $\text{MeLi} \cdot (\text{Et}_2\text{O})_{0.14}$ (1.43 g, 44.4 mmol) at 0 °C. The $\text{MeLi} \cdot (\text{Et}_2\text{O})_{0.137}$ was prepared from a known amount (60 mL) of standard MeLi solution in Et_2O (1.6 M) by evaporation of Et_2O in a dynamic vacuum to constant weight. The amount of Et_2O was determined by weight difference of the resulting solid and confirmed by ^1H NMR. This mixture was stirred for 16 h at 0 °C in the absence of light and finally filtered. The supernatant solution was concentrated to dryness, and the resulting solid was washed with *n*-hexane (3–10 mL). Yield: 4.65 g, 80%. Anal. Calcd for $\text{C}_{32}\text{H}_{50}\text{N}_2\text{Ti}$: C, 75.29; H, 9.80; N, 5.49. Found: C, 75.32; H, 9.83; N, 5.45. Mp: 113–114 °C. EI-MS: m/z (%) 511 (2) $[\text{M}]^+$, 495 (20) $[\text{M}^+ - \text{CH}_4]$, 481 (2) $[\text{M}^+ - \text{C}_2\text{H}_6]$, 476 (10) $[\text{M}^+ - 2\text{CH}_4 - 3\text{H}]$, 462 (30) $[\text{M}^+ - 3\text{CH}_4]$, 418 (30) $[\text{LH}^+]$, 403 (80) $[\text{LH}^+ - \text{Me}]$, 375 (20) $[\text{LH}^+ - \text{C}_3\text{H}_7]$, 202 (100) $[\text{LH}^+ -$

(31) Krause, E. *Ber. Deutsch. Chem. Ges.* **1918**, *51*, 1447–1456.

(32) Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P. *Dalton Trans.* **2001**, 3465–3469.

(33) Nikiforov, G. B.; Roesky, H. W.; Jones, P. G.; Oswald, R. B.; Noltemeyer, M. *Dalton Trans.* **2007**, 4149–4159.

(30) Frisch, M. J.; et al. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004 (Supporting Information).

$i\text{Pr}_2\text{C}_6\text{H}_3 - \text{C}_4\text{H}_7$. ^1H NMR (500.2 MHz, C_6D_6 , rt): δ_{H} (ppm) 7.10–7.16 (m, 6H, C_6H_3), 5.04 (s, 1H, $\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 3.27 (sept, 4H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2), 1.79 (s, 9H, Ti-CH_3), 1.62 (s, 6H, $\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 1.39 (d, 12H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2), 1.15 (d, 12H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2). ^{13}C NMR (125.76 MHz, C_6D_6 , rt): δ_{C} (ppm) 166.2 ($\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 149.4 (C_6H_3), 141.6 (C_6H_3), 126.5 (C_6H_3), 124.4 (C_6H_3), 98.6 ($\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 79.4 (Ti-CH_3), 28.7 (CHMe_2), 25.9 ($\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 24.8 (CH_3), 24.6 (CH_3), assignment was done using ^1H – ^{13}C correlation and available references.^{21a}

Synthesis of 2. LTiMe_3 (0.55 g, 1.1 mmol) was dissolved in toluene (50 mL). Then the solution was cooled to 0 °C, and the AlMe_3 (1: 2, 1.1 mL, 2 M, 2.2 mmol) in toluene was added under stirring. The resulting mixture was stirred for 0.5 h, warmed to room temperature, and left undisturbed for 1 day. Then the solution was concentrated (10 mL) and left at +2 °C for 1 week. The crystalline solid, which deposited, was filtered off from the supernatant and washed with *n*-hexane (2–5 mL). Yield: 0.56 g, 80%. Anal. Calcd for $\text{C}_{36}\text{H}_{60}\text{Al}_2\text{N}_2\text{Ti}$: C, 69.38; H, 9.64; N, 4.49. Found: C, 69.38; H, 9.67; N, 4.44. Decomposition without melting at a temperature above 100 °C was observed. Melting under decomposition to a black solid at 210 °C occurred. EI-MS: m/z (%) 459 (100) $[\text{AlMe}]^+$, 443 (70) $[\text{AlMe}^+ - \text{CH}_4]$, 427 (10) $[\text{AlMe}^+ - 2\text{CH}_4]$. ^1H NMR (500.2 MHz, C_6D_6 , rt): δ_{H} (ppm) 9.71 (s, 1H, Ti=CH , $J_{\text{C-H}} = 87.7$ Hz), 7.22–7.15 (m, aryl), 4.71 (s, 1H, $\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 3.45 (sept, 2H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2), 2.92 (sept, 2H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2), 1.64 (d, 6H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2), 1.55 (d, 6H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2), 1.43 (s, 3H, Ti-Me), 1.40 (s, 6H, $\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 1.08 (d, 6H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2), 0.95 (d, 6H, $^3J_{\text{H-H}} = 6.80$ Hz, CHMe_2), –0.51 (s, br, 15H, Al-Me). ^{13}C NMR (125.707 MHz, C_6D_6 , rt): δ_{C} (ppm) 290.5 (Ti=CH), 170.1 ($\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 143.1 (C_6H_3), 142.1 (C_6H_3), 141.4 (C_6H_3), 128.1 (C_6H_3), 125.2 (C_6H_3), 125.1 (C_6H_3), 96.8 ($\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 57.0 (Ti-CH_3), 29.1 (CHMe_2), 28.3 (CHMe_2), 23.7 ($\text{C}(\text{CH}_3)\text{CHC}(\text{CH}_3)$), 26.7 (CH_3), 24.4 (CH_3), 23.6 (CH_3), 23.5 (CH_3), –5.0 (Al-CH_3) assignment was done using ^1H – ^{13}C correlation. Note: (a) The cross-peak between ^1H and ^{13}C NMR resonances of the Ti=CH moiety was observed in the HMQC spectrum using the coupling constant $J_{\text{C-H}} = 87.7$ Hz. (b) Reaction of **1** and 4 equiv of AlMe_3 also produced **2** in 80% yield.

X-ray Crystallography. X-ray data were collected on a Bruker three-circle diffractometer with a mirror system equipped with a SMART 6000 area detector ($\lambda(\text{Cu K}\alpha) = 1.54184$ Å) using ω and θ scans. The crystal was cooled to 100 K with an Oxford Cryosystem. All calculations were carried out using SHELXTL software.³⁴ The data were integrated with SAINT³⁵ and corrected for absorption with SADABS³⁶ or TWINABS³⁷ in the case of the twinned crystal **2**. The structure of **2** was refined including twin fractions using a HKL5 format file. A twin factor of 52.6%:47.4% could be calculated.

Density Functional Calculations. Density functional calculations aimed at the analysis of the Ti-bonding situation and NMR spectra were carried out. The B3LYP^{38,39} functional as implemented in the Gaussian program package³⁰ was used throughout all the computations. Due to the atoms of the compound a basis of type LANL2DZ⁴⁰ for Ti and a modified 6-31G basis with additional diffuse functions^{41,42} for the remaining atoms was used to achieve the needed precision. In the first step the compound was fully

Table 1. Crystallographic Data and Structure Refinement Details for 1 and 2

	1	2
empirical formula	$\text{C}_{32}\text{H}_{50}\text{N}_2\text{Ti}$	$\text{C}_{36}\text{H}_{60}\text{Al}_2\text{N}_2\text{Ti}$
M_r	510.64	622.72
temp [K]	100(2)	100(2)
radiation used (λ [Å])	Cu K α (1.54184)	Cu K α (1.54184)
cryst size [mm]	$0.10 \times 0.10 \times 0.04$	$0.20 \times 0.15 \times 0.05$
cryst syst	orthorhombic	triclinic
space group	$Pnma$	$P\bar{1}$
a [Å]	14.245(3)	9.772(2)
b [Å]	22.068(4)	10.029(2)
c [Å]	10.071(2)	20.808(4)
α [deg]	90	87.45(3)
β [deg]	90	87.39(3)
γ [deg]	90	67.78(3)
V [Å ³]	3165.9(11)	1885.1(7)
Z	4	2
ρ_{calcd} [$\text{g}\cdot\text{cm}^{-3}$]	1.071	1.097
μ [mm^{-1}]	2.542	2.542
$F(000)$	1112	676
scan range θ [deg]	4.01 to 57.11	2.13 to 60.79
completeness to θ_{max} [%]	99.0	90.0
index ranges	$-15 \leq h \leq 15$ $-18 \leq k \leq 23$ $-10 \leq l \leq 10$	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-23 \leq l \leq 23$
total no. of reflns	18 161	28 002
no. of unique reflns	2180	5319
$R(\text{int})$	0.0723	0.0686
no. of data/restraints/params	2180/0/170	5319/6/398
goodness-of-fit on F^2	1.059	1.050
R_1, wR_2 [$I > 2\sigma(I)$] ^a	0.0448, 0.1001	0.0497, 0.1199
R_1, wR_2 (all data) ^a	0.0602, 0.1078	0.0656, 0.1311
max/min el dens [$\text{e}\cdot\text{\AA}^{-3}$]	0.380/–0.261	0.398/–0.391

^a $wR_2 = (\sum[w(F_o^2 - F_c^2)]/\sum[F_o^4])^{1/2}$, $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$, weight = $1/[\sigma^2(F_o^2) + (AP)^2 + (BP)]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$; for **1** $A = 0.0384$, $B = 3.2744$; for **2** $A = 0.0463$, $B = 0.8143$.

optimized to its equilibrium structure (coordinates are given in the Supporting Information). The following steps consisted of a NBO analysis⁴³ and the calculation of NMR shifts with the gauge-independent atomic orbital (GIAO) method⁴⁴ (see Supporting Information).

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Supporting Information Available: Complete ref 30, experimental procedures, NMR reaction *in situ*, spectroscopic data (IR), X-ray crystallographic data for **1** and **2**, ethylene polymerization data, and details of the DFT calculations including calculated ^{13}C NMR and IR spectra of $\text{LTi}(\text{Me})=\text{CH}(\text{Al}_2\text{Me}_5)$, comparison of Ti–C bonding in $\text{LTi}(\text{Me})=\text{CH}(\text{Al}_2\text{Me}_5)$ (**2**) and $^*\text{Ti}(\mu\text{-Me})(\mu\text{-NPr}_3)(\mu_3\text{-CH})(\text{AlMe}_2)_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM800144V

(41) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081–6090.

(42) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193–2218.

(43) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736–1740. (c) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

(44) (a) Dodds, J. L.; McWeeny, R.; Sadlej, A. J. *Mol. Phys.* **1980**, *41*, 1419–1430. (b) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260.

(34) Sheldrick, G. *SHELXTL 5.1*; Bruker AXS, Inc.: Madison, WI, 1997.

(35) SAINT 6.02; Bruker AXS, Inc.: Madison, WI, 1997–1999.

(36) Sheldrick, G. *SADABS*; Bruker AXS, Inc.: Madison, WI, 1999.

(37) Sheldrick, G. *TWINABS*; University of Göttingen: Germany, 2002.

(38) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(39) Michlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200–206.

(40) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283.