# Early Transition Metal Complexes Containing 1,2,4-Triazolato and Tetrazolato Ligands: Synthesis, Structure, and Molecular Orbital Studies

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Several early transition metal complexes bearing 1,2,4-triazolato and tetrazolato ligands have been prepared by reaction of the pyrazolato complexes $Ti(tBu_2pz)_{4-x}Cl_x$ ($tBu_2pz$ = 3,5-di-*tert*-butylpyrazolato; $x = 1, 2$) and $M(tBu_2pz)_{5-x}Cl_x$ (M = Nb, Ta: $x = 2, 3$) with the sodium or potassium salts derived from 1,2,4-triazoles and tetrazoles. The X-ray structure analysis of $Ti(tBu_2pz)_2(Me_2C_2N_3)_2$ shows $\eta^2$-coordination of the 1,2,4-triazolato ligands, while in $Ti(tBu_2pz)_3(C_2H_2N_3)$ and $Nb(tBu_2pz)_3(Me_2C_2N_3)_2$ the analogous groups are joined in a $\eta^1$-fashion in the solid-state structure. Solution NMR studies at different temperatures suggest transition states involving $\eta^2$-1,2,4-triazolato ligands for the complexes containing $\eta^1$-1,2,4-triazolato ligands in the solid state. X-ray crystal structures of analogous tetrazolato complexes $Ti(tBu_2pz)_3(PhCN_4)$ and $Nb(tBu_2pz)_3(PhCN_4)_2$ show $\eta^1$-coordination of the 2-nitrogen atoms of the tetrazolato ligands. Molecular orbital calculations have been carried out on several model titanium complexes and provide detailed insight into the bonding between early transition metal centers and 1,2,4-triazolato and tetrazolato ligands. The $\eta^2$-coordination mode of 1,2,4-triazolato and tetrazolato ligands is predicted to be more stable than the $\eta^1$-coordination mode by 13.8−5.2 kcal/mol.

## Introduction

There is considerable interest in the development of new nitrogen donor ligand sets for early transition metal complexes. Motivations in this area are diverse and include the preparation of new single-site olefin polymerization catalysts,[1−6] attempts to understand and mimic hydrodenitrogenation catalysts,[7−14] and the preparation of improved precursors to metal nitride phases,[15,16] to name a few. Examples of nitrogen donor ligands that have been reported recently include amidinate,[17−22] pyrazolylborate,[23−26] amido,[27−30] and others.[31−40] Our group has reported extensively about the use of pyrazolato ligands[41−44] among the transition,[45−50]

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(1) Schrock, R. R.; Casado, A. L.; Goodman, J. T.; Liang, L. C.; Bonitatebus, P. J.; Davis, W. M. *Organometallics* **2000**, *19*, 5325.
(2) Chen, R. F.; Qian, C. T.; Li, Y.; Zou, F. L. *Chin. J. Org. Chem.* **2000**, *20*, 712.
(3) Laine, T. V.; Piironen, U.; Lappalainen, K.; Klinga, M.; Aitola, E.; Leskela, M. *J. Organomet. Chem.* **2000**, *606*, 112.
(4) Shao, P. C.; Gendron, R. A. L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **2000**, *19*, 509.
(5) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.
(6) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415.
(7) Bianchini, C.; Meli, A.; Vizza, F. *Eur. J. Inorg. Chem.* **2001**, *3*, 43.
(8) Castro, A.; Galakhov, M. V.; Gómez, M.; Sánchez, F. *J. Organomet. Chem.* **1999**, *507*, 161.
(9) Vicic, D. A.; Jones, W. D. *Organometallics* **1999**, *18*, 134.
(10) Tayebani, M.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3002.
(11) Garcia, J. J.; Casado, A. L. *J. Organomet. Chem.* **1998**, *558*, 189.
(12) Fox, P. A.; Bruck, M. A.; Gray, S. D.; Gruhn, N. E.; Grittini, C.; Wigley, D. E. *Organometallics* **1998**, *17*, 2720.
(13) Weller, K. J.; Filippov, I.; Briggs, P. M.; Wigley, D. E. *Organometallics* **1998**, *17*, 322.
(14) Weller, K. J.; Fox, P. A.; Gray, S. D.; Wigley, D. E. *Polyhedron* **1997**, *16*, 3139.
(15) Winter, C. H. *Aldrichim. Acta* **2000**, *33*, 3.
(16) Hoffman, D. M. *Polyhedron* **1994**, *13*, 1169.
(17) Hagadorn, J. R.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1729.
(18) Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355.
(19) Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1997**, 3087.
(20) Littke, A.; Sleiman, N.; Bensimon, C.; Richeson, D. S.; Yap, G. P. A.; Brown, S. J. *Organometallics* **1998**, *17*, 446.
(21) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403.
(22) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219.
(23) Reger, D. L. *Coord. Chem. Rev.* **1996**, *147*, 571.
(24) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419.
(25) Parkin, G. *Adv. Organomet. Chem.* **1995**, *42*, 291.
(26) Trofimenko, S. *Scorpinates: Polypyrazolylborate Ligands and Their Coordination Chemistry*; Imperial College Press: London, 1999.
(27) Daniele, S.; Hitchcock, P. B.; Lappert, M. F.; Perle, P. G. *J. Chem. Soc., Dalton Trans.* **2001**, 13.
(28) Humphries, M. J.; Green, M. L. H.; Leech, M. A.; Gibson, V. C.; Jolly, M.; Williams, D. N.; Elsegood, M. R. J.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **2000**, 4044.
(29) Sanchez-Nieves, J.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **2000**, *19*, 3161.
(30) Sinnema, P. J.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2000**, *598*, 179.
(31) Gantzel, P.; Walsh, P. J. *Inorg. Chem.* **1998**, *37*, 3450.
(32) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1998**, *17*, 382.
(33) Fryzuk, M. D.; Love, J. B.; Rettig, S. J. *Organometallics* **1998**, *17*, 846.
(34) Scott, M. J.; Lippard, S. J. *Organometallics* **1998**, *17*, 1769.
(35) Muller, E.; Muller, J.; Olbrich, F.; Bruser, W.; Knapp, W.; Abeln, D.; Edelmann, F. T. *Eur. J. Inorg. Chem.* **1998**, *1*, 87.
(36) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *J. Chem. Soc., Chem. Commun.* **1998**, 199.
(37) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308.
(38) Armistead, L. T.; White, P. S.; Gagné, M. R. *Organometallics* **1998**, *17*, 216.
(39) Lee, C. H.; La, Y.-H.; Park, S. J.; Park, J. W. *Organometallics* **1998**, *17*, 3648.
(40) Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L.; Winter, C. H. *Polyhedron* **1997**, *16*, 4017.

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lanthanide,[51−54] and main group metals.[55−58] In particular, we[45−49] and others[59,60] have demonstrated that $\eta^2$-coordination of pyrazolato ligands is common in the early transition metals and that complexes containing this coordination mode bear significant structural and chemical resemblance to analogous cyclopentadienyl and $\beta$-diketonate derivatives. As part of this program, we sought to extend our exploration to complexes containing 1,2,4-triazolato and tetrazolato ligands.

The coordination chemistry of 1,2,4-triazolato and tetrazolato ligands has not been as widely studied as that of pyrazolato ligands, and there is more variability in the binding modes due to the increased number of nitrogen atoms and the attendant possibilities for isomerism.[61−92] Binding modes that have been observed for 1,2,4-triazolato ligands include $\eta^1$,[62−64] 1,2-$\mu$:$\eta^1$,$\eta^1$,[65−69] 1,4-$\mu$:$\eta^1$,$\eta^1$,[70−73] and 1,2,4-$\mu$:$\eta^1$,$\eta^1$,$\eta^1$.[74−78] The bridging coordination modes are by far the most common with 1,2,4-triazolato ligands; $\eta^1$ coordination is rare. A review article on the coordination chemistry of ligands derived from 1,2,4-triazoles has recently appeared and gives a comprehensive listing of known coordination modes.[61] Structurally characterized coordination modes among tetrazolato ligands include $\eta^1$,[79−82] 1,2-$\mu$:$\eta^1$,$\eta^1$,[83] 1,3-$\mu$:$\eta^1$,$\eta^1$,[84,85] 2,3-$\mu$:$\eta^1$,$\eta^1$,[86] 1,2,3-$\mu$:$\eta^1$,$\eta^1$,$\eta^1$,[87] 1,2,4-$\mu$:$\eta^1$,$\eta^1$,$\eta^1$,[88] $\mu$-1,2-$\eta^2$,3-$\eta^1$,[89,90] $\mu$-1,3-$\eta^1$,2,3-$\eta^2$,[91] and $\mu$:$\eta^1$,$\eta^1$,$\eta^1$,$\eta^1$.[92] The best documented coordination mode for tetrazolato ligands is $\eta^1$, although the number of crystallographically characterized complexes is small.

We are interested in the synthesis of complexes that possess only nitrogen atoms in the coordination sphere and their subsequent use as precursors for the deposition of thin films of nitride materials.[51−54,93] 1,2,4-Triazolato and tetrazolato ligands are potentially interesting for such applications, since they may form complexes that are analogous to complexes containing pyrazolato ligands. In addition, the higher nitrogen content in triazolato and tetrazolato complexes, compared to pyrazolato complexes, may lead to low film deposition temperatures and highly efficient precursor decomposition pathways that are driven by the formation of dinitrogen. Herein we describe the synthesis, structure, and properties of titanium, niobium, and tantalum complexes containing 1,2,4-triazolato and tetrazolato ligands. This is the first description of early transition metal complexes containing these ligands. Crystal structures of representative complexes document $\eta^1$- and $\eta^2$-coordination of 1,2,4-triazolato ligands, depending on the degree of steric crowding in the coordination sphere and $\eta^1$-coordination of the tetrazolato ligands. This study provides the first example of $\eta^2$-1,2,4-triazolato ligand coordination by any metal. NMR studies

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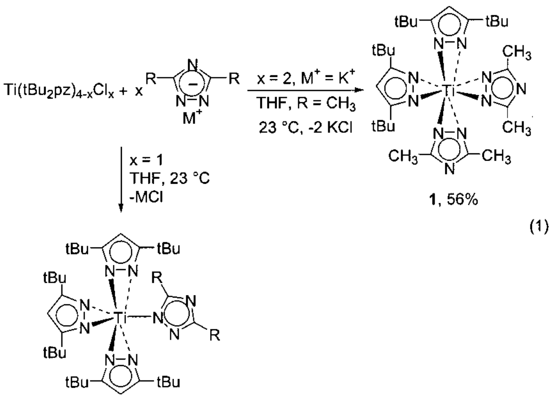
(41) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.
(42) Sadimenko, A. P.; Basson, S. S. *Coord. Chem. Rev.* **1996**, *147*, 247.
(43) La Monica, G.; Ardizzoia, G. A. *Progr. Inorg. Chem.* **1997**, *46*, 151.
(44) Cosgriff, J. E.; Deacon, G. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 286.
(45) Guzei, I. A.; Baboul, A. G.; Yap, G. P. A.; Rheingold, A. L.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1997**, *119*, 3387.
(46) Guzei, I. A.; Yap, G. P. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 1738.
(47) Guzei, I. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 4415.
(48) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1999**, *38*, 1871.
(49) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Organometallics* **1999**, *18*, 1168.
(50) Perera, J. R.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1999**, *121*, 4536.
(51) Pfeiffer, D.; Ximba, B. J.; Liable-Sands, L. M.; Rheingold, A. L.; Heeg, M. J.; Coleman, D. M.; Schlegel, H. B.; Kuech, T. F.; Winter, C. H. *Inorg. Chem.* **1999**, *38*, 4539.
(52) Cederberg, J. G.; Culp, T. D.; Bieg, B.; Pfeiffer, D.; Winter, C. H.; Bray, K. L.; Kuech, T. F. *J. Appl. Phys.* **1999**, *85*, 1825.
(53) Culp, T. D.; Cederberg, J. G.; Bieg, B.; Kuech, T. F.; Bray, K. L.; Pfeiffer, D.; Winter, C. H. *J. Appl. Phys.* **1998**, *83*, 4918.
(54) Cederberg, J. G.; Culp, T. D.; Bieg, B.; Pfeiffer, D.; Winter, C. H.; Bray, K. L.; Kuech, T. F. *J. Cryst. Growth* **1998**, *195*, 105.
(55) Yu, Z. K.; Wittbrodt, J. M.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **2000**, *122*, 9338.
(56) Pfeiffer, D.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **2000**, *39*, 2377.
(57) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1998**, *37*, 3892.
(58) Pfeiffer, D.; Heeg, M. J.; Winter, C. H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2517.
(59) Röttger, D.; Erker, G.; Grehl, M.; Frölich, R. *Organometallics* **1994**, *13*, 3897.
(60) Mösch-Zanetti, N. C.; Krätzer, R.; Lehmann, C.; Schneider, T. R.; Usón, I. *Eur. J. Inorg. Chem.* **2000**, *2*, 13.
(61) For a review of the coordination chemistry of 1,2,4-triazolato complexes, see: Haasnoot, J. G. *Coord. Chem. Rev.* **2000**, *200−202*, 131.
(62) Hage, R.; Haasnoot, J. G.; Reedijk, J.; Wang, R.; Ryan, E. M.; Vos, J. G.; Spek, A. L.; Duisenberg, A. J. M. *Inorg. Chim. Acta* **1990**, *174*, 77.
(63) Buchanan, B. E.; Vos, J. G.; Kaneko, M.; van der Putten, W. J. M.; Kelly, J. M.; Hage, R.; de Graaff, R. A. G.; Prins, R.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1990**, 2425.
(64) Hage, R.; Turkenburg, J. P.; De Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *Acta Crystallogr.* **1989**, *C45*, 381.
(65) Jahncke, M.; Neels, A.; Stoeckli-Evans, H.; Suss-Fink, G. *J. Organomet. Chem.* **1998**, *561*, 227.
(66) Slangen, P. M.; van Koningsbruggen, P. J.; Goubitz, K.; Haasnoot, J. G.; Reedijk J. *Inorg. Chem.* **1994**, *33*, 1121.
(67) Slangen, P. M.; van Koningsbruggen, P. J.; Haasnoot, J. G.; Jansen, J.; Gorter, S.; Reedijk, J.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chim. Acta* **1993**, *212*, 289.
(68) Antolini, L.; Fabretti, A. C.; Gatteschi, D.; Giusti, A.; Sessoli, R. *Inorg. Chem.* **1991**, *30*, 4858.
(69) Prins, R.; Birker, P. J. M. W. L.; Haasnoot, J. G.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 4128.
(70) Nomiya, K.; Tsuda, K.; Kasuga, N. C. *J. Chem. Soc., Dalton Trans.* **1998**, 1653.
(71) Pichierri, F.; Chiarparin, E.; Zangrando, E.; Randaccio, L.; Holthenrich, D.; Lippert, B. *Inorg. Chim. Acta* **1997**, *264*, 109.
(72) Biagini-Cingi, M.; Manotti-Lanfredi, A. M.; Ugozzoli, F.; Haasnoot, J. G. *Inorg. Chim. Acta* **1994**, *227*, 181.
(73) Oro, L. A.; Pinillos, M. T.; Tejel, C.; Foces-Foces, C.; Cano, F. H. *J. Chem. Soc., Dalton Trans.* **1986**, 2193.
(74) Hagrman, D.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1998**, 2005.
(75) Krober, J.; Bkouche-Waksman, I.; Pascard, C.; Thomann, M.; Kahn, O. *Inorg. Chim. Acta* **1995**, *230*, 159.
(76) Vreugdenhil, W.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chim. Acta* **1987**, *129*, 205.
(77) Oro, L. A.; Pinillos, M. T.; Tejel, C.; Foces-Foces, C.; Cano F. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1087.
(78) Drew, M. G. B.; Yates, P. C.; Trocha-Grimshaw, J.; McKillop, K. P.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1985**, 262.
(79) Demadis, K. D.; El Samanody, E.-S.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 838.
(80) Morosin, B.; Dunn, R. G.; Assink, R.; Massis, T. M.; Fronaberger, J.; Duesler, E. N. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1997**, *53*, 1609.
(81) Guilard, R.; Perrot, I.; Tabard, A.; Richard, P.; Lecomte, C.; Liu, Y. H.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 27.
(82) Das, R.; Paul, P.; Nag, K.; Venkatsubramanian, K. *Inorg. Chim. Acta* **1991**, *185*, 221.
(83) Palopoli, S. F.; Geib, S. J.; Rheingold, A. L.; Brill, T. B. *Inorg. Chem.* **1988**, *27*, 2963.
(84) Hill, M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1996**, 1857.
(85) Hill, M.; Mahon, M. F.; McGinley, J.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1996**, 835.
(86) John, E. O.; Willett, R. D.; Scott, B.; Kirchmeier, R. L.; Schreeve, J. M. *Inorg. Chem.* **1989**, *28*, 893.
(87) Munoz-Hernandez, M.-A.; Hill, M. S.; Atwood, D. A. *Polyhedron* **1998**, *17*, 2237.
(88) Oro, L. A.; Pinillos, M. T.; Tejel, C.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *J. Chem. Soc., Dalton Trans.* **1988**, 1927.
(89) Huang, X.-Y.; Zhou, X.-G.; Zhang, L.-X.; Feng, X.-J.; Cai, R.-F.; Huang, Z. E. *Chin. J. Struct. Chem.* **1998**, *17*, 449.
(90) Zhou, X.-G.; Huang, Z.-E.; Cai, R.-F.; Zhang, L.-X.; Hou, X.-F.; Feng, X.-J.; Huang, X.-Y. *J. Organomet. Chem.* **1998**, *563*, 101.
(91) Arp, H. P. H.; Decken, A.; Passmore, J.; Wood, D. J. *Inorg. Chem.* **2000**, *39*, 1840.
(92) Carlucci, L.; Ciani, G.; Prosperio, D. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3488.
(93) Scheper, J. T.; McKarns, P. J.; Lewkebandara, T. S.; Winter, C. H. *Mater. Sci. Semicond. Process.* **1998**, *2*, 149.

suggest that the $\eta^1$-1,2,4-triazolato ligands can access low-energy $\eta^2$-transition states that lead to site exchange of substituents in the 3- and 5- positions of these ligands. Finally, molecular orbital calculations demonstrate that $\eta^2$-coordination of 1,2,4-triazolato and tetrazolato ligands is more stable than the $\eta^1$-coordination mode, in the absence of steric effects.

## Results

**Synthesis of Complexes with 1,2,4-Triazolato Ligands.** Treatment of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) or chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) with excess potassium 3,5-dimethyl-1,2,4-triazolate or sodium 1,2,4-triazolate in tetrahydrofuran at room temperature for 48 h afforded the titanium triazolato derivatives **1**−**3** as yellow crystalline solids in 56−79% yields after workup (eq 1). Compounds **1**−**3** were characterized by spectroscopic and analytical techniques and by crystal structure determinations (vide infra)**.** Compound **1** possesses a structure with two $\eta^2$-di-*tert*-butylpyrazolato and two $\eta^2$-dimethyl-1,2,4-triazolato ligands. Consistent with this structure, the $^1$H NMR spectra of **1** are static between −80 and +20 °C in toluene-$d_8$ solution. Compounds **2** and **3** have structures with three $\eta^2$-di-*tert*-butylpyrazolato ligands and one $\eta^1$-dimethyl-1,2,4-triazolato (**2**) or one $\eta^1$-1,2,4-triazolato (**3**) ligand. The variable-temperature $^1$H NMR spectra of **2** are described below.

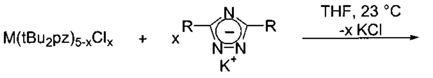


**1**, 56%

(1)

**2**, R = CH$_3$, M$^+$ = K$^+$, 58%
**3**, R = H, M$^+$ = Na$^+$, 79%

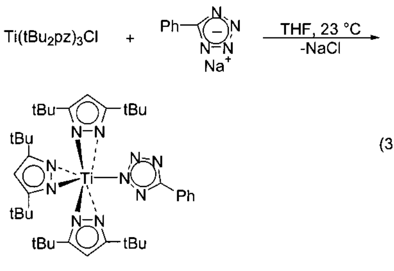
Analogous 1,2,4-triazolato derivatives of niobium and tantalum were prepared by reaction of dichlorotris(3,5-di-*tert*-butylpyrazolato)metal(V) and trichlorobis(3,5-di-*tert*-butylpyrazolato)metal(V) complexes with potassium 3,5-dimethyl-1,2,4-triazolate and potassium 3,5-diethyl-1,2,4-triazolate in tetrahydrofuran at ambient temperature (eq 2). Complexes **4**−**9** were obtained in 40−81% yields after crystallization from hexane at −20 °C. These compounds were characterized by spectroscopic and analytical techniques and by a crystal structure determination of **4** (vide infra)**.** On the basis of the crystal structure of **4** and NMR studies described below on **4** and **6**, **4**−**7** possess three $\eta^2$-di-*tert*-butylpyrazolato and two $\eta^1$-dialkyl-1,2,4-triazolato ligands. The formulation of **8** and **9** as monomeric complexes is proposed on the basis of spectral and analytical data and the similarity to **4**−**7**. Structural speculation about **8** and **9** from the low-temperature NMR spectra is described below.



M(tBu$_2$pz)$_{5-x}$(R$_2$C$_2$N$_3$)$_x$
**4**, M = Nb, R = CH$_3$, x = 2, 76%
**5**, M = Nb, R = CH$_2$CH$_3$, x = 2, 81%
**6**, M = Ta, R = CH$_3$, x = 2, 62%
**7**, M = Ta, R = CH$_2$CH$_3$, x = 2, 43%
**8**, M = Nb, R = CH$_3$, x = 3, 60%
**9**, M = Ta, R = CH$_3$, x = 3, 40%

(2)

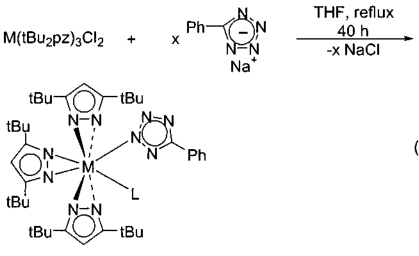
**Synthesis of Complexes with Tetrazolato Ligands.** Treatment of chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) with sodium 5-phenyltetrazolate in tetrahydrofuran at room temperature for 48 h afforded the titanium tetrazolato derivative **10** as yellow crystals in 74% yield after crystallization from hexane at −20 °C (eq 3). The structure of **10** was established from the spectral and analytical data. $\eta^1$-Coordination to the 2-nitrogen atom of the phenyltetrazolato ligand was determined from a low precision X-ray crystallographic structure determination.



**10**, 74%

(3)

Tetrazolato complexes of niobium and tantalum were prepared through treatment of dichlorotris(3,5-di-*tert*-butylpyrazolato)metal(V) with sodium 5-phenyltetrazolate in refluxing tetrahydrofuran for 40 h (eq 4). The complexes tris(3,5-di-*tert*-butylpyrazolato)bis(5-phenyltetrazolato)niobium(V) (**11**) and chlorotris(3,5-di-*tert*-butylpyrazolato)(5-phenyltetrazolato)tantalum(V) (**12**) were obtained as yellow crystals in 59 and 60% yields, respectively, after workup. Despite extended reflux of dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V) with excess sodium 5-phenyltetrazolate, only one chlorine atom could be replaced and **12** was the only product observed. The compositions of **11** and **12** were established through spectral and analytical data and from an X-ray crystal structure determination of **11** (vide infra).



(4)

**11**, M = Nb, x = 2, L = 2-(5-phenyltetrazolato), 59%
**12**, M = Ta, x = 1, L = Cl, 60%

**Crystal Structures of 1, 2, 4, and 11.** The X-ray crystal structures of **1**, **2**, **4**, and **11** were determined to establish the geometries about the metal centers as well as the bonding modes of the pyrazolato, 1,2,4-triazolato, and tetrazolato ligands. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2−5, and perspective views are presented in Figures 1−4. Further data are available in the Supporting Information. The X-ray crystal structures of **3** and **10** are presented in the Supporting Information. The molecular structure of **3** is very similar to that of **2**, while the structural data for **10** are of low precision (although the structure is unambiguously established).

The molecular structure of **1** is presented in Figure 1. The complex crystallizes with one and a half independent molecules in the asymmetric unit. The molecule exhibits distorted dodeca-

**Table 1.** Experimental Crystallographic Data for **1**, **2**, **4**, and **11**

| | **1** | **2** | **4** | **11** |
|---|---|---|---|---|
| empirical formula | $C_{30}H_{50}N_{10}Ti$ | $C_{37}H_{63}N_{9}Ti$ | $C_{41}H_{69}N_{12}Nb$ | $C_{47}H_{67}N_{14}Nb$ |
| fw | 598.70 | 681.86 | 822.99 | 921.06 |
| space group | $C2/c$ | $P2_1/n$ | $C222_1$ (No. 20) | $P2_1$ |
| *a* (Å) | 33.981(2) | 10.2054(11) | 14.2966(8) | 12.6843(2) |
| *b* (Å) | 16.2356(8) | 37.372(4) | 23.9396(14) | 18.3911(3) |
| *c* (Å) | 23.0511(11) | 10.8560(13) | 14.7500(8) | 13.1692(3) |
| $\beta$ (deg) | 121.6160(10) | 96.506(2) | 90 | 112.8500(10) |
| *V* (Å$^3$) | 10829.9(9) | 4113.8(8) | 5048.3(5) | 2831.00(9) |
| Z | 12 | 4 | 4 | 2 |
| *T* (K) | 295(2) | 295(2) | 295(2) | 295(2) |
| $\lambda$ (Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| $\rho_{calcd}$ (g cm$^3$) | 1.102 | 1.101 | 1.083 | 1.081 |
| $\mu$ (mm$^{-1}$) | 0.269 | 0.243 | 0.276 | 0.253 |
| *R*(*F*) (%) | 5.55 | 5.49 | 4.92 | 5.23 |
| $R_w(F)$ (%) | 13.66 | 10.53 | 9.10 | 13.88 |

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**

| | | | |
|---|---|---|---|
| Ti(1)−N(1) | 2.019(2) | Ti(1)−N(2) | 2.054(2) |
| Ti(1)−N(3) | 2.057(2) | Ti(1)−N(4) | 2.018(2) |
| Ti(1)−N(5) | 2.059(2) | Ti(1)−N(6) | 2.098(2) |
| Ti(1)−N(8) | 2.065(2) | Ti(1)−N(9) | 2.067(2) |
| N(1)−N(2) | 1.370(3) | N(3)−N(4) | 1.361(3) |
| N(5)−N(6) | 1.370(3) | N(8)−N(9) | 1.373(3) |
| N(1)−Ti(1)−N(2) | 39.30(7) | N(1)−Ti(1)−N(3) | 94.47(9) |
| N(1)−Ti(1)−N(4) | 120.71(9) | N(1)−Ti(1)−N(5) | 95.81(8) |
| N(1)−Ti(1)−N(6) | 134.26(8) | N(1)−Ti(1)−N(8) | 114.41(9) |
| N(1)−Ti(1)−N(9) | 89.53(9) | N(2)−Ti(1)−N(3) | 87.11(9) |
| N(2)−Ti(1)−N(4) | 92.26(9) | N(2)−Ti(1)−N(5) | 134.63(8) |
| N(2)−Ti(1)−N(6) | 172.26(8) | N(2)−Ti(1)−N(8) | 94.06(9) |
| N(2)−Ti(1)−N(9) | 92.92(9) | N(3)−Ti(1)−N(4) | 39.01(8) |
| N(3)−Ti(1)−N(5) | 91.73(9) | N(3)−Ti(1)−N(6) | 89.53(9) |
| N(3)−Ti(1)−N(8) | 134.84(8) | N(3)−Ti(1)−N(9) | 173.66(8) |
| N(4)−Ti(1)−N(5) | 114.48(9) | N(4)−Ti(1)−N(6) | 89.51(9) |
| N(4)−Ti(1)−N(8) | 95.90(8) | N(4)−Ti(1)-N(9) | 134.69(8) |
| N(5)−Ti(1)−N(6) | 38.47(7) | N(5)−Ti(1)−N(8) | 117.25(10) |
| N(5)−Ti(1)−N(9) | 92.75(9) | N(6)−Ti(1)−N(8) | 93.26(9) |
| N(6)−Ti(1)−N(9) | 91.19(9) | N(8)−Ti(1)−N(9) | 38.83(8) |
| Ti(1)−N(1)−N(2) | 71.72(13) | Ti(1)−N(2)−N(1) | 68.97(13) |
| Ti(1)−N(3)−N(4) | 68.95(12) | Ti(1)−N(4)−N(3) | 72.04(12) |
| Ti(1)−N(5)-N(6) | 72.32(13) | Ti(1)−N(6)−N(5) | 69.21(13) |
| Ti(1)−N(8)−N(9) | 70.67(13) | Ti(1)−N(9)−N(8) | 70.50(13) |

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

| | | | |
|---|---|---|---|
| Ti−N(1) | 2.020(4) | Ti−N(4) | 2.016(4) |
| Ti−N(5) | 2.042(4) | Ti−N(6) | 1.986(4) |
| Ti−N(7) | 2.036(4) | Ti−N(8) | 1.999(4) |
| Ti−N(9) | 2.018(4) | N(1)−N(2) | 1.392(5) |
| N(4)−N(5) | 1.362(4) | N(6)−N(7) | 1.360(4) |
| N(8)−N(9) | 1.375(4) | | |
| N(1)−Ti−N(4) | 94.78(15) | N(1)−Ti−N(5) | 130.90(15) |
| N(1)−Ti−N(6) | 110.49(16) | N(1)−Ti−N(7) | 89.45(16) |
| N(1)−Ti−N(8) | 115.25(16) | N(1)−Ti−N(9) | 87.92(15) |
| N(4)−Ti−N(5) | 39.22(11) | N(4)−Ti−N(6) | 129.31(15) |
| N(4)−Ti−N(7) | 101.07(15) | N(4)−Ti−N(8) | 96.91(15) |
| N(4)−Ti−N(9) | 130.17(15) | N(5)−Ti−N(6) | 96.06(14) |
| N(5)−Ti−N(7) | 85.86(15) | N(5)−Ti−N(8) | 91.76(16) |
| N(5)−Ti−N(9) | 131.17(15) | N(6)−Ti−N(7) | 39.50(11) |
| N(6)−Ti−N(8) | 109.54(14) | N(6)−Ti−N(9) | 95.06(14) |
| N(7)−Ti−N(8) | 148.04(14) | N(7)−Ti−N(9) | 128.74(15) |
| N(8)−Ti−N(9) | 40.02(13) | Ti−N(1)−N(2) | 111.0(3) |
| Ti−N(4)−N(5) | 71.4(2) | Ti−N(5)−N(4) | 69.4(2) |
| Ti−N(6)−N(7) | 72.2(2) | Ti−N(7)−N(6) | 68.3(2) |
| Ti−N(8)−N(9) | 70.7(3) | Ti−N(9)−N(8) | 69.2(3) |

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

| | | | |
|---|---|---|---|
| Nb−N(1) | 2.114(2) | Nb−N(2) | 2.073(2) |
| Nb−N(3) | 2.094(3) | Nb−N(4) | 2.194(3) |
| N(1)−N(1)#1 | 1.358(5) | N(2)−N(3) | 1.388(4) |
| N(4)−N(5) | 1.403(4) | | |
| N(1)−Nb−N(2) | 91.23(13) | N(1)−Nb−N(3) | 126.24(13) |
| N(1)−Nb−N(4) | 83.68(10) | N(1)−Nb−N(1)′ | 37.47(13) |
| N(2)−Nb−N(3) | 38.90(10) | N(2)−Nb−N(4) | 90.58(9) |
| N(2)−Nb−N(2)′ | 178.8(2) | N(2)−Nb−N(3)′ | 139.86(11) |
| N(2)−Nb−N(1)′ | 89.95(13) | N(3)−Nb−N(1)′ | 127.55(12) |
| N(3)−Nb−N(3)′ | 101.32(14) | N(3)−Nb−N(4) | 79.60(10) |
| N(3)−Nb−N(4)′ | 84.73(10) | N(4)−Nb−N(1)′ | 121.14(10) |
| N(4)−Nb−N(2)′ | 89.15(9) | N(4)−Nb−N(4)′ | 155.2(2) |
| Nb−N(4)−N(5) | 112.9(2) | Nb−N(1)−N(1)′ | 71.26(7) |
| Nb−N(2)−N(3) | 71.40(14) | Nb−N(3)−N(2) | 69.7(2) |

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for **11**

| | | | |
|---|---|---|---|
| Nb−N(1) | 2.092(5) | Nb−N(2) | 2.054(4) |
| Nb−N(3) | 2.096(4) | Nb−N(4) | 2.080(4) |
| Nb−N(5) | 2.056(4) | Nb−N(6) | 2.093(4) |
| Nb−N(7) | 2.198(5) | Nb−N(11) | 2.179(5) |
| N(1)−N(2) | 1.377(6) | N(3)−N(4) | 1.368(6) |
| N(5)−N(6) | 1.396(6) | N(7)−N(8) | 1.336(6) |
| N(7)−N(10) | 1.306(6) | N(9)−N(10) | 1.338(7) |
| N(11)−N(12) | 1.336(6) | N(11)−N(14) | 1.354(6) |
| N(13)−N(14) | 1.346(6) | | |
| N(1)−Nb−N(2) | 38.8(2) | N(1)−Nb−N(3) | 127.5(2) |
| N(1)−Nb−N(4) | 125.3(2) | N(1)−Nb−N(5) | 139.7(2) |
| N(1)−Nb−N(6) | 101.1(2) | N(1)−Nb−N(7) | 78.5(2) |
| N(2)−Nb−N(3) | 89.7(2) | N(2)−Nb−N(4) | 92.2(2) |
| N(2)−Nb−N(5) | 178.4(2) | N(2)−Nb−N(6) | 139.3(2) |
| N(2)−Nb−N(7) | 91.5(2) | N(3)−Nb−N(4) | 38.2(2) |
| N(3)−Nb−N(5) | 91.9(2) | N(3)−Nb−N(6) | 126.7(2) |
| N(3)−Nb−N(7) | 122.4(2) | N(4)−Nb−N(5) | 89.9(2) |
| N(4)−Nb−N(6) | 128.1(2) | N(4)−Nb−N(7) | 84.2(2) |
| N(5)−Nb−N(6) | 39.3(2) | N(5)−Nb−N(7) | 87.6(2) |
| N(6)−Nb−N(7) | 83.7(2) | Nb−N(1)−N(2) | 69.1(3) |
| Nb−N(2)−N(1) | 72.1(2) | Nb−N(3)−N(4) | 70.2(2) |
| Nb−N(4)−N(3) | 71.5(2) | Nb−N(5)−N(6) | 71.8(2) |
| Nb−N(6)−N(5) | 68.9(2) | Nb−N(7)−N(8) | 123.0(3) |
| Nb−N(7)−N(10) | 125.2(3) | Nb−N(11)−N(12) | 123.9(3) |
| Nb−N(11)−N(14) | 125.2(3) | | |

hedral geometry, similar to that found in eight-coordinate pyrazolato complexes of the formula $Ti(R_2pz)_4$ ($R = CH_3, C_6H_5$) that we have previously reported.[45] The titanium atom in **1** is bound to two pyrazolato and two triazolato ligands with $\eta^2$-coordination to both types of ligands. The geometry about the titanium center is distorted tetrahedral, if the center of each nitrogen−nitrogen bond in the ligands is considered to be a monodentate donor. The titanium−nitrogen bond lengths associated with the triazolato ligands (range 2.059−2.098 Å) are slightly longer than the analogous values in the pyrazolato ligands (range 2.018−2.057 Å). Within each pyrazolato ligand, one titanium−nitrogen bond is 0.035−0.039 Å longer than the other. Within the triazolato ligands, the ligand containing N(5) and N(6) shows a similar asymmetric bonding to titanium (difference 0.031 Å), while the ligand containing N(8) and N(9) exhibits ideal $\eta^2$-bonding. The nitrogen−nitrogen bond lengths

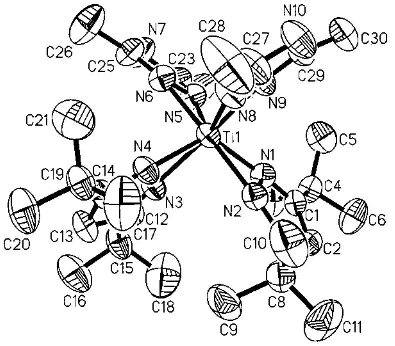


**Figure 1.** Perspective view of Ti(tBu$_2$pz)$_2$(Me$_2$C$_2$N$_3$)$_2$ (**1**) with thermal ellipsoids at the 50% probability level.

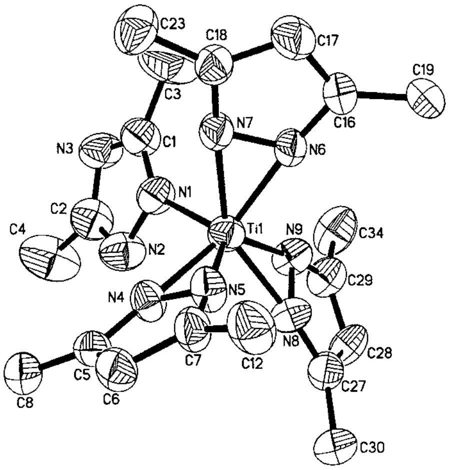


**Figure 2.** Perspective view of Ti(tBu$_2$pz)$_3$(Me$_2$C$_2$N$_3$) (**2**) with thermal ellipsoids at the 50% probability level.

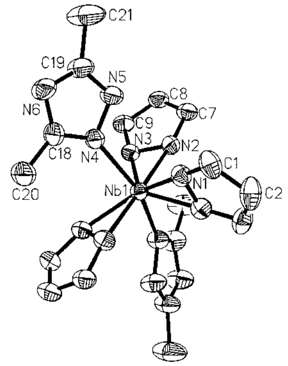


**Figure 3.** Perspective view of Nb(tBu$_2$pz)$_3$(Me$_2$C$_2$N$_3$)$_2$ (**4**) with thermal ellipsoids at the 50% probability level.

in the pyrazolato and triazolato groups are almost identical (1.361(3)−1.373(3) Å).

Complex **2** crystallizes as a 7-coordinate monomer with three $\eta^2$-di-*tert*-butylpyrazolato ligands and one $\eta^1$-dimethyl-1,2,4-triazolato ligand (Figure 2). The geometry about the titanium center is distorted tetrahedral, if the center of each nitrogen−nitrogen bond in the 3,5-di-*tert*-butylpyrazolato ligands is considered to be a monodentate donor. The titanium−nitrogen bond length to the $\eta^1$-triazolato ligand (2.020(4) Å) is similar to the values for the $\eta^2$-pyrazolato ligands (1.986(4)−2.042(4) Å). The metal−nitrogen bond lengths in **2** are slightly shorter than those found in **1**, probably due to the less crowded 7-coordinate metal center in **2**.

The molecular structure of **4** is presented in Figure 3. The coordination sphere of **4** contains two $\eta^1$-triazolato and three $\eta^2$-pyrazolato groups. The geometry about the niobium atom is best described as distorted trigonal bipyramidal, if the centers of the nitrogen−nitrogen bonds of the $\eta^2$-pyrazolato ligands are considered as monodentate donors. The equatorial plane is defined by two approximately coplanar di-*tert*-butylpyrazolato ligands and one di-*tert*-butylpyrazolato ligand whose plane is approximately perpendicular to the plane of the other two. We have previously observed a similar arrangement of $\eta^2$-pyrazolato ligands in lanthanide complexes of the formula Ln(tBu$_2$pz)$_3$(py)$_2$;[51] such a disposition of these ligands is apparently due to steric accommodation of the *tert*-butyl groups. The $\eta^1$-triazolato ligands occupy the axial positions. The N(4)−Nb−N(4)′ angle is 155.2(2)° and is less than the idealized 180°, apparently due to avoidance of steric interactions with the *tert*-butyl groups of one of the pyrazolato ligands. The 3,5-di-*tert*-butylpyrazolato ligands are symmetrically bound in a $\eta^2$-fashion, with the niobium−nitrogen distances ranging from 2.073(2) to 2.114(2) Å. The values described thus far for **4** are very similar to the related values for dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V), whose structure we have recently reported.[48] The niobium−nitrogen bond length for the $\eta^1$-dimethyl-1,2,4-triazolato ligand is 2.194(3) Å. The second nitrogen on each triazolato ligand is clearly not coordinated to the niobium center. The crowded coordination sphere that is present in **4** probably causes the lengthening of the niobium−nitrogen bond for the triazolato ligand compared to the pyrazolato ligands.

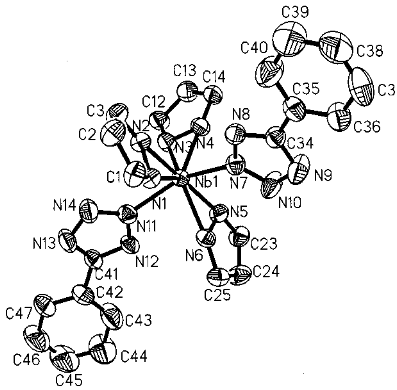


**Figure 4.** Perspective view of Nb(tBu$_2$pz)$_3$(PhCN$_4$)$_2$ (**11**) with thermal ellipsoids at the 50% probability level.

The molecular structure of **11** is presented in Figure 4. The coordination sphere contains two $\eta^1$-tetrazolato and three $\eta^2$-pyrazolato groups. The coordination geometry is very similar to those found in **4** and dichloro(3,5-di-*tert*-butylpyrazolato)niobium(V).[48] Again, the equatorial plane is comprised of two approximately coplanar pyrazolato ligands and a third pyrazolato ligand whose five-membered ring approximately bisects the plane of the other two. The angle between the coordinated nitrogen atoms of the axial tetrazolato ligands is 152.2(2)°. The niobium−nitrogen bond lengths for the pyrazolato ligands range from 2.054(4) to 2.096(4) Å and are slightly shorter than those found in **4**. The niobium−nitrogen bond lengths in the $\eta^1$-tetrazolato groups (2.179(5) and 2.198(5) Å) are similar to the related bond length for the $\eta^1$-triazolato ligands in **4**.

**Variable-Temperature NMR Behavior.** We sought to explore solution structures and exchange processes that might occur in the new compounds. Kinetics of methyl site exchange in the dimethyl-1,2,4-triazolato ligands of **4** and **6** was studied and is described below. In addition, solution structures for **8** and **9** are proposed on the basis of the low-temperature NMR spectra. In **2**, a single sharp resonance was observed at −80 °C in toluene-$d_8$ for the 1,2,4-triazolato ligand methyl groups,

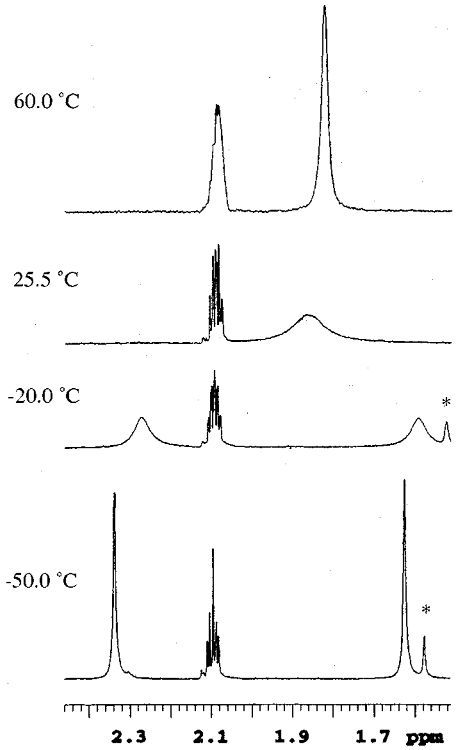


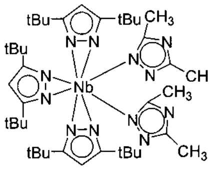
**Figure 5.** Variable-temperature $^1$H NMR Spectra for **4**. The resonance at $\delta$ 2.08 corresponds to the residual hydrogen atoms on the methyl group of toluene-$d_8$, and the resonance denoted with an asterisk is an impurity.

**Table 6.** Rate Constants Data for Interconversion of Triazolato Ligand Methyl Sites for **4** and **6**

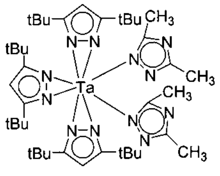
| temp (K) | rate const (s$^{-1}$) | temp (K) | rate const (s$^{-1}$) |
|---|---|---|---|
| | (a) Data for **4** | | |
| 223.4 | 0.00 | 293.2 | 972 |
| 234.0 | 5.36 | 303.7 | 1600 |
| 244.6 | 13.9 | 308.5 | 2500 |
| 255.3 | 34.7 | 324.4 | 6610 |
| 265.9 | 113 | 340.4 | 13900 |
| 276.6 | 259 | | |
| | (b) Data for **6** | | |
| 247.6 | 7.2 | 305.8 | 259 |
| 259.2 | 12 | 311.6 | 462 |
| 270.9 | 26.4 | 317.5 | 590 |
| 282.5 | 67.5 | 323.3 | 972 |
| 288.3 | 104 | 329.1 | 1190 |
| 298.8 | 148 | | |

suggesting that there is a low barrier for exchange between the two possible sites in the $\eta^1$-3,5-dimethyl-1,2,4-triazolato ligand.

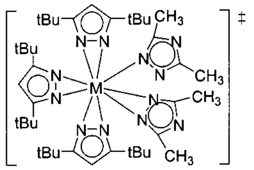
In the $^1$H NMR spectra in toluene-$d_8$, the methyl groups of the 3,5-dimethyl-1,2,4-triazolato ligands in **4** and **6** undergo site exchange between −50 and 60 °C. To gain further insight into the dynamic processes, the line-broadening kinetics was studied for these events. Details of the analyses are presented in the Experimental Section and in the Supporting Information. Rate constants were determined by simulating the $^1$H NMR spectra at various temperatures using the program gNMR.[94] Figure 5 shows the $^1$H NMR spectra for **4** that were taken at various temperatures. Consistent with these spectra, the process was modeled as a two-site AB exchange. Rate constants are presented in Table 6. The $^1$H NMR spectra for **6** were very similar to those for **4,** and a kinetics analysis was performed in an analogous fashion. Eyring analysis of the rate data for **4** afforded the activation parameters $\Delta H^\ddagger = 11.4 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -6.2 \pm 0.1$ cal/(K·mol), and $\Delta G^\ddagger(298\text{ K}) = 13.2 \pm 0.1$ kcal/mol. The activation parameters for **6** were $\Delta H^\ddagger = 10.0 \pm 0.2$ kcal/mol, $\Delta S^\ddagger = -14.6 \pm 0.2$ cal/(K·mol), and $\Delta G^\ddagger(298\text{ K}) = 14.3 \pm 0.2$ kcal/mol. These data allow us to offer some insight into the character of the transition states that interconvert the triazolato methyl sites in **4** and **6**. The transition state most likely corresponds to a nine-coordinate structure **13** that contains one $\eta^2$-triazolato ligand. The more ordered nature of the transition states, compared to the ground-state structures of **4** and **6**, is reflected in the negative entropies of activation for the kinetic processes. An ionic transition state that entails dissociation of a dimethyl-1,2,4-triazolate ion, followed by recoordination to the other nitrogen atom, is unlikely since such a process should exhibit a large positive entropy of activation. A transition state that involves substantial $\eta^1$-pyrazolato ligand character is also unlikely in view of the negative entropies of activation.



**4**



**6**



**13**

We have recently reported that the starting material used to prepare **4**, dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium, undergoes a Berry pseudorotation-type process in toluene-$d_8$ between −50 and −30 °C that interconverts the separate sites for the *tert*-butyl groups.[48] In **4** and **6**, three types of *tert*-butyl sites were observed in toluene-$d_8$ at temperatures up to about 60 °C. Between 60 and 100 °C, the *tert*-butyl resonances began to broaden slightly, suggesting that the di-*tert*-butylpyrazolato ligands in these complexes undergo an exchange process at higher temperatures. However, even at 120 °C in *o*-xylene-$d_{10}$, line broadening had not occurred sufficiently to allow kinetics determinations with gNMR. Accordingly, kinetics studies for these processes were not carried out. The much higher temperatures required for a *tert*-butyl site interconversion in **4** and **6**, compared to the case for dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium, is consistent with the much more crowded coordination spheres in the former complexes.

The $^1$H and $^{13}$C{$^1$H} NMR spectra of complexes **8** and **9** were complicated and temperature dependent. Spectra obtained for **8** and **9** in toluene-$d_8$ between −90 and +60 °C were virtually identical, and only the spectra for **9** are discussed herein. At 60 °C, the $^1$H NMR spectrum of **9** revealed sharp resonances for one type of pyrazolato ligand ($\delta$ 6.44 (2 C*H*), 1.11 (4 C(C*H*$_3$)$_3$)) and one type of triazolato ligand ($\delta$ 2.03 (6 C*H*$_3$)). Upon cooling of the sample to −65 °C, each of these resonances gradually broadened and coalesced into new resonances. Between −65 and −90 °C, the $^1$H NMR spectra were essentially static with only small chemical shift differences. At −90 °C, the $^1$H NMR spectrum revealed resonances for two equal intensity pyrazolato methine groups ($\delta$ 6.53, 6.34), six equal intensity methyl groups ($\delta$ 2.76, 2.64, 2.48, 2.24, 2.02, 1.28), and four equal intensity

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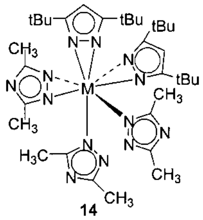
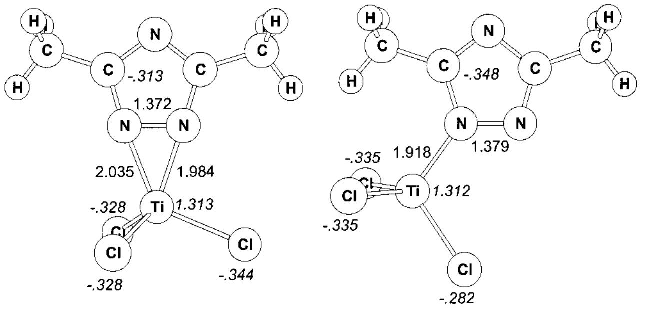
[94] gNMR; version 4; Cherwell Scientific Publishing: Oxford, U.K., 1997.

*tert*-butyl groups ($\delta$ 1.29, 1.20, 1.18, 0.75). In particular, the methyl resonance at $\delta$ 1.28 and the *tert*-butyl resonance at $\delta$ 0.75 are shifted substantially upfield from the normal chemical shifts for these groups. The upfield shifts suggest that these groups are positioned in the shielding region of an aromatic pyrazolato or triazolato ligand. A monomeric structure consistent with these spectral data is represented by **14**. The proposed structure possesses approximate trigonal pyramidal geometry, with $\eta^2$-pyrazolato, $\eta^2$-triazolato, and $\eta^1$-triazolato ligands in the equatorial plane. The axial ligands comprise $\eta^2$-pyrazolato and $\eta^1$-triazolato ligands. If the $\eta^2$-pyrazolato and $\eta^2$-triazolato ligands are approximately coplanar in the equatorial plane, then it is likely that the equatorial $\eta^1$-triazolato ligand will lie approximately perpendicular to the equatorial plane. Such a disposition would place one methyl group from the $\eta^2$-triazolato ligand and one *tert*-butyl group from the $\eta^2$-pyrazolato ligand within the shielding cone of the equatorial $\eta^1$-triazolato ligand and could account for the observed unusually large upfield shifts. It is necessary to propose an axial $\eta^2$-pyrazolato ligand to arrive at a structure that fits the low-temperature $^1$H NMR spectrum. We caution that we have only considered monomeric structures. While the crowded coordination spheres of **8** and **9** are likely to disfavor oligomeric structures, we cannot rule out such species at low temperature.



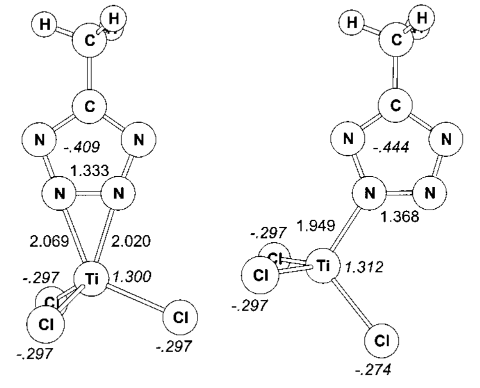
**14**

The $^1$H NMR spectra of **11** in toluene-$d_8$ were recorded between +40 and −80 °C. At or below −60 °C, the $^1$H NMR spectra of **11** showed three different *tert*-butyl group sites ($\delta$ 1.15, 1.12, 0.92 at −60 °C) and two different CH fragments of the pyrazolato rings ($\delta$ 6.98 and 6.45 at −60 °C in a 2:1 proportion). Between −60 and −50 °C the *tert*-butyl resonances at $\delta$ 1.15 and 1.12 merged to a single resonance, while warming to between −50 and −30 °C led to coalescence of the two remaining *tert*-butyl resonances into a single broad peak at $\delta$ 1.08. Between −50 and −30 °C the pyrazolato C−H resonances at $\delta$ 6.98 and 6.45 gradually broadened. At −20 °C, a broad pyrazolato C−H resonance was centered at $\delta$ 6.8. At 40 °C, sharp singlets for *tert*-butyl and pyrazolato C−H groups were observed at $\delta$ 1.07 and 6.83, respectively. Such dynamic behavior for **11** is very similar to the pseudorotation-type process that we have previously reported for dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium.[48] It is particularly striking that the pseudorotation rate constant for **11** is qualitatively similar to that of dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium,[48] while the related process for **4** and **6** is significantly slower. A possible explanation is that the low energy $\eta^2$-triazolato ligand transition states for **4** and **6** lead to more steric congestion about the metal centers than is present in **11** and dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium. Such a proposal suggests that a similar $\eta^2$-tetrazolato ligand transition state is not accessible for **11**. Along these lines, the tetrazolato phenyl resonances of **11** appeared at multiplets centered at $\delta$ 8.2 (4H), 7.15 (4 H), and 7.05 (2H) between +40 and −80 °C. These resonances did not undergo any changes other than small chemical shift differences with temperature (±$\delta$ 0.1 over 100 °C).

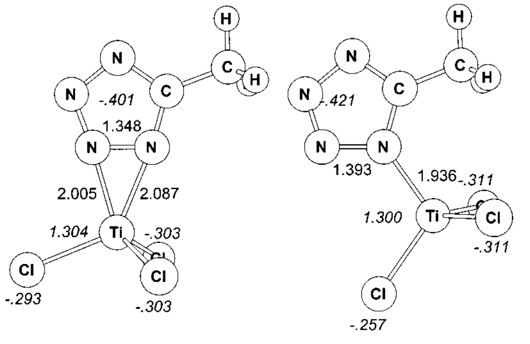


15a (0.0 kcal/mol) 15b (13.8 kcal/mol)

**Figure 6.** Calculated Structures for trichloro(3,5-dimethyl-1,2,4-triazolato)titanium(IV) (**15**; Ti−N and N−N bond lengths in Å, charges on Ti, Cl, and the ring in italics, relative energies in bold). The $\eta^1$-structure **15b** is not a minimum, since the Ti−N−N bond angle was constrained to 126°.



16a (0.0 kcal/mol) 16b (5.2 kcal/mol)



17a (0.8 kcal/mol) 17b (8.6 kcal/mol)

**Figure 7.** Calculated structures for trichloro(5-methyltetrazolato)-titanium(IV) (**16** and **17**; Ti−N and N−N bond lengths in Å, charges on Ti, Cl, and the ring in italics, relative energies in bold). The $\eta^1$-structures **16b** and **17b** are not minima, since the Ti−N−N bond angles were constrained to 126°.

**Molecular Orbital Calculations.** To help in understanding the bonding between the titanium(IV) center and the triazolato and tetrazolato ligands, we carried out a series of ab initio molecular orbital calculations on model compounds containing a single 3,5-dimethyltriazolato or methyltetrazolato ligand complexed with the trichlorotitanium(IV) fragment. Thus considered were the 1,2-$\eta^2$- and 1-$\eta^1$-3,5-dimethyltriazolato (**15**), 2,3-$\eta^2$- and 2-$\eta^1$-methyltetrazolato (**16**), and 1,2-$\eta^2$- and 1-$\eta^1$-3,5- methyltetrazolato (**17**) complexes. The optimized geometries are shown in Figures 6 and 7. In each case, the equilibrium geometry is $\eta^2$. To simulate $\eta^1$ bonding, the titanium−nitrogen−nitrogen angle was constrained to 126° and the remaining coordinates were reoptimized. We have carried out similar calculations previously on trichloro(3,5-dimethylpyrazolato)-titanium(IV).[45] The two $\eta^2$ isomers **16a** and **17a** differ in energy by less than 0.8 kcal/mol, with the 2,3-isomer **16a** being more stable. Since these structures are separated by the $\eta^1$ structure

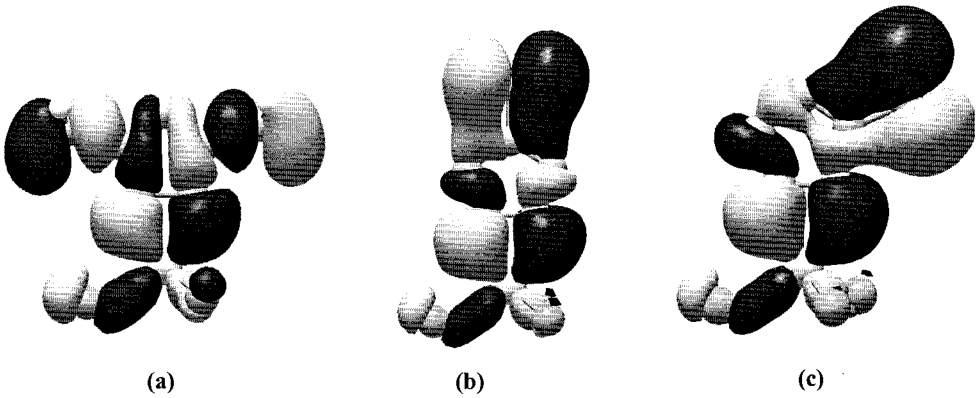
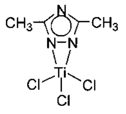
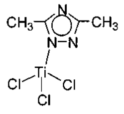


**Figure 8.** Calculated occupied orbitals for (a) trichloro(3,5-dimethyl-1,2,4-triazolato)titanium(IV) and (b, c) two isomers of trichloro(5-methyltetrazolato)titanium(IV) showing the interaction of the antisymmetric combination of the nitrogen lone pairs with the titanium $d_{xz}$ orbital.

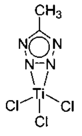
**16b** that is only 5.2 kcal/mol higher in energy, interconversion between **16a** and **17a** should be rapid at temperatures that are accessible in normal NMR solvents.



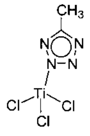
**15a**



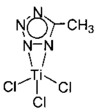
**15b**



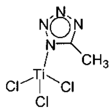
**16a**



**16b**



**17a**



**17b**

The calculated titanium−nitrogen bond lengths for the triazolato complexes **15** are about 0.06 Å shorter than in the crystal structure for **1**; a similar trend was found previously for the analogous pyrazolato complex.[45] The difference can probably be attributed to the use of chloride for three of the ligands in the computational models. Chloride is a less sterically demanding ligand than those that are present in **1**, and it is likely that the trichlorotitanium(IV) fragment is a stronger Lewis acid than the related fragment in **1**. Both of these factors would lead to shorter titanium−nitrogen bond lengths in the model complex **15a**. The average titanium−nitrogen bond lengths calculated for the $\eta^2$ complexes are ca. 0.1 Å longer than for the $\eta^1$ structures; a similar trend is also observed in the crystal structures, but the change is at the limit of experimental error (0.05 Å). The titanium−nitrogen bond lengths increase in going from triazolato to tetrazolato ligands, and this increase is larger for the $\eta^2$ complexes than for the $\eta^1$ structures. The charge on the ring also increases in the series. The charge on the ring in the $\eta^1$ structures is slightly higher than for $\eta^2$, presumably because of a greater opportunity to share charge through bonding in the latter.

The energy difference between the $\eta^1$ and $\eta^2$ structures is largest for trichloro(3,5-dimethylpyrazolato)titanium(IV) (16.5 kcal/mol)[45] and triazolato complexes **15** (13.8 kcal/mol) and smallest for tetrazolato complexes **16** and **17** (5.2 and 8.6 kcal/mol). This is in accord with the fact that sterically crowded complexes **1** and **2** are observed to have both $\eta^2$ and $\eta^1$ bonding of the triazolato ligands, but **11** has only $\eta^1$ bonding of the tetrazolato ligand. However, the trend in the $\eta^1-\eta^2$ energy difference in **15-17** is not merely the result of sterics, since **15b** has steric interactions that are essentially the same as in the $\eta^1$ structure of trichloro-3,5-dimethylpyrazolatotitanium(IV), but the $\eta^1-\eta^2$ energy difference is about 3 kcal/mol less. Thus, electronic factors must make a significant contribution.

Figure 8 shows the molecular orbitals for **15a**, **16a**, and **17a** consisting of bonding between the antisymmetric combination of the nitrogen lone pairs and the empty titanium $d_{xz}$ orbital. A similar bonding arrangement occurs between the symmetric combination of the lone pairs and the titanium $d_{z^2}$ orbital, but this interaction mixes with several other orbitals and is correspondingly difficult to visualize. The related molecular orbitals for trichloro(3,5-dimethylpyrazolato)titanium(IV) have been reported previously.[45] The shapes of these orbitals are very similar and do not immediately supply an explanation for the observed trends. However, an inspection of the lone pair orbital energies does reveal the necessary differences. As expected from the increased electronegativity, the lone pair orbitals on the ring become more stable as the number of nitrogens increases. This increases the energy difference between the occupied nitrogen lone pair orbitals and the empty titanium d orbitals and, consequently, the stabilizing interaction becomes weaker. The weaker interaction is manifested by longer and weaker titanium−nitrogen bonds: 1.991, 2.010, 2.044, and 2.046 Å for the average titanium−nitrogen bond lengths in trichloro(3,5-dimethylpyrazolato)titanium(IV),[45] **15a**, **16a**, and **17a**, respectively. The trend in the bond strengths can be gauged by the energy needed to break one of the $\eta^2$ titanium−nitrogen bonds to form the $\eta^1$ structure: 16.5 kcal/mol for pyrazolato; 13.8 kcal/mol for **16a**; 5.2−8.6 kcal/mol for **16a** and **17a**. The weaker orbital interaction also diminishes the sharing of charge between the ring and the trichlorotitanium(IV) fragment, thus accounting for the trend in the charges as well.

## Discussion

The complexes described herein are the first early transition metal compounds that contain 1,2,4-triazolato and tetrazolato ligands. Our initial synthetic attempts to prepare homoleptic 1,2,4-triazolato and tetrazolato complexes led to insoluble or poorly soluble, intractable products. The tractable complexes described herein were only obtained when bulky 3,5-di-*tert*-butylpyrazolato ligands were included in the coordination spheres. Thus, very bulky ligands appear to be required to disfavor bridging coordination modes of 1,2,4-triazolato and tetrazolato ligands. It is likely that 3,5-disubstituted 1,2,4-triazolato ligands with large alkyl or aryl groups should also provide sufficient steric bulk to allow the formation of homoleptic monomeric early transition metal complexes. Since tetrazolato ligands contain only one group attached to carbon, as opposed to the two substituents in 3,5-disubstituted pyrazolato and 1,2,4-triazolato ligands, a very bulky group is probably required to obtain tractable homoleptic early transition derivatives. Finally, because bulky ligands are required to obtain monomeric complexes, as noted above, it is very likely that both $\eta^1$- and $\eta^2$-1,2,4-triazolato and tetrazolato ligands are higher in energy than bridging coordination modes of these ligands, in the absence of steric effects. Accordingly, we predict that $\eta^1$- and $\eta^2$-coordination of these ligands will only be observed in early transition metal complexes when bulky substituents are present in the coordination sphere to disfavor bridging ligands.

The theoretical results demonstrate that there is a strong thermodynamic driving force for $\eta^2$-coordination of 1,2,4-triazolato and tetrazolato ligands over the $\eta^1$-coordination mode. On the basis of the theoretical results described herein, the similarity between orbital interactions of $\eta^2$-1,2,4-triazolato and $\eta^2$-tetrazolato ligands with those of $\eta^2$-pyrazolato ligands[45] and the widespread occurrence of $\eta^2$-pyrazolato ligands among early transition metal complexes,[44−49,59,60] we predict that $\eta^2$-coordination of 1,2,4-triazolato and tetrazolato ligands will be common in early transition metal complexes. At the same time, the energy difference between $\eta^2$- and $\eta^1$-coordination is smaller for 1,2,4-triazolato and tetrazolato ligands (13.8−5.2 kcal/mol) than for pyrazolato ligands (16.5 kcal/mol), and therefore, $\eta^2$-coordination of 1,2,4-triazolato and tetrazolato ligands should be much more sensitive to steric crowding than are pyrazolato ligands. Complexes **1**−**12** reflect the fine balance between $\eta^2$- and $\eta^1$-coordination modes. Consistent with the higher calculated bond energies, the pyrazolato ligands in **2**−**4**, **10**, and **11** are $\eta^2$-bonded. Apparently, the tris($\eta^2$-3,5-di-*tert*-butylpyrazolato)metal fragment is too bulky to allow a fourth or fifth ligand to bond in a $\eta^2$-fashion, so $\eta^1$-coordination of the 1,2,4-triazolato and tetrazolato ligands is observed. We have previously noted that only three 3,5-di-*tert*-butylpyrazolato ligands can be placed around a titanium(IV) center[57] and that pentakis(3,5-dimethylpyrazolato)tantalum(V) contains three $\eta^2$- and two $\eta^1$-pyrazolato ligands.[46]

The calculated charges on the $\eta^2$-heterocyclic ligands in trichloro($\eta^2$-dimethylpyrazolato)titanium[45] and **15**−**17** follow the order pyrazolato < 1,2,4-triazolato < tetrazolato. This order reflects the ability of the ligands to stabilize a negative charge and also follows the order of p$K_a$s of the parent heterocycles.[95] The calculated charges also predict that the order of electron-withdrawing character for these ligands will follow the order pyrazolato < 1,2,4-triazolato < tetrazolato. Accordingly, 1,2,4-triazolato and tetrazolato ligand sets in early transition metal complexes should confer unique electronic character to the metal centers. Such ideas may contribute to the development of new ancillary ligand sets that can support useful reactivity in early transition metal complexes.[1−39]

The NMR kinetics studies of **4** and **6** suggest that methyl site exchange in these complexes occurs through 9-coordinate transition states that contain $\eta^2$-dimethyl-1,2,4-triazolato ligands. The enthalpy of activation for these processes (10.0−11.4 kcal/mol) must represent the upper limit for the energy difference between the ground state and the transition state for methyl site exchange. Hence, the $\eta^1$-dimethyl-1,2,4-triazolato ligands in **4** and **6** are stabilized by up to 11 kcal/mol compared to the $\eta^2$-ligand. In sterically unencumbered **15**, the $\eta^2$-coordination mode is 13.8 kcal/mol more stable than the $\eta^1$-ligand. Accordingly, the tris($\eta^2$-3,5-di-*tert*-butylpyrazolato)metal(V) fragment in **4** and **6** may destabilize the $\eta^2$-coordination mode by up to 25 kcal/mol. In a study relevant to this work, Chisholm and Extine prepared complexes of the formula $M(O_2CN(CH_3)_2)_5$ (M = Nb, Ta) and found that the niobium complex possessed a structure with three $\eta^2$- and two $\eta^1$-dimethylcarbamato ligands.[96] Such a structure is similar to **4** and **6**. $M(O_2CN(CH_3)_2)_5$ was found to undergo dynamic exchange of the $\eta^2$- and $\eta^1$-dimethylcarbamato ligands with interconversion barriers of 11−12 kcal/mol, and the exchange was suggested to entail a bidentate transition state or intermediate. These exchanges are remarkably similar to those documented herein for **4** and **6** and suggest considerable similarity between five membered heterocyclic ligands and dialkylcarbamato ligands in group 5 metal(V) complexes.

As described herein, **1** contains the first example of terminal $\eta^2$-1,2,4-triazolato ligand coordination to any metal, while **2**−**4** provide additional examples of the rare $\eta^1$-coordination mode of this ligand. We were unable to prepare and characterize crystallographically any complexes containing $\eta^2$-tetrazolato ligands, since the bulky pyrazolato ligand spheres required for monomeric complexes also promoted $\eta^1$-coordination. A search of the Cambridge Crystallographic Database did not reveal any examples of $\eta^2$-bonding interactions within bridging 1,2,4-triazolato ligands. Crystallographically characterized tetrazolato complexes containing $\eta^2$-bonding interactions within a bridging coordination mode are limited to two examples. The 1- and 2-nitrogen atoms of each phenyltetrazolato ligand in the dimeric complexes $[(C_5H_4(CH_3))_2Ln(PhCN_4)]_2$ (Ln = Yb, Er) are $\eta^2$-bonded to each lanthanide(III) center, while the 3-nitrogen atom bridges to the other lanthanide(III) ion of the dimeric unit with a $\eta^1$-interaction.[88,89] The 2- and 3-nitrogen atoms in cesium 5-cyanotetrazolate are bonded to the cesium ion in a $\eta^2$-fashion.[90] The bonding of cesium and lanthanide(III) ions to nitrogen donor ligands is predominately ionic, so the interaction of tetrazolato ligands with these metals is different than the more covalent bonding observed in d-block metal complexes. Accordingly, the observation of a $\eta^2$-1,2,4-triazolato ligand in **1** and the prediction that $\eta^2$-coordination of 1,2,4-triazolato and tetrazolato ligands should be common among the early transition metals represent novel and unexpected findings given the current state of the literature in this area.

The long-term goal of our research is to explore new nitrogen source compounds that can be used to grow metal nitride phases by chemical vapor deposition techniques. While ammonia is by far the most widely used nitrogen source compound in film growth, the high stability of ammonia and concomitant high film deposition temperatures has led to increasing consideration of alternative nitrogen source compounds in the past several years within the context of GaN and TiN film growth.[86,97−107] Hydrazine and alkylhydrazines have been the focus of most of

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(95) Grimmett, M. R. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, U.K., 1979; Vol. 4, p 365.

(96) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 782.

(97) Auvray, L.; Dumont, H.; Dazord, J.; Monteil, Y.; Bouix, J.; Bru-Chevallier, C.; Grenoullet, L. *Mater. Sci. Semicond. Process.* **2000**, *3*, 505.

(98) Friedman, D. J.; Norman, A. G.; Geisz, J. F.; Kurtz, S. R. *J. Cryst. Growth* **2000**, *208*, 11.

(99) Nakamura, K.; Sasaki, T. *J. Solid State Chem.* **2000**, *154*, 101.

(100) Sussek, H.; Stark, O.; Devi, A.; Pritzkow, H.; Fischer, R. A. *J. Organomet. Chem.* **2000**, *602*, 29.

(101) Peters, D. W.; Bourret, E. D.; Power, M. P.; Arnold, J. *J. Organomet. Chem.* **1999**, *582*, 108.

(102) Sato, S.; Satoh, S. *J. Cryst. Growth* **1998**, *192*, 381.

(103) Beaumont, B.; Vaille, M.; Lorenzini, P.; Gibart, P. *Internet J. Nitride Semicond. Res.* **1997**, *1*, 17.

(104) Hill, M.; Jegier, J.; Munoz-Hernandez, M. A.; Rutherford, D.; Singer, A.; Atwood, D. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1997**, *125*, 183.

(105) Amato-Wierda, C.; Wierda, D. A. *J. Mater. Res.* **2000**, *15*, 2414.

(106) Juppo, M.; Ritala, M.; Leskela, M. *J. Electrochem. Soc.* **2000**, *147*, 3377.

the effort; however, nitrogen heterocycles such as those described herein are potentially useful source compounds.[86,104]

## Experimental Section

**General Considerations.** All manipulations were carried out under argon using Schlenk line or glovebox techniques. Hexane and toluene were distilled from sodium, while diethyl ether and tetrahydrofuran were distilled from purple solutions of sodium benzophenone ketyl immediately prior to use. Potassium hydride (35% dispersion in mineral oil) and sodium hydride (60% dispersion in mineral oil) were purchased from Aldrich Chemical Co. and were washed with hexane prior to use to remove the mineral oil. (1,2,4-Triazolato)sodium was purchased from Aldrich Chemical Co. and was used as received. 3,5-Dimethyl-1,2,4-triazole was prepared according to a published procedure.[108,109] 3,5-Diethyl-1,2,4-triazole was prepared in 49% yield in a similar fashion using propionamide and hydrazine hydrate. Potassium 3,5-dimethyl-1,2,4-triazolate, potassium 3,5-diethyl-1,2,4-triazolate, and sodium 5-phenyltetrazolate were prepared by treatment of 3,5-dimethyl-1,2,4-triazole, 3,5-diethyl-1,2,4-triazole, and 5-phenyl-1*H*-tetrazole (Aldrich Chemical Co.) with 1 equiv of potassium hydride or sodium hydride in tetrahydrofuran and were isolated as a white solids after removing the volatile components under vacuum. The insoluble salts were used without further purification or characterization. $Ti(tBu_2pz)_{4-x}Cl_x$ ($x = 1, 2$), and $M(tBu_2pz)_{5-x}Cl_x$ ($M = Nb, Ta$; $x = 2, 3$) were prepared according to our previously reported procedures.[48]

Infrared spectra were recorded as Nujol mulls. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were determined at 500, 300, 125, or 75 MHz in the indicated solvents. Chemical shifts ($\delta$, ppm) are given relative to residual protons or the carbon atoms of solvent. Melting points were determined in sealed capillary tubes under argon and are uncorrected. Microanalyses were performed by Midwest Microlab, Indianapolis, IN.

**Preparation of Bis(3,5-di-*tert*-butylpyrazolato)bis(3,5-dimethyl-1,2,4-triazolato)titanium(IV) (1).** A 100-mL Schlenk flask was charged with dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (1.00 g, 2.09 mmol), potassium 3,5-dimethyl-1,2,4-triazolate (0.71 g, 5.25 mmol), and tetrahydrofuran (70 mL). The reaction mixture was stirred at room temperature for 48 h. The volatile components were removed under reduced pressure, and the resultant yellow solid was extracted with hexane (90 mL). Filtration of the hexane extract through a 2-cm pad of Celite on a coarse glass frit gave a yellow solution. Cooling the solution to −20 °C afforded **1** as yellow crystals (0.70 g, 56%): mp 154 °C dec; IR (Nujol, $cm^{-1}$) 1523 (m), 1498 (s), 1407 (w), 1364 (s), 1242 (s), 1206 (w), 1130 (w), 1016 (m), 1002 (w), 806 (s), 738 (m), 688 (w); $^1H$ NMR ($C_6D_6$, 22 °C, $\delta$) 6.25 (s, 2 H, pyrazolato ring $CH$), 2.32 (s, 12 H, triazolato $CH_3$), 1.31 (s, 36 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 22 °C, ppm) 157.12 (s, $CC(CH_3)_3$), 154.25 (s, triazolato $CCH_3$), 108.88 (s, pyrazolato ring $CH$), 32.26 (s, $C(CH_3)_3$), 30.70 (s, $C(CH_3)_3$), 13.89 (s, triazolato $CH_3$).

Anal. Calcd for $C_{30}H_{50}N_{10}Ti$: C, 60.19; H, 8.42; N, 23.40. Found: C, 59.86; H, 8.42; N, 23.67.

**Preparation of Tris(3,5-di-*tert*-butylpyrazolato)(3,5-dimethyl-1,2,4-triazolato)titanium(IV) (2).** In a fashion similar to the preparation of **1**, treatment of chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.60 g, 0.97 mmol) with potassium 3,5-dimethyl-1,2,4-triazolate (0.21 g, 1.55 mmol) in tetrahydrofuran (60 mL) afforded **2** as yellow crystals (0.38 g, 58%): mp 291 °C dec; IR (Nujol, $cm^{-1}$) 1507 (m), 1398 (w), 1365 (s), 1291 (m), 1252 (m), 1233 (m), 1204 (w), 1112 (w), 1019 (m), 989 (m), 843 (w), 810 (m), 802 (s), 754 (w), 722 (m), 693 (w); $^1H$ NMR ($C_6D_6$, 22 °C, $\delta$) 6.41 (s, 3 H, pyrazolato ring $CH$), 2.32 (s, 6 H, triazolato $CCH_3$), 1.21 (s, 54 H, $C(CH_3)_3$; $^{13}C\{^1H\}$ NMR ($C_6D_6$, 22 °C, $\delta$) 158.63 (s, $CC(CH_3)_3$), 156.06 (s, triazolato $CCH_3$), 110.48 (s, pyrazolato ring $CH$), 32.32 (s, $C(CH_3)_3$), 30.55 (s, $C(CH_3)_3$), 14.18 (s, triazolato $CH_3$).

Anal. Calcd for $C_{37}H_{63}N_9Ti$: C, 65.18; H, 9.31; N, 18.49. Found: C, 65.14; H, 9.35; N, 18.56.

**Preparation of Tris(3,5-di-*tert*-butylpyrazolato)(1,2,4-triazolato)-titanium(IV) (3).** In a fashion similar to the preparation of **1**, treatment of chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.60 g, 0.97 mmol) with (1,2,4-triazolato)sodium (0.13 g, 1.43 mmol) in tetrahydrofuran (60 mL) afforded **3** as yellow crystals (0.50 g, 79%): mp 247 °C; IR (Nujol, $cm^{-1}$) 1507 (m), 1481 (m), 1364 (s), 1287 (w), 1251 (s), 1233 (m), 1205 (w), 1175 (m), 1141 (w), 1064 (m), 1019 (m), 988 (m), 955 (w), 861 (m), 816 (m), 809 (s), 716 (w), 670 (m); $^1H$ NMR ($C_6D_6$, 22 °C, $\delta$) 8.43 (s, 2 H, triazolato ring $CH$), 6.48 (s, 3 H, pyrazolato ring $CH$), 1.13 (s, 54 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 22 °C, ppm) 159.65 (s, $CC(CH_3)_3$), 150.34 (s, triazolato ring $CH$), 111.76 (s, pyrazolato ring $CH$), 32.31 (s, $C(CH_3)_3$), 30.31 (s, $C(CH_3)_3$).

Anal. Calcd for $C_{35}H_{59}N_9Ti$: C, 64.30; H, 9.10; N, 19.28. Found: C, 64.21; H, 9.09; N, 19.20.

**Preparation of Tris(3,5-di-*tert*-butylpyrazolato)bis(3,5-dimethyl-1,2,4-triazolato)niobium(V) (4).** A 100-mL Schlenk flask was charged with dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) (0.50 g, 0.71 mmol), potassium 3,5-dimethyl-1,2,4-triazolate (0.24 g, 1.8 mmol), and tetrahydrofuran (80 mL). The reaction mixture was stirred for 3 days at room temperature, and the volatile components were removed under reduced pressure. The resultant orange solid was extracted with hexane (90 mL), and the hexane extract was filtered through a 2-cm pad of Celite on a coarse glass frit. Crystallization at −20 °C for 24 h afforded **4** as orange crystals (0.45 g, 76%): mp: 210 °C dec; IR (Nujol, $cm^{-1}$) 3080 (m), 1522 (m), 1500 (m), 1402 (m), 1306 (m), 1261 (m), 1232 (m), 1204 (w), 1100 (s), 1020 (s), 965 (m), 902 (w), 800 (s), 752 (w), 722 (w); $^1H$ NMR ($C_6D_6$, 22 °C, $\delta$) 6.60 (s, 2 H, pyrazolato ring $CH$), 6.54 (s, 1 H, pyrazolato ring $CH$), 1.91 (s broad, 12 H, triazolato $CH_3$), 1.14 (s, 18 H, $C(CH)_3)_3$), 1.08 (s, 18 H, $C(CH)_3)_3$), 1.01 (s, 18 H, $C(CH_3)_3$; $^{13}C\{^1H\}$ NMR ($C_6D_6$, 22 °C, ppm) 161.58 (s, triazolato $CCH_3$), 160.25 (s, $CC(CH_3)_3$), 158.69 (s, $CC(CH_3)_3$), 156.04 (s, $CC(CH_3)_3$), 118.38 (s, 2 pyrazolato ring $CH$), 116.06 (s, 1 pyrazolato ring $CH$), 32.47 (s, $C(CH_3)_3$), 32.25 (s, $C(CH_3)_3$), 32.15 (s, $C(CH_3)_3$), 30.03 (s, $C(CH_3)_3$), 29.98 (s, $C(CH_3)_3$), 29.98 (s, $C(CH_3)_3$), 12.94 (broad s, triazolato $CH_3$).

Anal. Calcd for $C_{41}H_{69}N_{12}Nb$: C, 59.84; H, 8.45; N, 20.42. Found: 59.60; H, 8.41; N, 20.34.

**Preparation of Tris(3,5-di-*tert*-butylpyrazolato)bis(3,5-diethyl-1,2,4-triazolato)niobium(V) (5).** In a fashion similar to the preparation of **4**, treatment of dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) (0.50 g, 0.71 mmol) with potassium 3,5-diethyl-1,2,4-triazolate (0.29 g, 1.78 mmol) in tetrahydrofuran (80 mL) afforded **5** as orange crystals (0.51 g, 81%): mp 227−229 °C dec; IR (Nujol, $cm^{-1}$) 3079 (m), 1522 (m), 1492 (s), 1415 (s), 1365 (s), 1351 (m), 1260 (m), 1232 (m), 1204 (w), 1027 (m), 967 (s), 812 (m), 727 (m); $^1H$ NMR ($C_6D_6$, 22 °C, $\delta$) 6.61 (s, 2 H, pyrazolato ring $CH$), 6.54 (s, 1 H, pyrazolato ring $CH$), 2.20 (broad s, 8 H, $CCH_2CH_3$), 1.34 (t, $J = 7.5$ Hz, 12 H, $CCH_2CH_3$), 1.15 (s, 18 H, $C(CH)_3)_3$), 1.07 (s, 18 H, $C(CH)_3)_3$), 1.03 (s, 18 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (toluene-$d_8$, 80 °C, ppm) 163.27 (s, triazolato $CCH_2CH_3$), 161.59 (s, $CC(CH_3)_3$), 160.26 (s, $CC(CH_3)_3$), 156.29 (s, $CC(CH_3)_3$), 118.12 (s, 2 pyrazolato ring $CH$), 115.78 (s, 1 pyrazolato ring $CH$), 32.18 (s, $C(CH_3)_3$), 32.08 (s, $C(CH_3)_3$), 31.62 (s, $C(CH_3)_3$), 29.97 (s, 3 $C(CH_3)_3$ overlapped), 20.36 (s, $CH_2CH_3$), 12.97 (s, $CH_2CH_3$).

Anal. Calcd for $C_{45}H_{77}N_{12}Nb$: C, 61.48; H, 8.83; N, 19.12. Found: C, 62.68; H, 9.21; N, 18.10.

**Preparation of Tris(3,5-di-*tert*-butylpyrazolato)bis(3,5-dimethyl-1,2,4-triazolato)tantalum(V) (6).** In a fashion similar to the preparation of **4**, treatment of dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V) (0.50 g, 0.63 mmol) with potassium 3,5-dimethyl-1,2,4-triazolate (0.21 g, 1.58 mmol) in tetrahydrofuran (80 mL) afforded **6** as colorless crystals (0.36 g, 62%): dec pt 112 °C; IR (Nujol, $cm^{-1}$) 3085 (m), 1525 (s), 1511 (m), 1403 (s), 1365 (s), 1308 (s), 1263 (m), 1233 (s), 1203 (w), 1158 (w), 1105 (w), 1068 (w), 1033 (w), 999 (w), 967 (s), 901 (m), 811 (s), 752 (m), 723 (w), 697 (w), 619 (w); $^1H$ NMR ($C_6D_6$, 22 °C, $\delta$) 6.74 (s, 1 H, pyrazolato ring $CH$), 6.68 (s, 2 H, pyrazolato ring $CH$), 2.25 (broad s, 6 H, triazolato $CH_3$), 1.62 (broad s, 6 H, triazolato $CH_3$), 1.14 (s, 18 H, $C(CH)_3)_3$), 1.07 (s, 18 H, $C(CH)_3)_3$), 1.01 (s, 18 H, $C(CH_3)_3$; $^{13}C\{^1H\}$ NMR (toluene-$d_8$, 60 °C, ppm) 160.95 (s, triazolato $CCH_3$), 161.18 (s, $CC(CH_3)_3$), 159.56 (s, $CC(CH_3)_3$), 156.98 (s, $CC(CH_3)_3$), 117.34 (s, 2 pyrazolato ring $CH$), 115.51 (s, 1

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(107) Amato-Wierda, C.; Norton, E. T.; Wierda, D. A. *Electrochem. Solid State Lett.* **1999**, *2*, 613.

(108) Jones, R. E.; Rees, C. W. *J. Chem. Soc. C* **1969**, 2251.

(109) Macleod, I. T.; Tiekink, E. R. T.; Young, C. G. *J. Organomet. Chem.* **1996**, *506*, 301.

pyrazolato ring C*H*), 32.30 (s, *C*(CH$_3$)$_3$), 32.12 (s, *C*(CH$_3$)$_3$), 32.02 (s, *C*(CH$_3$)$_3$), 29.85 (s, 3 C(*C*H$_3$)$_3$ overlapped), 12.46 (broad s, triazolato *C*H$_3$).

Anal. Calcd for $C_{41}H_{69}N_{12}Ta$: C, 54.05; H, 7.63; N, 18.45. Found: C, 53.80; H, 7.57; N, 18.85.

**Preparation of Tris(3,5-di-*tert*-butylpyrazolato)bis(3,5-diethyl-1,2,4-triazolato)tantalum(V) (7).** In a fashion similar to the preparation of **4**, treatment of dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V) (0.50 g, 0.63 mmol) with potassium 3,5-diethyl-1,2,4-triazolate (0.26 g, 1.6 mmol) in tetrahydrofuran (70 mL) afforded **7** as colorless crystals (0.26 g, 43%): dec pt. 273−275 °C; IR (Nujol, cm$^{-1}$) 3083 (m), 1524 (m), 1494 (m), 1415 (m), 1261 (m), 1233 (w), 1026 (s), 968 (m), 801 (s), 727 (m); $^1$H NMR (C$_6$D$_6$, 22 °C, $\delta$) 6.73 (s, 1 H, pyrazolato ring C*H*), 6.70 (s, 2 H, pyrazolato ring C*H*), 2.69 (broad s, 4 H, C*H$_2$*CH$_3$), 1.53 (broad s, 4 H, C*H$_2$*CH$_3$), 1.34 (broad s, 12 H, CH$_2$C*H$_3$*), 1.15 (s, 18 H, C(C*H*)$_3$)$_3$), 1.06 (s, 18 H, C(C*H*)$_3$)$_3$), 1.02 (s, 18 H, C(C*H$_3$*)$_3$); $^{13}$C{$^1$H} NMR (toluene-*d*$_8$, 50 °C, ppm) 164.42 (s, triazolato *C*CH$_2$-CH$_3$), 160.80 (s, *C*C(CH$_3$)$_3$), 159.97 (s, *C*C(CH$_3$)$_3$), 156.84 (s, *C*C-(CH$_3$)$_3$), 117.43 (s, 2 pyrazolato ring *C*H), 115.42 (s, 1 pyrazolato ring *C*H), 32.34 (s, *C*(CH$_3$)$_3$), 32.16 (s, *C*(CH$_3$)$_3$), 32.07 (s, *C*(CH$_3$)$_3$), 29.96 (s, CC(*C*H$_3$)$_3$), 29.92 (s, 2 C(*C*H$_3$)$_3$ overlapped), 22.64 (s, *C*H$_2$CH$_3$), 12.96 (broad s, CH$_2$*C*H$_3$).

Anal. Calcd for $C_{45}H_{77}N_{12}Ta$: C, 55.89; H, 8.03; N, 17.38. Found: C, 55.91; H, 8.21; N, 17.22.

**Preparation of Bis(3,5-di-*tert*-butylpyrazolato)tris(3,5-dimethyl-1,2,4-triazolato)niobium(V) (8).** A 100-mL Schlenk flask was charged with trichlorobis(3,5-di-*tert*-butylpyrazolato)niobium(V) (0.30 g, 0.55 mmol), potassium 3,5-dimethyl-1,2,4-triazolate (0.29 g, 2.15 mmol), and tetrahydrofuran (50 mL). The mixture was stirred at room temperature for 48 h to give a red suspension. The volatile components were removed under reduced pressure, and the resultant solid was extracted with hexane (90 mL). The hexane extract was filtered through a 2-cm pad of Celite on a coarse glass frit. The red filtrate was concentrated to a volume of about 10 mL. Crystallization at −20 °C for 48 h afforded **8** as red blocks (0.24 g, 60%): dec pt 148 °C; IR (Nujol, cm$^{-1}$) 3081 (m), 1508 (vs), 1398 (vs), 1306 (s), 1286 (s), 1256 (w), 1238 (s), 1204 (w), 1143 (w), 1115 (w), 1103 (w), 1019 (m), 994 (m), 983 (m), 877 (w), 823 (m), 754 (m), 735 (m), 694 (w), 668 (w), 617 (s); $^1$H NMR (C$_6$D$_6$, 22 °C, $\delta$) 6.41 (broad s, 2 H, pyrazolato ring C*H*), 2.11 (broad s, 18 H, triazolato C*H$_3$*), 1.10 (s, 36 H, C(C*H$_3$*)$_3$); $^{13}$C{$^1$H} NMR (toluene-*d*$_8$, 80 °C, ppm) 158.82 (s, *C*C(CH$_3$)$_3$), 157.11 (s, triazolato *C*CH$_3$), 116.30 (s, pyrazolato ring *C*H), 32.22 (s, *C*(CH$_3$)$_3$), 29.68 (s, C(*C*H$_3$)$_3$), 12.91 (broad s, triazolato *C*H$_3$).

Anal. Calcd for $C_{34}H_{56}N_{13}Nb$: C, 55.20; H, 7.63; N, 24.61. Found: 55.11; H, 7.55; N, 24.60.

**Preparation of Bis(3,5-di-*tert*-butylpyrazolato)tris(3,5-dimethyl-1,2,4-triazolato)tantalum(V) (9).** In a fashion similar to the preparation of **8**, treatment of trichlorobis(3,5-di-*tert*-butylpyrazolato)tantalum(V) (0.60 g, 0.93 mmol) with potassium 3,5-dimethyl-1,2,4-triazolate (0.50 g, 3.72 mmol) in tetrahydrofuran (70 mL) afforded **9** as pale yellow crystals (0.31 g, 40%): dec pt 162−164 °C; IR (Nujol, cm$^{-1}$) 3085 (m), 1508 (s), 1399 (s), 1308 (m), 1292 (s), 1257 (m), 1238 (m), 1205 (w), 1108 (w), 1023 (w), 994 (m), 983 (w), 823 (w), 755 (m), 736 (w), 721 (m); $^1$H NMR (C$_6$D$_6$, 22 °C, $\delta$) 6.50 (s, 2 H, pyrazolato ring C*H*), 2.12 (broad s, 18 H, triazolato C*H$_3$*), 1.10 (s, 36 H, C(C*H$_3$*)$_3$); $^{13}$C{$^1$H} NMR (toluene-*d*$_8$, 80 °C, ppm) 158.62 (s, *C*C(CH$_3$)$_3$), 158.03 (s, triazolato *C*CH$_3$), 115.19 (s, pyrazolato ring *C*H), 32.20 (s, *C*(CH$_3$)$_3$), 29.68 (s, C(*C*H$_3$)$_3$), 12.91 (broad s, triazolato *C*H$_3$).

Anal. Calcd for $C_{34}H_{56}N_{13}Ta$: C, 49.33; H, 6.82; N, 21.99. Found: C, 48.36; H, 7.06; N, 21.29.

**Preparation of Tris(3,5-di-*tert*-butylpyrazolato)(5-phenyltetrazolato)titanium(IV) (10).** In a fashion similar to the preparation of **1**, treatment of chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.52 g, 0.84 mmol) with sodium 5-phenyltetrazolate (0.21 g, 1.2 mmol) in tetrahydrofuran (60 mL) afforded **10** as yellow crystals (0.45 g, 74%): mp 201 °C dec; IR (Nujol, cm$^{-1}$) 1559 (w), 1540 (w), 1508 (m), 1365 (s), 1256 (s), 1236 (m), 1205 (w), 1168 (w), 1073 (w), 1027 (m), 991 (w), 976 (w), 852 (w), 800 (s), 731 (m), 721 (w), 695 (m); $^1$H NMR (C$_6$D$_6$, 22 °C, $\delta$) 7.67 (m, 2 H, *ortho*-C*H* of Ph ring), 7.24 (m, 2 H, *meta*-C*H* of Ph ring), 7.10 (m, 1 H, *para*-C*H* of Ph ring), 6.52 (s, 3 H, pyrazolato ring C*H*), 1.16 (s, 54 H, C(C*H$_3$*)$_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$, 22 °C, ppm) 161.45 (s, *C*Ph), 159.23 (s, *C*C(CH$_3$)$_3$), 129.96 (s, ipso-*C* of Ph ring), 128.41 (s, *para*-*C*H of Ph ring), 128.36 (s, *meta*-*C*H of Ph ring), 126.86 (s, *ortho*-*C*H of Ph ring), 112.63 (s, pyrazolato ring *C*H), 32.15 (s, *C*(CH$_3$)$_3$), 30.06 (s, C(*C*H$_3$)$_3$).

Anal. Calcd for $C_{40}H_{62}N_{10}Ti$: C, 65.73; H, 8.55; N, 19.16. Found: C, 65.61; H, 8.57; N, 18.79.

**Preparation of Tris(3,5-di-*tert*-butylpyrazolato)bis(5-phenyltetrazolato)niobium(V) (11).** A 100-mL Schlenk flask was charged with dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) (0.52 g, 0.74 mmol), sodium 5-phenyltetrazolate (0.36 g, 2.14 mmol), and tetrahydrofuran (70 mL). After being stirred at ambient temperature for 2 h, the reaction mixture was refluxed for 40 h. The volatile components were removed under reduced pressure, and the resultant yellow solid was extracted with toluene (50 mL). Filtration of the toluene extract through a 2-cm pad of Celite on a coarse glass frit gave a yellow solution. Removal of the toluene under reduced pressure afforded **11** as a yellow solid (0.40 g, 59%). An analytical sample was obtained by recrystallization from hexane at −20 °C: dec pt 216 °C; IR (Nujol, cm$^{-1}$) 1522 (m), 1507 (m), 1257 (m), 1232 (m), 1165 (w), 1068 (w), 1026 (s), 962 (m), 800 (m), 731 (s), 693 (m); $^1$H NMR (C$_6$D$_6$, 22 °C, $\delta$) 8.38 (m, 4 H, *ortho*-C*H* of Ph ring), 7.17 (m, 4 H, *meta*-C*H* of Ph ring), 7.04 (m, 2 H, *para*-C*H* of Ph ring), 6.85 (s, 3 H, pyrazolato ring C*H*), 1.08 (s, 54 H, C(C*H$_3$*)$_3$); $^{13}$C{$^1$H} (C$_6$D$_6$, 22 °C, ppm) 163.17 (s, *C*Ph), 159.20 (s, *C*C(CH$_3$)$_3$), 130.63 (s, ipso-*C* of Ph ring), 128.85 (s, *meta*-*C*H of Ph ring), 128.29 (s, *para*-*C*H of Ph ring), 126.78 (s, *ortho*-*C*H of Ph ring), 119.53 (s, pyrazolato ring *C*H), 32.35 (s, *C*(CH$_3$)$_3$), 30.07 (s, C(*C*H$_3$)$_3$).

Anal. Calcd for $C_{47}H_{67}N_{14}Nb$: C, 61.29; H, 7.33; N, 21.29. Found: C, 61.30; H, 7.37; N, 21.28.

**Preparation of Chlorotris(3,5-di-*tert*-butylpyrazolato)(5-phenyltetrazolato)tantalum(V) (12).** In a fashion similar to the preparation of **11**, treatment of dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V) (0.60 g, 0.76 mmol) with sodium 5-phenyltetrazolate (0.38 g, 2.26 mmol) in tetrahydrofuran (70 mL) afforded **12** as pale-yellow crystals (0.43 g, 60%) after crystallization from hexane at −20 °C: dec pt 196 °C; IR (Nujol, cm$^{-1}$) 1524 (s), 1485 (m), 1365 (s), 1283 (w), 1256 (s), 1235 (s), 1201 (w), 1173 (w), 1126 (w), 1075 (w), 1035 (m), 1001 (w), 973 (s), 842 (w), 822 (m), 815 (m), 732 (m), 722 (w), 694 (m); $^1$H NMR (C$_6$D$_6$, 22 °C, $\delta$) 8.35 (m, 2 H, *ortho*-C*H* of Ph ring), 7.17 (m, 2 H, *meta*-C*H* of Ph ring), 7.02 (m, 1 H, *para*-C*H* of Ph ring), 6.88 (s, 3 H, pyrazolato C*H*), 1.20 (s, 54 H, C(C*H$_3$*)$_3$; $^{13}$C{$^1$H} (C$_6$D$_6$, 22 °C, ppm) 163.55 (s, *C*Ph), 158.12 (s, *C*C(CH$_3$)$_3$), 130.92 (s, ipso-*C* of Ph ring), 128.80 (s, *meta*-*C*H of Ph ring), 128.67 (s, *para*-*C*H of Ph ring), 126.64 (s, *ortho*-*C*H of Ph ring), 116.77 (s, pyrazolato ring *C*H), 32.31 (s, *C*(CH$_3$)$_3$), 30.37 (s, C(*C*H$_3$)$_3$).

Anal. Calcd for $C_{40}H_{62}ClN_{10}Ta$: C, 53.42; H, 6.95; N, 15.57. Found: C, 53.52; H, 6.88; N, 15.54.

**Kinetics Measurements on 4.** A 5-mm NMR tube was charged with **4** (0.015 g, 0.018 mmol) and toluene-*d*$_8$ (0.80 mL) and was fitted with a rubber septum. The tube was transferred to the NMR probe, and the $^1$H NMR spectra were recorded between −50 and 67 °C. At −50 °C the 3,5-dimethyl-1,2,4-triazolato methyl resonances were observed at $\delta$ 2.34 and 1.63. Upon warming, the methyl resonances became broad and coalesced into one peak at 20 °C to give a broad peak at $\delta$ 1.86. At 67 °C, the 3,5-dimethyl-1,2,4-triazolato methyl resonances were observed as a single peak at $\delta$ 1.82. The dynamic process was modeled as an AB exchange using the program gNMR.[94] The same coalescence temperatures were observed in a sample of **4** (0.008 g, 0.010 mmol) in toluene-*d*$_8$ (0.80 mL) that was about half as concentrated, suggesting that the observed kinetic event was intramolecular. For further data, see the Supporting Information. Errors in kinetic data are reported at the 95% confidence level.

**Kinetics Measurements on 6.** A 5-mm NMR tube was charged with **6** (0.015 g, 0.016 mmol) and toluene-*d*$_8$ (0.80 mL) and was fitted with a rubber septum. The tube was transferred to the NMR probe, and the $^1$H NMR spectra were recorded between −60 and 70 °C. At −60 °C the 3,5-dimethyl-1,2,4-triazolato methyl resonances were observed at $\delta$ 2.40 and 1.65. Upon warming, the methyl resonances became broad and coalesced into one peak at 38 °C to give a broad peak at $\delta$ 1.84. At 70 °C, the 3,5-dimethyl-1,2,4-triazolato methyl resonance was observed as a single peak at $\delta$ 1.84. The dynamic process was modeled as an AB exchange using the program gNMR.[94] The same coalescence temperature was observed in a sample of **6** (0.008 g, 0.008 mmol) in toluene-$d_8$ (0.80 mL) that was about half as concentrated. For further data, see the Supporting Information. Errors in kinetic data are reported at the 95% confidence level

**Molecular Orbital Calculations.** Electronic structure calculations were carried out with the GAUSSIAN 98[110] series of programs using the B3LYP density functional method[111−113] and the 6-311G(d) basis set[114−116] (for titanium, this corresponds to the Wachters−Hay basis set[117,118] augmented with an f-type Gaussian shell with an exponent of 0.690). Equilibrium geometries were optimized using redundant internal coordinates. Charge distributions were obtained by Mulliken population analysis.

**Crystallographic Determinations.** Crystalline samples were mounted in sealed thin walled capillary tubes under a nitrogen atmosphere for X-ray data collection. All crystal structures were collected at room temperature on a Bruker P4/CCD diffractometer equipped with Mo radiation. For each collection, frames were collected at 10 s/frame with 0.3° between each frame. The frame data was integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program, and the structure was solved and refined using the programs of SHELX-97. Hydrogen atoms were placed in calculated positions. All molecules crystallized as neutral compounds with no associated ions or solvent. Complex **1** crystallized as irregular yellow fragments. 1390 frames yielded 52110 reflections, which averaged into 11478 unique data points. The asymmetric unit contains 1.5 molecules; the half molecule occupies a crystallographic 2-fold axis. Complex **2** crystallized as yellow rods. 1650 frames yielded 30 245 reflections, which averaged into 10 060 unique reflections. Three *tert*-butyl groups were badly disordered and their best representation involved partial occupancy positions and isotropic refinement. The asymmetric unit contains one general molecule. Complex **4** crystallized as orange multifaceted crystals with 24 787 reflections measured on 1390 frames. The molecule occupies a crystallographic 2-fold axis. Complex **11** crystallized as orange rhomboids with 1470 frames of data yielding 16 587 integrated intensities. The complex displays typical disorder in the position of the *tert*-butyl groups; one of them is described in 0.5 occupancy positions and isotropic.

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**Supporting Information Available:** Figures and tables presenting kinetic data for **4** and **6,** tables of Cartesian coordinates for **15−17, and** X-ray crystallographic files for **1**−**4**, **10**, and **11**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(110) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(111) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(112) Lee, C.; Yang, W.; Parr, R. D. *Phys. Rev. B* **1988**, *37*, 785.

(113) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(114) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(115) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(116) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(117) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

(118) Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, *91*, 1062.