Insertion and Coordination Reactions of Titanium(IV) Metallocene Zwitterions

Gregory S. Hair, Richard A. Jones,* Alan H. Cowley,* and Vincent Lynch

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

Received March 16, 2000

Reaction of the titanium borate zwitterion complex (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$) (**1**) with carbon monoxide results in the formation of the novel titanium−acyl borate complex (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_3(CH)_3CH_2COB(C_6F_5)_3$) (**2**). Addition of 1 equiv of PMe_3 to **1** results in the loss of $B(C_6F_5)_3$ to give (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(1,3-pentadiene) and $Me_3P\cdot B(C_6F_5)_3$. Addition of $(CH_3)_3CN{\equiv}C$ to **1** results in the formation of the isocyanide adduct (η^5-$C_5Me_4SiMe_2N^tBu$)Ti($CNC(CH_3)_3$)(η^3-$C_5H_8B(C_6F_5)_3$) (**3**). The X-ray crystal structures of **2** and **3** were determined.

Introduction

Intermediate π-complexes play an important role in the mechanism of olefin polymerization by Ziegler−Natta catalysts. In many cases, relatively stable complexes with CO, isocyanide, or phosphine ligands have been isolated that provide insight into the nature of the coordination of the olefin to the catalytically active center.

Recently, several examples of d^0 metal−carbonyl complexes have been isolated. In 1992, Jordan et al.[1] reported the first stable d^0 metal−carbonyl complex, $[Cp_2Zr(CO)(\eta^2\text{-}C,N\text{-}CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})]^+$, by treatment of $[Cp_2Zr(\eta^2\text{-}C,N\text{-}CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})]^+$ with CO. In 1994, Stryker et al.[2] treated $[Cp^*_2Zr(\eta^3\text{-}C_3H_5)]^+$ with CO at room temperature to yield the d^0 Zr−CO complex $[Cp^*_2Zr(\eta^3\text{-}C_3H_5)(CO)]^+$. Jordan et al.[3] also reported the reaction of $Cp^*_2Zr(CH_3)(\mu\text{-}CH_3)B(C_6F_5)_3$ with CO at room temperature to form an η^2-acyl carbonyl complex, $[Cp^*_2Zr(CO)(\eta^2\text{-}COCH_3)]^+$. In addition, in 1995, Erker et al.[4] reported the isolation of $Cp_2Hf(CO)(\eta^3\text{-}C_4H_6)B(C_6F_5)_3$, the first zwitterionic d^0 metallocene carbonyl complex from the reaction of $Cp_2Hf(\eta^3\text{-}C_4H_6)B(C_6F_5)_3$ with CO.

The isocyanide ligand is similar to CO but undergoes migratory insertions more readily.[5] Bochmann et al.[6] have prepared several isocyanide compounds of Ti(IV) by treatment of cationic alkyl bis(cyclopentadienyl)titanium complexes with isocyanides. In 1986, Takaya et al.[7] isolated a mixed titanium−rhenium complex that featured an isocyanide ligand coordinated to a d^0 Ti center. Also, recently Jordan's group[3] have prepared an iminoacyl isocyanide complex of Zr(IV) via the reaction of $Cp_2Zr(CH_3)(THF)^+$ with *tert*-butyl isocyanide.

Recently, considerable interest has been shown in the use of zwitterionic metallocene compounds for use as Ziegler−Natta catalysts. We recently described the preparation of a titanium borate zwitterion[8] and describe here the insertion and coordination reactions of CO and *tert*-butyl isocyanide with this complex. Of related interest is the alkyl cation chemistry of monocyclopentadienyl-bridged titanium complexes recently described by Okuda[9] and Marks.[10]

Results and Discussion

Synthesis and Structure of (2). The reaction of the titanium borate zwitterion (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$) (**1**)[8] with 40 psi of CO in toluene at room temperature results in the uptake of one molecule of CO (on the basis of elemental analysis) and the formation of a new complex (**2**). The $^{13}C\{^1H\}$ NMR spectrum of **2** exhibited a chemical shift of δ 140.87 ppm for the carbonyl carbon atom. By comparison, Zr(IV) carbonyl compounds exhibit CO chemical shifts above ~200 ppm for the terminal carbonyl group.[11] For η^2-acyl compounds of Ti(IV) and Zr(IV), the acyl carbon is observed at low field (~300 ppm).[12]

The IR spectrum was investigated to help elucidate the structure of **2**. A ν_{CO} band for **2** appears at 1546 cm^{-1}. This is considerably lower in energy than that expected for a Ti(IV) terminal carbonyl (Zr(IV) ≈ 2100 cm^{-1}, Hf(IV) ≈ 2000−2050 cm^{-1}, free CO = 2143 cm^{-1}).[13] However, it is in the range expected for an η^2-acyl compound (1554−1630 cm^{-1}).[14] The IR data there-

---

[1] Guram, A. S.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1992**, *114*, 8991.

[2] Antonelli, D. M.; Tjaden, E. B.; Stryker, J. M. *Organometallics* **1994**, *13*, 763.

[3] Guo, Z.; Swenson, D. C.; Guram, A. S.; Jordan, R. F. *Organometallics* **1994**, *13*, 766.

[4] Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755.

[5] See for example: Collman, J. P.; Hegedus; L. S. Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed., 1987; p 377.

[6] (a) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Montevalli, M. *Organometallics* **1988**, *7*, 1148.

[7] Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *Organometallics* **1987**, *6*, 885.

[8] Cowley, A. H.; Hair, G. S.; McBurnett, B. G.; Jones, R. A. *Chem. Comm.* **1999**, 437.

[9] Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836.

[10] Chen, X.-Y.; Marks, T. J. *Organometallics* **1997**, *16*, 3649.

[11] For example: ($[Cp_2Zr(CO)(\eta^2\text{-}C,N\text{-}CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})]^+$) δ 206.1 ppm, (ref 1); ($[Cp^*_2Zr(\eta^3\text{-}C_3H_5)(CO)]^+$) δ 218.7 ppm, (ref 2); ($[Cp^*_2Zr(CO)(\eta^2\text{-}COCH_3)]^+$) δ 204.5 ppm, (ref 3); and ($[Cp_3Zr(CO)]^+$) δ 206.9 ppm, (ref 21).

[12] See for example: ($[Cp^*_2Zr(CO)(\eta^2\text{-}COCH_3)]^+$) δ 299.0, (ref 3); ($Cp^*TiCl_2(\eta^2\text{-}COCH_3)$) δ 306.6, (ref 15); and ($[Cp_2Ti(\eta^2\text{-}CO^iPr)]^+$) δ 301.4 ppm, (ref 16).

10.1021/om0002327 CCC: $20.00
Publication on Web 12/06/2000

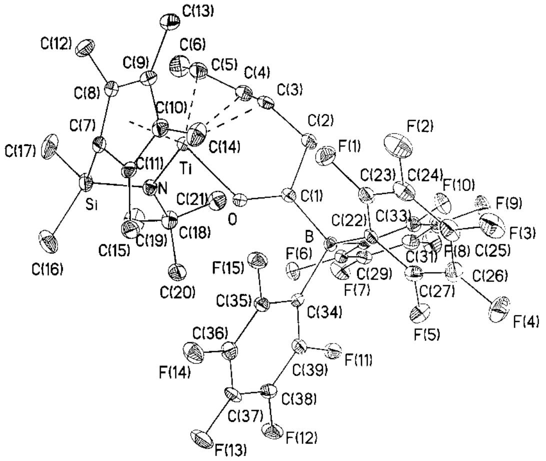


Figure 1. Molecular structure and atom-numbering scheme for (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_3(CH)_3CH_2COB(C_6F_5)_3$) (**2**). The thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms have been omitted for clarity.

fore eliminate the possibility of a simple, terminal Ti(IV) carbonyl structure for **2**. In addition, monitoring of reaction solutions via IR or by low-temperature NMR spectroscopy failed to show evidence of a labile CO adduct. Since IR and NMR data appear contradictory, an X-ray crystallographic study of **2** was undertaken.

Table 1. Crystal Data and Structure Refinement for 2 and 3

	2	3
empirical formula	$C_{39}H_{35}BF_{15}NOSiTi$	$C_{43}H_{44}BF_{15}N_2SiTi$
fw	905.48	960.60
temp	193(2) K	198(2) K
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
unit cell dimens		
a	10.6936(13) Å	10.999(1) Å
b	14.4516(11) Å	21.845(3) Å
c	24.998(2) Å	18.440(2) Å
α	90°	90°
β	94.266(8)°	92.47(1)°
γ	90°	90°
volume	3852.4(6) Å^3	4426.5(9) Å^3
Z	4	4
density (calcd)	1.561 Mg/m^3	1.44 Mg/m^3
abs coeff	0.360 mm^{-1}	0.32 mm^{-1}
F(000)	1840	1968
θ range for data collection	1.63−27.50°	2.1−25.0°
no. of reflns collected	11 064	9048
no. of ind reflns	8843 [*R*(int) = 0.0585]	7231 [*R*(int) = 0.066]
abs corr	none	Gaussian
no. of data/restraints/params	8839/0/532	7227/0/589
goodness-of-fit on F^2	1.013	1.025
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0718, wR2 = 0.1276	R1 = 0.0784, wR2 = 0.116
R indices (all data)	R1 = 0.1738, wR2 = 0.1771	R1 = 0.208, wR2 = 0.160
largest diff peak and hole	0.440 and −0.470 e Å^{-3}	0.31 and −0.30 e Å^{-3}

Table 2. Selected Bond Lengths (Å) for 2

Ti−N	1.938(4)	N−C(18)	1.495(6)
Ti−O	2.121(3)	C(28)−B	1.650(7)
Ti−C(4)	2.340(5)	C(34)−B	1.650(7)
Ti−C(3)	2.375(5)	C(1)−C(2)	1.525(6)
Ti−C(5)	2.383(5)	C(1)−B	1.645(7)
Si−N	1.747(4)	C(3)−C(4)	1.389(7)
Si−C(17)	1.858(6)	C(3)−C(2)	1.489(7)
Si−C(7)	1.861(5)	C(22)−B	1.640(7)
Si−C(16)	1.865(6)	C(4)−C(5)	1.365(7)
O−C(1)	1.246(5)	C(5)−C(6)	1.487(8)

Table 3. Selected Bond Angles (deg) for 2

N−Ti−O	98.3(2)	Si−N−Ti	102.4(2)
N−Ti−C(4)	111.4(2)	O−C(1)−C(2)	115.2(4)
O−Ti−C(4)	94.2(2)	O−C(1)−B	124.6(4)
N−Ti−C(3)	137.5(2)	C(2)−C(1)−B	119.7(4)
O−Ti−C(3)	70.6(2)	C(4)−C(3)−C(2)	121.1(5)
C(4)−Ti−C(3)	34.2(2)	C(4)−C(3)−Ti	71.5(3)
N−Ti−C(5)	101.3(2)	C(2)−C(3)−Ti	111.8(3)
O−Ti−C(5)	127.8(2)	C(5)−C(4)−C(3)	126.6(6)
C(4)−Ti−C(5)	336(2)	C(5)−C(4)−Ti	74.9(3)
C(3)−Ti−C(5)	62.3(2)	C(3)−C(4)−Ti	74.3(3)
N−Si−C(17)	113.7(3)	C(22)−B−C(1)	113.9(4)
N−Si−C(7)	92.2(2)	C(22)−B−C(28)	110.6(4)
C(17)−Si−C(7)	114.8(3)	C(1)−B−C(28)	102.2(4)
N−Si−C(16)	118.9(3)	C(22)−B−C(34)	105.3(4)
C(17)−Si−C(16)	105.8(3)	C(1)−B−C(34)	109.6(4)
C(7)−Si−C(16)	111.4(3)	C(28)−B−C(34)	115.5(4)
N−Si−Ti	41.17(14)	C(3)−C(2)−C(1)	110.5(4)
C(1)−O−Ti	128.9(3)	C(4)−C(5)−C(6)	123.1(6)
C(18)−N−Si	124.8(3)	C(4)−C(5)−Ti	71.5(3)
C(18)−N−Ti	132.5(3)	C(6)−C(5)−Ti	124.4(4)

X-ray Crystal Structure of 2. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell; the molecular geometry is shown in Figure 1. The crystal data are shown in Table 1, and selected bond lengths and angles are presented in Tables 2 and 3, respectively. The hydrogen atoms of the allyl group (C(2)−C(6)) were located and refined. Instead of a d^0 titanium carbonyl compound or a η^2-acyl titanium compound, **2** is, in fact, a titanium−η^2-acyl borate. The C=O unit is bound through the oxygen atom with a formal dative bond to the titanium center. The Ti−O bond length is 2.123(3) Å which is similar to those observed for other titanium compounds featuring Ti−O=C bonds (av = 2.114 Å).[18] The Ti−O−C(1) bond angle is 128.9(3)°, indicating little or no Ti−O π interaction. The C=O bond length is 1.246(5) Å (C=O = 1.21 Å av),[19] which rules out any possibility of a titanium enolate complex, as does the observed C(1)−C(2) bond length of 1.525(6) Å (typical C(sp^2)−C(sp^3) = 1.51 Å).[19] The slightly longer Ti−O, C=O, and C(1)−C(2) bond lengths can most likely be attributed to the presence of the $B(C_6F_5)_3$ group. The remaining structural features of **2** are very similar to those found in the starting material (**1**), except for the lack of agostic H interactions with the titanium atom.[8] The overall reaction for the formation of **2** is shown in Scheme 1. Although the precise mechanistic details of the formation of **2** are not clear, the isolation of an isocyanide adduct of **1,** compound **3**,

---

(13) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.

(14) The ν_{CO} band for η^2-acyls has been observed at 1554 (Cp*TiCl$_2$-(η^2-COCH$_3$)),[15] 1613 ([Cp$_2$Ti(η^2-CO^{i}Pr)]$^+$),[16] 1580 (Cp$_2$Ti(η^2-COPh)Cl),[17] 1620 (Cp$_2$Ti(η^2-COCH$_3$)Cl),[17] 1630 (Cp$_2$Ti(η^2-COCH$_3$)(N≡CCH$_3$)),[6a] and 1576 cm^{-1} (Cp*$_2$Zr(CO) (η^2-COCH$_3$))[3].

(15) Martin, A.; Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2117.

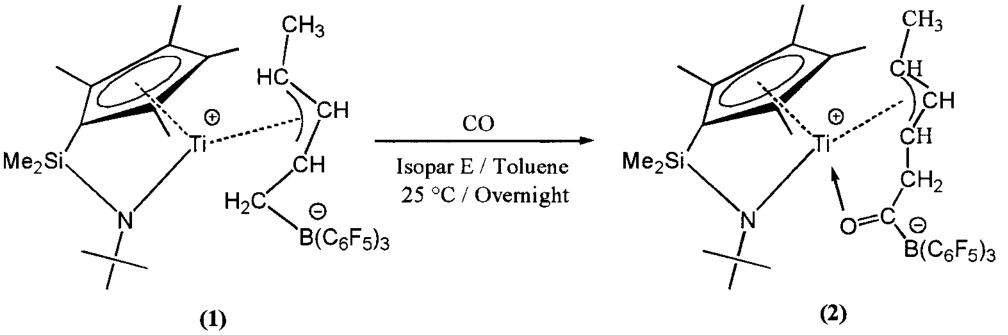
(16) Pankowski, M.; Cabestaing, C.; Jaouen, G. *J. Organomet. Chem.* **1996**, *516*, 11.

(17) Fachinetti, G.; Floriani, C.; Evans, H. S. *J. Chem. Soc., Dalton Trans.* **1977**, 2297.

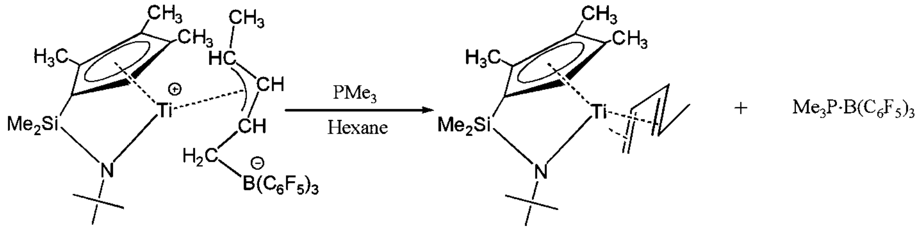
(18) Cozzi, P. G.; Solari, E.; Floriani, C.; Villa, A. C.; Rizzoli, C. *Chem. Ber.* **1986**, *129*, 1361. Maier, G.; Seipp, U.; Boese, R. *Tetrahedron Lett.* **1987**, *28*, 4515. Bachand, B.; Gariépy, F. B.; Wuest, J. D. *Organometallics* **1990**, *9*, 2860. Utko, J.; Sobota, P.; Lis, T. *J. Organomet. Chem.* **1987**, *334*, 341.

(19) Giacovazzo, C.; Monaco, H. L.; Viterbo, D.; Scordari, F.; Gilli, G.; Zanotti, G.; Catti, M. *Fundamentals of Crystallography*; Oxford University Press: New York, 1994; p 503.

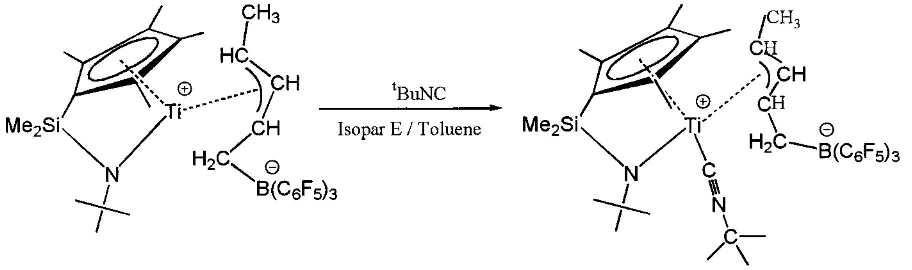
Scheme 1. Synthesis of (η^5C$_5$Me$_4$SiMe$_2$N^{t}Bu)Ti(η-CH$_3$(CH)$_3$CH$_2$COB(C$_6$F$_5$)) (2).



Scheme 2. Reaction of PMe$_3$ with 1



Scheme 3. Synthesis of (η^5C$_5$Me$_4$SiMe$_2$N^{t}Bu)-Ti(CNC(CH$_3$)$_3$)(η^3-C$_5$H$_8$B(C$_6$F$_5$)$_3$) (3).



described below suggests that the formation of **2** proceeds through an intermediate terminal carbonyl complex. The unstable compound reacts readily, eventually giving the observed structure, possibly through an acyl intermediate.

Reaction of 1 with PMe$_3$. The addition of PMe$_3$ to a hexane solution of **1** resulted in the formation of a dark red crystalline compound, as well as the adduct Me$_3$P·B(C$_6$F$_5$)$_3$. Analysis of the red complex showed it to be the diene complex (η^5-C$_5$Me$_4$SiMe$_2$N^{t}Bu)Ti(1,3-pentadiene). In this case, the addition of PMe$_3$ resulted in cleavage of the boron−carbon bond of **1** and formation of the adduct Me$_3$P·B(C$_6$F$_5$)$_3$ (Scheme 2). The spectroscopic data for the product are in agreement with published data[20] for (η^5-C$_5$Me$_4$SiMe$_2$N^{t}Bu)Ti(1,3-pentadiene). This observation suggests that the boron−C(1) bond of **1** can be cleaved under suitable reaction conditions. The reaction of **2** with PMe$_3$ in order to form a vinyl ketene complex was also investigated; however we were unable to isolate any tractable products.

Synthesis of (η^5-C$_5$Me$_4$SiMe$_2$N^{t}Bu)Ti(CNC(CH$_3$)$_3$)(η^3-C$_5$H$_8$B(C$_6$F$_5$)$_3$) (3). Since PMe$_3$ does not form an adduct with **1**, an alternative Lewis base was tested. The addition of one or more equivalents of *tert*-butyl isocyanide to a toluene solution of **1** resulted in the immediate formation of a dark green precipitate. Recrystallization of this precipitate from dichloromethane resulted in dark green, air-stable crystals of **3** (Scheme 3). The IR spectrum of **3** revealed a strong band at 2191 cm^{-1}, which was assigned to the C≡N stretching vibration. The $\nu_{C\equiv N}$ for the free *tert*-butyl isocyanide ligand occurs at 2125 cm^{-1}. Such a shift to a higher wavenumber is expected for a d^0 metal−isocyanide complex where there is no π back-bonding from the metal to the ligand. The IR spectrum of **3** also ruled out the possibility of isocyanide insertion into a titanium−carbon bond to form an iminoacyl complex (C=N). Most metal−iminoacyl bands are found in the 1550−1750 cm^{-1} range. No bands were found in the IR spectrum of **3** in this range that were not present in the starting material, **1**. ^{1}H NMR analysis of the product was consistent with the formation of an isocyanide adduct of **1**. The ^{13}C{^{1}H} NMR spectrum exhibited a resonance at δ 159.4 which was assigned to the *C*N^{t}Bu carbon atom. This chemical shift is consistent with the formation of an isocyanide adduct of **1**, as opposed to an iminoacyl compound, which would be expected to exhibit a ^{13}C NMR resonance in the range δ 200−250.[1,3] In the case of [Cp$_3$Zr(CN^{t}Bu)]$^+$ [21] the *C*N^{t}Bu carbon atom was observed at δ 145.4 ppm. To confirm the structure, an X-ray diffraction study was undertaken.

X-ray Crystal Structure of 3. Compound **3** crystallizes in the monoclinic space group *P*2$_1$/*c* with four molecules per unit cell; the molecular geometry and atom numbering scheme are shown in Figure 2. The

---

[20] Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132.

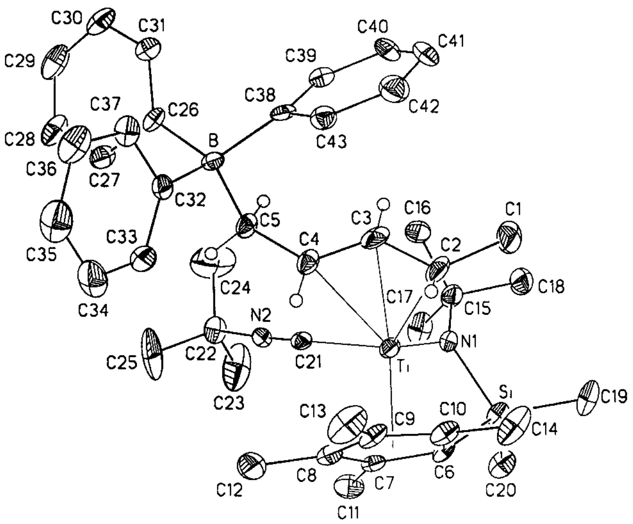


Figure 2. Molecular structure and atom-numbering scheme for $(\eta^5\text{-}C_5Me_4SiMe_2N^tBu)Ti(CNC(CH_3)_3)(\eta^3\text{-}C_5H_8B(C_6F_5)_3)$ (**3**). The F atoms and most hydrogen atoms have been omitted for clarity. The thermal ellipsoids are scaled to the 30% probability level.

Table 4. Selected Bond Lengths (Å) for 3

Ti−N(1)	1.914(6)	N(2)−C(21)	1.146(7)
Ti−C(21)	2.165(7)	N(2)−C(22)	1.447(8)
Ti−C(2)	2.279(8)	B−C(38)	1.631(10)
Ti−C(3)	2.343(7)	B−C(32)	1.649(10)
Ti−C(4)	2.522(7)	B−C(26)	1.662(9)
Si−N(1)	1.756(5)	B−C(5)	1.673(10)
Si−C(20)	1.845(7)	C(1)−C(2)	1.491(11)
Si−C(19)	1.851(7)	C(2)−C(3)	1.412(10)
Si−C(6)	1.870(7)	C(3)−C(4)	1.358(10)
N(1)−C(15)	1.503(8)	C(4)−C(5)	1.478(9)

Table 5. Selected Bond Angles (deg) for 3

N(1)−Ti−C(21)	94.0(2)	C(26)−B−C(5)	107.5(5)
N(1)−Ti−C(2)	102.9(3)	C(3)−C(2)−C(1)	121.8(9)
C(21)−Ti−C(2)	131.0(3)	C(3)−C(2)−Ti	74.7(4)
N(1)−Ti−C(3)	110.8(3)	C(1)−C(2)−Ti	122.8(6)
C(21)−Ti−C(3)	95.4(3)	C(4)−C(3)−C(2)	126.2(9)
C(2)−Ti−C(3)	35.5(2)	C(4)−C(3)−Ti	81.2(5)
N(1)−Ti−C(4)	134.3(2)	C(2)−C(3)−Ti	69.7(4)
C(21)−Ti−C(4)	73.5(2)	C(3)−C(4)−C(5)	123.9(8)
C(2)−Ti−C(4)	61.7(3)	C(3)−C(4)−Ti	66.6(4)
C(3)−Ti−C(4)	32.2(2)	C(5)−C(4)−Ti	131.5(5)
N(1)−Si−C(20)	117.0(3)	C(4)−C(5)−B	113.1(6)
N(1)−Si−C(19)	113.8(3)	N(2)−C(21)−Ti	172.5(6)
C(20)−Si−C(19)	104.8(4)		
N(1)−Si−C(6)	92.7(3)		
C(15)−N(1)−Si	124.7(4)		
C(15)−N(1)−Ti	133.7(4)		
Si−N(1)−Ti	101.4(2)		
C(21)−N(2)−C(22)	177.4(7)		
C(38)−B−C(32)	112.8(5)		
C(38)−B−C(26)	115.4(5)		
C(32)−B−C(26)	101.7(6)		
C(38)−B−C(5)	103.8(6)		
C(32)−B−C(5)	115.9(6)		

crystal data are presented in Table 1, and selected bond lengths and angles are listed in Tables 4 and 5, respectively. The hydrogen atoms on the allyl group (C(2)−C(5)) were located and refined. The *tert*-butyl isocyanide ligand is coordinated directly to the titanium atom and does not undergo an insertion reaction. The reason for this may be steric in nature. The Ti−C bond length for the coordinated isocyanide ligand is 2.165(7) Å, which may be compared with those of the similar isocyanide compounds $[Cp_2Ti\{\eta^2\text{-}C(N^tBu)Me\}(CN^tBu)]^+$ (Ti−C = 2.192(6) Å)[6a] and $Cp^*_2Ti\{\eta^2\text{-}C(N^tBu)CH_2CH_2CORe_2(CO)_9\}(CN^tBu)$ (Ti−C = 2.17(2) Å).[7] The isocyanide ligand is bonded to the titanium atom in an almost linear geometry with a Ti−C−N bond angle of 172.5(6)°, which is similar to that in $[Cp_2Ti\{\eta^2\text{-}C(N^tBu)Me\}(CN^tBu)]^+$ (Ti−C−N = 174.4(3)°).[6a] The C≡N distance of 1.146(7) Å is typical of those reported for coordinated isocyanides (C≡N = 1.16 Å av).[6]

Experimental Section

General Synthetic Considerations. All reactions were performed under a dry, oxygen-free nitrogen atmosphere or under vacuum using standard Schlenk line and drybox techniques, unless otherwise indicated. All solvents were dried prior to use by distillation from molten sodium or sodium benzophenone ketyl under nitrogen. The diene $\eta^5\text{-}C_5Me_4SiMe_2N^tBu)Ti(1,3\text{-pentadiene})$ and $B(C_6F_5)_3$ were prepared by standard literature methods.[8,22] All other reagents were purchased from commercial suppliers and used without further purification.

NMR measurements were performed at room temperature on either a Varian Inova-500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) or a General Electric QE300 (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{11}B, 96 MHz; ^{19}F, 282 MHz) spectrometer. Chemical shifts are reported in ppm with positive values corresponding to downfield shifts from the standard. Chemical shifts are reported relative to tetramethylsilane (TMS, δ = 0.00) and are referenced to the residual protons of C_6D_6 (^{1}H, δ = 7.15, ^{13}C, δ = 128.0) or CD_2Cl_2 (^{1}H, δ = 5.32; ^{13}C, δ = 54.0).

IR measurements were performed with a Digilab FTS-40 spectrometer as Nujol mulls with KBr plates. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. High- and low-resolution mass spectra were obtained with a VG Analytical ZAB2-E mass spectrometer in chemical ionization mode with CH_4 as the ionizing gas.

Synthesis of $(\eta^5\text{-}C_5Me_4SiMe_2N^tBu)Ti(\eta^3\text{-}CH_3(CH)_3CH_2C(O)B(C_6F_5)_3)$ (2). A solution of $B(C_6F_5)_3$ (45.75 mL, 2.68 mmol, 3% solution in Isopar E) was added to a solution of $(\eta^5\text{-}C_5Me_4SiMe_2N^tBu)Ti(1,3\text{-pentadiene})$ (10.0 g, 2.68 mmol, 9.8% solution in Isopar E) in a Fischer−Porter bottle, along with 30 mL of toluene. With stirring, the bottle was first evacuated briefly, then pressurized to 40 psi with carbon monoxide. The solution was allowed to stir overnight, then excess carbon monoxide was vented. The solution was concentrated 50% and stored for 3 days at −30 °C, resulting in the formation of dark green crystals of **2** (1.29 g 53.2% yield), mp 165−166 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 0.10 (s, SiCH_3, 3H), 0.35 (s, SiCH_3, 3H), 0.90 (s, N^{t}Bu, 9H), 1.33 (s, CpCH_3, 3H), 1.38 (s, CpCH_3, 3H), 1.59 (s, CpCH_3, 3H), 1.74 (s, CpCH_3, 3H), 2.20 (s, CH_3-diene, 3H), 2.89 (br s, CH-diene, 1H), 3.00 (br s, CH-diene, 1H), 3.11 (br s, CH_2-diene, 1H), 3.65 (d, CH_2-diene, 1H, ^3J = 16.3 Hz), 5.25 (br s, CH-diene, 1H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 4.70 (s, SiCH_3), 5.46 (s, SiCH_3), 10.94 (s, CpCH_3), 11.99 (s, CpCH_3), 14.44 (s, CH_3-diene), 14.77 (s, CpCH_3), 20.00 (s, CpCH_3), 33.12 (s, CH_3-^{t}Bu), 52.93 (s, CH_2-diene), 63.72 (s, C-^{t}Bu), 87.86 (s, CH-diene), 109.43 (s, CH-diene + C(Cp)), 131.38 (s, CMe(Cp)), 132.32 (s, CMe(Cp)), 134.00 (s, CMe(Cp)), 136.53 (m, C_6F_5), 138.49 (m, C_6F_5), 138.88 (s, CMe(Cp)), 140.87 (s, CO), 147.48 (m, C_6F_5), 149.38 (m, C_6F_5), 151.20 (s, CH-diene). ^{19}F NMR (282 MHz, C_6D_6): δ −123.9 (m, *o*-F, 6F), −154.6 (m, *p*-F, 3F), −159.1 (m, *m*-F, F), −160.5 (m, *m*-F, F). ^{11}B NMR (96.3 MHz, C_6D_6): δ − 10.6. IR (cm^{-1}, Nujol): 2934 (s), 2857 (s), 1645 (m), 1546(m), 1515 (s), 1465 (s), 1377 (s), 1316 (w), 1283 (m), 1256 (m), 1231 (w), 1217 (w), 1184 (m),

---

(21) Brackemeyer, T.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 531.

(22) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc., London* **1963**, 212. Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

1094 (s), 1060 (m), 1032 (m), 979 (s), 850 (m), 812 (w), 774 (w), 756 (s), 728 (w), 707 (w), 684 (m), 660 (w), 634 (w), 611 (w), 575 (w), 504 (m), 484 (w), 454 (w). Anal. Found: C, 51.85; H, 3.94; N, 1.59. Calcd: C, 51.71; H, 3.90; N, 1.54. MS-CI (CH_4): *m/z* 905 [M^+]. HRMS (CI) for $C_{39}H_{35}BF_{15}NOSiTi$: *m/z* (calcd) 905.1820; *m/z* (obsd) 905.1815.

Synthesis of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(CNC(CH_3)$_3$)(C_5H_8B-(C_6F_5)$_3$) (3). To a stirred 25 °C toluene solution of (η^5-C_5Me_4-$SiMe_2N^tBu$)Ti(η^3-$C_5H_8B(C_6F_5)_3$) (0.53 g, 0.60 mmol) was added 2 equiv of *tert*-butyl isocyanide (0.13 mL, 1.20 mmol) via syringe. Using an excess of isocyanide produces the same product. A dark green precipitate formed immediately upon addition of the isocyanide. The mixture was allowed to stir for 1 h, and then the supernatant was decanted. The green precipitate was washed with hexane and dried in vacuo. The precipitate was dissolved in dichloromethane (15 mL), filtered, and stored overnight at −30 °C. The supernatant was decanted from the resulting dark green needles which formed (0.42 g, 73.1% yield), mp 159−160 °C. ^1H NMR (500 MHz, C_6D_6): δ 0.08 (s, SiCH_3, 3H), 0.26 (s, SiCH_3, 3H), 0.67 (s, CN-^{t}Bu, 9H), 1.05 (s, N^tBu, 9H), 1.15 (s, CpCH_3, 3H), 1.47 (s, CpCH_3, 3H), 1.52 (d, CH_3-diene, 3H, ^3J = 12.4 Hz), 1.94 (s, CpCH_3, 3H), 1.99 (s, CpCH_3, 3H), 2.36 (m, CH_2-diene, 2H), 2.49 (m, C*H*-diene, 1H), 3.40 (br s, C*H*-diene, 1H), 4.51 (dd, C*H*-diene, 1H, ^3J = 13.4 Hz). $^{13}C\{^1H\}$NMR (125 MHz, C_7D_8): δ 4.34 (s, Si*C*H_3), 5.73 (s, Si*C*H_3), 11.48 (s, Cp*C*H_3), 11.55 (s, Cp*C*H_3), 15.38 (s, Cp*C*H_3), 17.17 (s, Cp*C*H_3), 21.27 (s, *C*H_3-diene), 30.13 (s, *C*H_3-^{t}Bu), 33.94 (s, *C*H_3-CN^{t}Bu + *C*H_2-diene), 60.16 (s, *C*-^{t}Bu), 63.55 (s, *C*-CN^{t}Bu), 82.48 (s, *C*H-diene), 108.40 (s, *C*(Cp)), 129.86 (s, *C*Me(Cp)), 130.34 (s, *C*Me(Cp)), 131.41 (s, *C*Me(Cp)), 131.46 (s, *C*H-diene), 133.89 (s, *C*H-diene), 136.17 (m, C_6F_5), 137.55 (m, C_6F_5), 139.50 (m, C_6F_5), 147.66 (m, C_6F_5), 149.59 (m, C_6F_5). ^{19}F NMR (282 MHz, C_6D_6): δ −128.4 (d, *o*-F, 6F, ^3J = 22.9 Hz), −159.8 (t, *p*-F, 3F, ^3J = 17.8 Hz), −163.4 (t, *m*-F, 6F, ^3J = 18.4 Hz). ^{11}B NMR (96.3 MHz, C_6D_6): δ −16.3. IR (cm^{-1}, Nujol): 2952 (s), 2855 (s), 2727 (w), 2191 (m), 1640 (m), 1558 (w), 1511 (m), 1460 (s), 1377 (s), 1311 (w), 1273 (m), 1261 (m), 1255 (m), 1183 (m), 1164 (w), 1078 (m), 1033 (w), 972 (m), 918 (w), 844 (m), 824 (m), 815 (m), 805 (m), 774 (w), 746 (m), 724 (m), 680 (m), 654 (m). Anal. Found: C, 53.85; H, 4.65; N, 2.89. Calcd: C, 53.76; H, 4.62; N, 2.91. MS-CI(CH_4): *m/z* = 960 [M^-].

Acknowledgment. We thank the Robert A. Welch Foundation (Grant F-816 and F-135) and the Science and Technology Center Program of the National Science Foundation (Grant No. CHE-08920120) for support.

Supporting Information Available: Details of the X-ray structure determinations of the structures of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0002327