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Insertion Reactions of Nitriles in Cationic Alkylbis(cyclopentadienyl)titanium Complexes: The Facile Synthesis of Azaalkenylidene Titanium Complexes and the Crystal and Molecular Structure of $[(\text{Indenyl})_2\text{Ti(NCMePh)(NCPh)}]\text{BPh}_4$

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The cationic methylbis(cyclopentadienyl)titanium nitrile complexes $[\text{Cp}_2\text{TiMe(N}{\equiv}\text{CR)}]\text{BPh}_4$ (R = Me, *n*-Pr, *t*-Bu, Ph) are readily converted to the azaalkenylidene complexes $[\text{Cp}_2\text{Ti(N}{=}\text{CMeR)(NCR)}]\text{BPh}_4$ as the products of a migratory insertion of nitriles into the Ti–methyl bond. The kinetics of the insertion reactions show a first-order dependence on the titanium alkyl and zero-order in the concentration of free nitrile. The reaction rates increase in the order Me ≪ *t*-Bu < Ph < *n*-Pr. Trimethylsilyl cyanide isomerizes to the isocyanide and forms the η^2-iminoacyl complex $[\text{Cp}_2\text{Ti(Me}_3\text{SiN}{=}\text{CMe)(C}{\equiv}\text{NSiMe}_3)]\text{BPh}_4$. Bis(indenyl) complexes are more reactive than their cyclopentadienyl analogues, with reaction rates increasing for R = *t*-Bu < Me < Ph. The role of these complexes as models for the mechanism of the $\text{Cp}_2\text{TiCl}_2/\text{AlR}_3$-catalyzed polymerization of ethylene is discussed. The structure of the complex $[(\text{C}_9\text{H}_7)_2\text{Ti(NCMePh)(NCPh)}]\text{BPh}_4$ was determined by X-ray crystallography. The complex crystallizes in the triclinic system, space group $P1$, with $a = 9.713$ (1) Å, $b = 11.143$ (2) Å, $c = 11.363$ (2) Å, $\alpha = 102.63$ (1)°, $\beta = 109.57$ (1)°, $\gamma = 80.91$°, $Z = 1$, and $D_{\text{calcd}} = 1.21$ g cm^{-3}. The Ti–azavinylidene arrangement is linear with a short Ti–N double bond (1.851 Å); the Me and Ph substituents adopt a "Me-outside" conformation in the plane bisecting the indenyl–Ti–indenyl angle.

Introduction

The mechanism of the alkene polymerization by $\text{Cp}_2\text{TiCl}_2/\text{AlR}_3$-based soluble Ziegler–Natta catalysts has remained a topic of continuous debate[1–4] since the discovery of these systems three decades ago.[5] Most reaction schemes proposed in the past have attempted to explain the process of alkene insertion into a titanium–carbon σ-bond on the basis of electroneutral complexes.[1] The chemistry of cationic titanium complexes and their possible role in polymerization reactions has, however, remained largely unexplored, in spite of an early proposal by Breslow and Newburg of an alkene polymerization mechanism involving (partially) charged intermediates[6] (eq 1) and supporting electrochemical evidence.[7]

(1)

More recently, the involvement of ionic species $[\text{Cp}_2\text{Ti–R}]^+[\text{AlR}_n\text{Cl}_{4-n}]^-$ was supported by the synthesis of $[\text{Cp}_2\text{TiC(SiMe}_3){=}\text{CMePh}]\text{AlCl}_4$ from $\text{Me}_3\text{SiC}{\equiv}\text{CPh}$ and a $\text{Cp}_2\text{TiCl}_2/\text{AlMeCl}_2$ mixture[8] and by the polymerization of ethylene by $[\text{Cp}_2\text{ZrMe(THF)}]\text{BPh}_4$ in the absence of aluminium alkyls.[3] We have earlier reported the preparation of a series of cationic methylbis(cyclopentadienyl)titanium complexes $[\text{Cp}_2\text{TiMe(L)}]^+$[9] and describe here the insertions of alkyl and aryl nitriles into the titanium–methyl bonds of these complexes and the possible role of this reaction as a mechanistic model for the olefin insertion step in soluble titanium polymerization catalysts.

Results

Preparation of Complexes. The nitrile complexes $[\text{Cp}_2\text{TiMe(NCR)}]\text{BPh}_4$ (**1**) react with excess nitrile in dichloromethane solution at room temperature to give the azaalkenylidene[10] complexes **2** as yellow to light brown

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(1) (a) Boor, J. *Ziegler-Natta Catalysts and Polymerization*; Academic: New York, 1979; p 325. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (c) Reichert, K. H. *Transition Metal Catalysed Polymerisations. Alkenes and Dienes Part B*; Quirk, R. P., Ed.; Harwood Academic: New York, 1983; p 465. (d) Fink, G. *Ibid.* p 495.

(2) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377.

(3) Jordan, R. F.; Bajgur, C. S.; Willet, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. Jordan, R. F.; LaPonte, R. E.; Baigur, C. S.; Echols, S. F.; Willet, R. *Ibid.* **1987**, *109*, 4111. Cationic Th alkyl complexes also exhibit ethylene polymerisation activity: Lin, Z.; Le Marechal, J. F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.

(4) (a) Fink, G.; Rottler, R. *Angew. Makromol. Chem.* **1981**, *94*, 25. (b) Fink, G.; Fenzl, W.; Mynott, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 158.

(5) (a) Natta, G.; Pino, P.; Mazzanti, G.; Giannini, U. *J. Am. Chem. Soc.* **1957**, *79*, 2975. (b) Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* **1957**, *79*, 5072.

(6) Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* **1959**, *81*, 81.

(7) Dyachkovski, F. S.; Shilova, A. K.; Shilov, A. E. *J. Polym. Sci., Part C* **1967**, *16*, 2333.

(8) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

(9) (a) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556.

(10) The –N=CRR′ ligand has been called variously the methyleneamido,[11] alkylideneamido,[11,12a] ketimido,[13] or azomethine[14] group. Werner has pointed out the close relationship between this ligand and the alkylidene group C=CRR′;[15] we prefer to follow his suggestion and use the terms *azaalkenylidene* and *azavinylidene*.

(11) (a) Erker, G.; Frömberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68. (b) Frömberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343.

(12) (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (b) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E. *Organometallics* **1987**, *6*, 1041.

(13) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 377.

(14) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

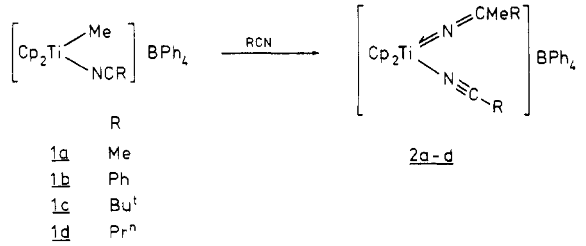
Table I. Selected Spectroscopic Data of Titanium Azaalkylidene Complexes

compound	IR,[a] cm^{-1}	^{1}H NMR,[b] ppm	^{13}C NMR,[c] ppm
[Cp$_2$Ti(NCMe)(N=CMe$_2$)]BPh$_4$ (**2a**)	2280 (w), 2310 (m), 1685 (m), 1700 (m)	1.57 (s, 3 H, =CMe$_2$), 1.85 (s, 3 H, =CMe$_2$), 1.87 (s, 3 H, MeC≡N), 5.92 (s, 10 H, Cp)	2.8 (*Me*CN), 24.8 and 26.6 (=C*Me*$_2$), 110.8 (Cp), 117.1 (MeCN), 172.2 (N=CMe$_2$)
[Cp$_2$Ti(NCPh)(N=CMePh)]BPh$_4$ (**2b**)	2262 (m), 1660 (s)	2.31 (s, 3 H, =C*Me*), 6.10 (s, 10 H, Cp), 7.7 (m, 10 H, C*Ph*)	25.1 (=C*Me*), 108.3 (*C*C≡N), 111.4 (Cp), 132.8–127.1 (m, Ph), 170.0 (N=*C*<)
[Cp$_2$Ti(NC-*t*-Bu)(N=CMe-*t*-Bu)]BPh$_4$ (**2c**)	2270 (m), 1679 (s)	1.12 (s, 9 H, =C-*t*-*Bu*), 1.40 (s, 9 H, N≡C-*t*-*Bu*), 1.84 (s, 3 H, =C*Me*), 5.93 (s, 10 H, Cp)	
[Cp$_2$Ti(NC-*n*-Pr)(N=CMe-*n*-Pr)]BPh$_4$ (**2d**)	2282 (m), 1682 (s)	1.05, 1.56 and 2.20 (m, 14 H, *n*-Pr), 1.85 (s, 3 H, =C*Me*)	13.5 and 14.1 ((CH$_2$)$_2$*Me*), 18.7, 19.3, and 20.0 (CH$_2$), 26.0 (=C*Me*), 41.5 (=C*CH*$_2$), 110.8 (Cp), 175.6 (N=*C*<)
[Ind$_2$Ti(NCMe)(N=CMe$_2$)]BPh$_4$ (**4a**)	2282 (w), 2310 (m), 1678 (s)	1.65 (s, 3 H, *Me*C≡N), 1.48 (s, 3 H, =C*Me*$_2$), 1.78 (s, 3 H, =C*Me*$_2$), 5.9 (m, 6 H, Ind), 6.2 (m, 8 H, Ind)	
[Ind$_2$Ti(NCPh)(N=CMePh)]BPh$_4$ (**4b**)	2270 (m), 1645 (s)	1.91 (s, 1.1 H, =C*Me*), 2.31 (s, 1.9 H, =C*Me*), 5.98 (m, 6 H, Ind), 6.24 (m, 8 H, Ind)	24.8 (=C*Me*), 108.6 (*C*C≡N), 101.9, 115.5, 115.8, 125–113 (Ind), 130–135 (Ph), 170.6 (N=*C*<)
[Ind$_2$Ti(NC-*t*-Bu)(N=CMe-*t*-Bu)]BPh$_4$ (**4c**)	2270 (m), 1665 (s)	0.92 (s, 9 H, =C-*t*-*Bu*), 1.37 (s, 9 H, *t*-*Bu*C≡N), 1.90 (s, 3 H, =C*Me*), 5.8 (m, 6 H, Ind), 6.10 (m, 8 H, Ind)	27.0 (=C*Me*), 27.6 and 28.2 (C*Me*$_3$), 43.8 and 56.3 (*C*Me$_3$), 100.7, 101.1, 115.3, and 124.6–133.8 (Ind), 185.5 (N=*C*<)
[CpCp*Ti(NCPh)(N=CMePh)]BPh$_4$ (**5**)	2260 (m), 1652 (m), 1658 (sh)	1.96 (s, 15 H, C$_5$Me$_5$), 2.10 (s, ca. 1.5 H, =C*Me*), 2.38 (s, ca. 1.5 H, =C*Me*), 5.9 (s, 5 H, Cp)	
[Cp$_2$Ti(CNSiMe$_3$)(η^2-MeC=NSiMe$_3$)]BPh$_4$ (**6**)	2140 (s), 1715 (s)	0.38 (s, 9 H, =NSi*Me*$_3$), 0.60 (s, 9 H, *Me*$_3$SiN≡C), 2.84 (s, 3 H, =C*Me*), 5.38 (s, 10 H, Cp)	

[a] CCl$_4$ mull; KBr plates. [b] In CD$_2$Cl$_2$ relative to SiMe$_4$, 60 MHz. [c] In CD$_2$Cl$_2$, relative SiMe$_4$, 100 MHz.

crystals. The reaction is usually complete in 24 h, except for the acetonitrile complex **1a** where the insertion proceeds slowly over a period of 2 weeks. The yields are quantitative according to NMR measurements. The bis(indenyl)complexes [Ind$_2$TiMe(NCR)]BPh$_4$ (**3a**, R = Me; **3b**, R = Ph; **3c**, R = *t*-Bu) react with nitriles similarly to give an analogous series of complexes **4a–c**. In this case, however, nitrile insertion into the titanium–methyl bond occurs considerably faster and requires less than 1 h. For comparison, the mixed-ligand complex [CpCp*Ti(NCMePh)(NCPh)]BPh$_4$ (**5**) (Cp* = C$_5$Me$_5$) was prepared from CpCp*TiMeCl, NaBPh$_4$, and PhCN in THF. The reaction is complete after the mixture was stirred at room temperature for ca. 20 h.

Attempts were made to isolate the products of nitrile insertion in the absence of added nitrile. IR data indicate the complete disappearance of coordinated nitrile and the formation of azavinylidene complexes. However, pure complexes could not be isolated.



(2)

Selected spectroscopic data are collected in Table I. The infrared C≡N stretching frequencies of the coordinated nitrile ligands in the complexes **2a–d**, **4a–c**, and **5** occur at higher wavenumbers than in the free nitriles ($\Delta(\nu_{C\equiv N})$ = ca. 30 cm^{-1}) and are close to those observed for the methyl complexes **1a–d**. The C=N frequencies of the azavinylidene ligands are observed between 1645 and 1700 cm^{-1}; they decrease in the order R = Me > *n*-Pr > *t*-Bu > Ph and are lower in the indenyl complexes than in the cyclopentadienyl compounds. The ^{1}H NMR reveals the presence of the azavinylidene methyl groups at ca. δ 1.8–1.9 (R = alkyl) and 2.3 (R = Ph), respectively.

As the crystal structure of **4b** shows, the Ti—N=C arrangement is linear, with the substituents Me and R roughly in the plane bisecting the Cp–Ti–Cp angle. Rotation about the Ti–N bond is hindered by its double-bond character, and two stereoisomers are therefore possible, i.e. "Me-inside" and "Me-outside". Most of the azavinylidene complexes exist as one stereoisomer, as indicated by the observation of only one singlet for the N=CMeR methyl group in the ^{1}H NMR spectrum. The exceptions are **4b** and the C$_5$Me$_5$ complex **5** where two methyl singlets are observed in 7:4 and 1:1 ratios, respectively. While it could be argued that the signal splitting in **4b** might be caused by the indenyl ligands adopting different relative orientations, such considerations are ruled out by **5** where the ring ligands have no conformational preferences. In the solid state **4b** adopts the "Me-outside" configuration (see below) and it is assumed that this geometry is also present in the other complexes.

Attempts to extend the nitrile insertion reaction of **1a** to Me$_3$SiCN did not yield a product of type **2**; instead, the

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(15) Werner, H.; Knaup, W.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 248.

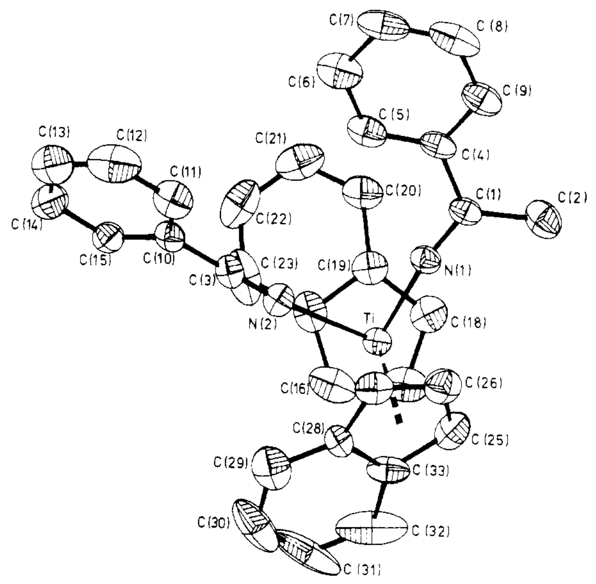
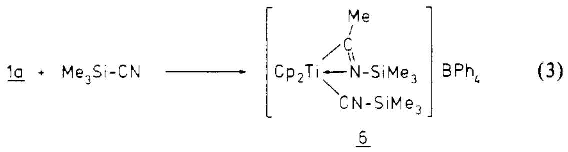


Figure 1. The structure of the $[Ind_2Ti(N{=}CMePh)(NCPh)]^+$ cation, showing the atomic numbering scheme. Thermal ellipsoids correspond to 50% probability.

η^2-iminoacyl isocyanide complex **6** was isolated as colorless crystals. The spectroscopic data of **6** resemble closely



$$\underline{1a} + Me_3Si{-}CN \longrightarrow \left[Cp_2Ti(\eta^2\text{-}C(Me){=}N{-}SiMe_3)(CN{-}SiMe_3) \right] BPh_4 \qquad (3)$$

6

those of the *t*-BuNC complex $[Cp_2Ti(t\text{-}BuNCMe)(t\text{-}CNBu)]BPh_4$.[9] Trimethylsilyl cyanide is known to exist in equilibrium with small amounts of $Me_3Si{-}NC$[16] which reacts preferentially with **1a**. It interesting that in these systems the formation of titanium–carbon bonds is favored with respect to titanium–nitrogen bonds, contrary to the sequence of bond energies in TiX_4 compounds.[17]

Molecular Structure of 4b. The molecular structure of $[Ind_2Ti(N{=}CMePh)(NCPh)]BPh_4$ (**4b**) was established by single-crystal X-ray diffraction and is shown in Figure 1. Selected bond distances and angles are given in Table II.

The indenyl ligands are oriented in such a way as to reduce interactions of their C_6 rings with each other. The midpoints of the five-membered rings (Cp centroids) and Ti form an angle of 135.8°. The bonding between titanium and the η^5-indenyl rings is slightly distorted, with longer bonds between Ti and those carbons shared with the six-membered rings. As a result, the lines between titanium and the Cp centroids are tilted by 5.18 and 8.01° with respect to axes normal to the C_5 ring planes, a common feature in indenyl complexes which probably helps to increase the aromatic character of the benzenoid rings.[18] The benzonitrile ligand is end-on bonded and nearly linear, with a short C(3)–N(2) distance typical of a C≡N triple bond (1.137 Å). The N(2)–Ti bond [2.175 (7) Å] is slightly longer than the Ti–N interaction in η^2-iminoacyl complexes[9b] but significantly shorter than in the pyridine complex $Ti(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)(OC_6H_3\text{-}t\text{-}Bu_2)(CH_2SiMe_3)(py)$ [2.293 (5) Å].[19]

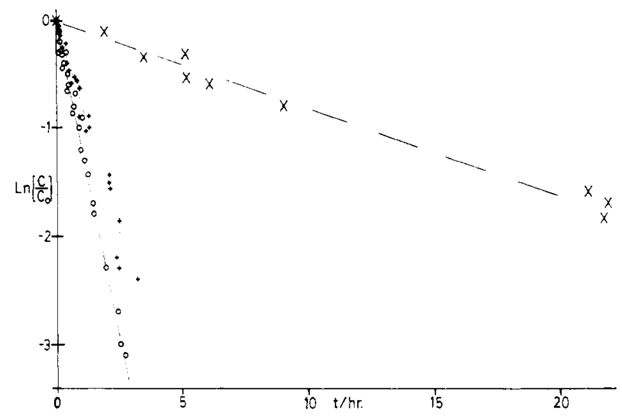


Figure 2. Reaction of RCN with $[Cp_2TiMe(NCR)]^+$ in CH_2Cl_2 at 35 °C: ○, R = *n*-Pr; +, R = Ph; ×, R = *t*-Bu. The points on each curve are the superimposed data from several measurements at different concentrations of titanium complex and nitrile.

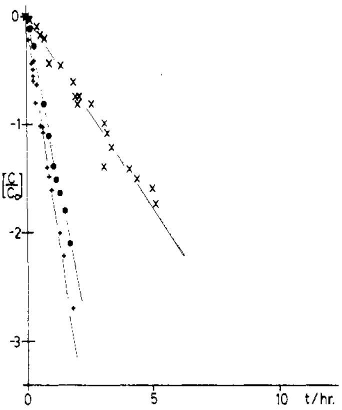


Figure 3. Reaction of RCN with $[Ind_2TiMe(NCR)]^+$: ○, R = Me; +, R = Ph; ×, R = *t*-Bu. Measuring conditions were those of Figure 2.

The azavinylidene moiety Ti–N(1)–C(1) in **4b** is η^1-coordinated and is close to linear [171.6 (4)°]. The methyl and phenyl substituents on C(1) lie in the N(1)–Ti–N(2) plane, with the methyl group pointing outward. The dihedral angle between the plane of the phenyl ring and this reference plane is 19.0°. By comparison, the C_6 ring of the benzonitrile ligand shows a tilt angle of 42.8°. Few complexes containing the azaalkenylidene ligand have been structurally characterized; Table III contains a comparison of the geometric features of this ligand in **4b** with Ti(IV), Zr(IV), Mo(II), and Os(II) compounds. In each case and irrespective of the d-electron count of the metal center or of the overall charge the M–N bond is short [<1.9 Å, except for $Cp_2ZrCl(NCHPh)$] and indicates substantial double-bond (d_π–p_π) character and sp hybridization of the nitrogen, as would be expected of a "heteroallene" $M{=}N{=}CR_2$. The Ti–N bond in **4b** is in fact slightly shorter than the Ti–N distances in $Fe[C_5H_4Ti(NEt_2)_3]_2$ (1.89 Å)[21] and in $ClTi[N(SiMe_3)_2]_3$ (1.940 Å) for which Ti–N bond orders higher than 1 have been discussed because of nitrogen lone pair–metal interactions.[22] The C(1)–N(1) distance indicates a double bond and agrees well with the bond lengths in $[R_2C{=}N{=}CR_2]^+$ ions.[23]

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(16) Seckar, J. A.; Thayer, J. S. *Inorg. Chem.* **1976**, *15*, 501.

(17) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219.

(18) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929.

(19) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981.

(20) (a) Kilner, M.; Midcalf, C. *J. Chem. Soc. A* **1971**, 292. (b) Shearer, H. M. M.; Sowerby, J. D. *J. Chem. Soc., Dalton Trans.* **1973**, 2629.

(21) Thewalt, U.; Schomburg, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *30B*, 636.

(22) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Praisthloy, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

Table II. Selected Bond Lengths and Bond Angles for $[(\mathrm{Indenyl})_2\mathrm{Ti(NCMePh)(NCPh)}]\mathrm{BPh}_4$

a. Bond Lengths (Å)

N(1)–Ti(1)	1.872 (7)	N(2)–Ti(1)	2.175 (7)
C(16)–Ti(1)	2.346 (8)	C(17)–Ti(1)	2.299 (8)
C(18)–Ti(1)	2.334 (9)	C(19)–Ti(1)	2.463 (8)
C(24)–Ti(1)	2.515 (9)	C(25)–Ti(1)	2.328 (8)
C(26)–Ti(1)	2.367 (9)	C(27)–Ti(1)	2.359 (9)
C(28)–Ti(1)	2.457 (8)	C(33)–Ti(1)	2.460 (8)
C(1)–N(1)	1.244 (8)	C(3)–N(2)	1.137 (8)
C(2)–C(1)	1.514 (10)	C(4)–C(1)	1.488 (8)
C(10)–C(3)	1.413 (7)	C(17)–C(16)	1.410 (10)
C(24)–C(16)	1.425 (9)	C(18)–C(17)	1.389 (9)
C(19)–C(18)	1.422 (9)	C(20)–C(19)	1.414 (9)
C(24)–C(19)	1.415 (9)	C(21)–C(20)	1.337 (9)
C(22)–C(21)	1.396 (11)	C(23)–C(22)	1.365 (10)
C(24)–C(23)	1.431 (9)	C(26)–C(25)	1.340 (11)
C(33)–C(25)	1.469 (10)	C(27)–C(26)	1.374 (10)
C(28)–C(27)	1.421 (9)	C(29)–C(28)	1.398 (9)
C(33)–C(28)	1.420 (9)	C(30)–C(29)	1.426 (11)
C(31)–C(30)	1.377 (13)	C(32)–C(31)	1.340 (12)
C(33)–C(32)	1.396 (10)		
C(111)–B(1)	1.680 (9)	C(221)–B(1)	1.706 (8)
C(311)–B(1)	1.682 (8)	C(411)–B(1)	1.703 (8)

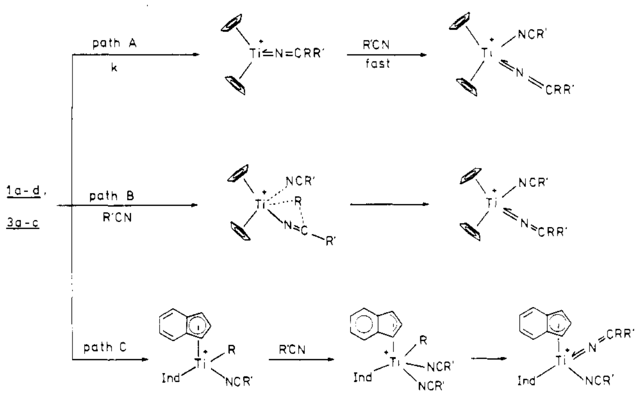
b. Bond Angles (deg)

N(2)–Ti(1)–N(1)	92.9 (3)	Cp(1)–Ti(1)–N(1)[a]	105.4 (5)
Cp(1)–Ti(1)–N(2)	104.2 (5)	Cp(2)–Ti(1)–N(1)[b]	107.8 (6)
Cp(2)–Ti(1)–N(2)	102.5 (6)	Cp(1)–Ti(1)–Cp(2)	135.8 (6)
C(1)–N(1)–Ti(1)	171.6 (4)	C(2)–C(1)–N(1)	120.2 (6)
C(10)–C(3)–N(2)	177.4 (6)	C(5)–C(4)–C(1)	118.7 (4)
C(9)–C(4)–C(1)	121.2 (4)	C(11)–C(10)–C(3)	120.7 (4)
C(3)–N(2)–Ti(1)	173.4 (5)	C(15)–C(10)–C(3)	119.3 (4)
C(24)–C(16)–C(17)	106.9 (6)	C(18)–C(17)–C(16)	109.3 (6)
C(19)–C(18)–C(17)	108.0 (6)	C(20)–C(19)–C(18)	132.7 (6)
C(24)–C(19)–C(18)	107.5 (6)	C(24)–C(19)–C(20)	119.7 (6)
C(21)–C(20)–C(19)	120.6 (7)	C(22)–C(21)–C(20)	120.7 (7)
C(23)–C(22)–C(21)	121.5 (7)	C(24)–C(23)–C(22)	119.4 (7)
C(19)–C(24)–C(16)	107.9 (6)	C(23)–C(24)–C(16)	133.9 (6)
C(23)–C(24)–C(19)	118.2 (6)	C(33)–C(25)–C(26)	109.5 (7)
C(27)–C(26)–C(25)	108.9 (7)	C(28)–C(27)–C(26)	109.5 (7)
C(29)–C(28)–C(27)	134.0 (6)	C(33)–C(28)–C(27)	106.9 (6)
C(33)–C(28)–C(29)	119.1 (7)	C(30)–C(29)–C(28)	118.3 (8)
C(31)–C(30)–C(29)	119.4 (7)	C(32)–C(31)–C(30)	123.8 (8)
C(33)–C(32)–C(31)	118.0 (8)	C(28)–C(33)–C(25)	104.8 (6)
C(32)–C(33)–C(25)	133.8 (6)	C(32)–C(33)–C(28)	121.2 (7)
C(211)–B(1)–C(111)	109.7 (5)	C(311)–B(1)–C(111)	108.8 (5)
C(311)–B(1)–C(211)	108.9 (4)	C(411)–B(1)–C(111)	108.4 (4)
C(411)–B(1)–C(211)	110.4 (4)	C(411)–B(1)–C(311)	110.6 (5)

[a] Cp(1) is defined as the midpoint of C16,C17,C18,C19,C24. [b] Cp(2) is defined as the midpoint of C25,C26,C27,C28,C33.

Kinetic Studies. The rates of the insertion of nitriles into the titanium–methyl bonds were measured by following the conversion of the complexes **1a–d** and **3a–c** by ^{1}H NMR in sealed tubes at 35 °C. The concentrations of the titanium starting materials ranged from 0.043 to 0.18 M and the concentrations of added nitrile from 0 to 6.1 M. Solutions were prepared in dichloromethane-d_2 except in the case of the acetonitrile complex **1a** where measurements were carried out in neat acetonitrile-d_3 because of poor solubility in other solvents. In all cases the rates are independent of the concentration of free nitrile and are first-order in the concentration of the titanium methyl complexes. The first-order ln C/C_0 vs t plots for the cyclopentadienyl complexes **1b–d** and the indenyl compounds **3a–c** are shown in Figures 2 and 3, respectively; they are linear over at least 3 half-lives (C_0 = concentration of starting complex at t = 0). The rate of insertion of acetonitrile into **1a** is very slow and could only be followed for about 1 half-life; it is omitted from Figure 2. The reason for this anomalously slow reaction is not clear; by contrast, the insertion of acetonitrile into **3a** is comparable to that of benzonitrile, as expected. The slopes in Figures 2 and 3 correspond to the least-squares values of k given in Table IV. Experiments with $[\mathrm{Ind_2TiMe(NCCD_3)}]\mathrm{BPh_4}$ in $\mathrm{CD_2Cl_2}$ provided no evidence for reversibility of the methyl migration step; there is no formation of $[\mathrm{Ind_2TiCD_3(NCMe)}]\mathrm{BPh_4}$.

Scheme I



Discussion

Azaalkenylidene complexes may be prepared by a number of routes, for example, by N–N bond cleavage of $R_2C{=}NN{=}CR_2$,[24] by dehydrohalogenation of metal imides,[25] from oximes[15] or via hydrometalation of nitriles.[11,12,14] The most generally applicable method, however, is the reaction of metal halides with $\mathrm{LiN{=}CR_2}$ or $\mathrm{Me_3SiN{=}CR_2}$.[13,20a,26] Nitriles will only react readily with metal–carbon bonds in alkene, alkyne, and related complexes of formally divalent metals of the titanium triad (under oxidative coupling and formation of metallacycles[27,28]) and with electron-deficient alkyl complexes of trivalent metals, notably $\mathrm{Cp^*_2ScMe}$;[14] pseudotetrahedral complexes such as $\mathrm{Cp_2TiMeCl}$, $\mathrm{Cp^*_2ZrMe_2}$, and $\mathrm{Cp^*_2HfMe_2}$ do not react.[14,26] Only if a coordination site cis to the metal–alkyl bond is available to the nitrile, as is the case in the scandium complexes and the isoelectronic $[\mathrm{Cp_2Ti{-}R}]^+$ cations, can a 1,3-alkyl shift take place to form an azavinylidene complex.[29] The titanium complexes are less reactive than their scandium counterparts, possibly for steric reasons, and double nitrile insertions and formation of metallaheterocycles[14] are not observed. The azaalkenylidene moiety in the cationic titanium complexes described here as well as in earlier reported cases[11,13-15,20,26] is η^1-coordinated and linear with a short metal–nitrogen double bond. However, a comparison of the isoelectronic series of complexes $\mathrm{Cp^*_2Sc{-}L}$, $\mathrm{Cp_2Y{-}L}$, $\mathrm{Cp^*_2Y{-}L}$, and $[\mathrm{Cp_2Ti{-}L}]^+$ (L = $\mathrm{NCR_2}$) reveals significant differences. Although excess nitrile is present during the preparation in all cases and scandium nitrile complexes $\mathrm{Cp^*_2ScR(NCR)}$ (R = p-tolyl) can be isolated, the compounds $\mathrm{Cp^*_2ScNCR_2}$ are monomeric and nitrile-free[14] with a formal electron

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[23] Al-Talib, M.; Jibril, I.; Würthwein, E. U.; Jochims, J. C.; Huttner, G. *Chem. Ber.* **1984**, *117*, 3365.

[24] Bright, D.; Mills, O. *J. Chem. Soc., Chem. Commun.* **1967**, 245.

[25] Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435.

[26] Collier, M. R.; Lappert, M. F.; McMeeking, J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 689.

[27] Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

[28] (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) *Ibid.* **1987**, *109*, 2544. (c) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Ibid.* **1987**, *109*, 1590.

[29] The slow insertion of $\mathrm{CD_3CN}$ into $[\mathrm{Cp_2ZrMe(NCMe)_2}]^+$ has recently been noted.[12b]

Table III. Bonding Parameters of Azaalkenylidene Ligands

compd	$\nu_{C=N}$, cm^{-1}	r_{C-N}, Å	r_{M-N}, Å	∠M–N–C, deg	ref
4b	1645	1.283	1.851	170.75	this work
$CpCl_2TiN{=}C$-*t*-Bu-*n*-Bu	1640				
	1650 br	1.267	1.872	171.3	13
$Cp_2ClZrN{=}CHPh$	1678	1.259 (7)	2.013 (5)	170.5 (5)	11a
$Cp(CO)_2MoN{=}C$-*t*-Bu_2	1616	1.26 (1)	1.892 (5)	171.8	20b
$[C_6H_6(PMe$-*t*-$Bu_2)OsN{=}CPh_2]^+$		1.270 (9)	1.882 (6)	168.8 (5)	15

Table IV. Rates[a] of Nitrile Insertion into Titanium–Methyl Bonds

compd	nitrile	k_{obsd}, s^{-1}
1a	MeCN	$(3.26 \pm 0.10) \times 10^{-6}$
1b	PhCN	$(2.40 \pm 0.16) \times 10^{-4}$
1c	*t*-BuCN	$(2.11 \pm 0.11) \times 10^{-5}$
1d	*n*-PrCN	$(3.38 \pm 0.11) \times 10^{-4}$
3a	MeCN	$(3.63 \pm 0.13) \times 10^{-4}$
3b	PhCN	$(3.99 \pm 0.18) \times 10^{-4}$
3c	*t*-BuCN	$(9.52 \pm 0.44) \times 10^{-5}$

[a] Least-squares values and standard deviations of k_{obsd} from measurements at three or more different concentrations.

count of 16 (if the nitrogen lone pair is fully taken into account); the sterically less crowded yttrium Cp complexes exist as 16-electron dimers,[12a] whereas the very bulky Cp* yttrium complexes[30] and the titanium compounds described here retain terminally coordinated nitrile ligands to form 18-electron complexes.

Several mechanistic pathways for the insertion of nitriles into titanium–carbon σ-bonds may be envisaged (Scheme I), e.g. 1,3-alkyl shift to give a 16-electron azavinylidene complex, followed by nitrile coordination in a fast subsequent step (path A) or an alkyl migration induced by a second nitrile molecule (path B). Similarly, the significantly faster nitrile insertion in the case of the indenyl complexes **3a–c** compared to the cyclopentadienyl compounds may be interpreted as the result of an $\eta^5 \rightarrow \eta^3$-indenyl rearrangement[18] combined with the coordination of a second nitrile ligand which would accelerate the methyl migration (path C). The kinetic results show, however, that the rate-limiting nitrile-insertion step into the titanium–methyl bond proceeds in the absence of free nitrile and that the rates are independent of the nitrile concentration within wide limits in all cases, thus dismissing pathways B and C. The observed acceleration of nitrile insertion in the indenyl complexes is likely to be the result of the electron-withdrawing properties of the indenyl ligand.[31]

The formation of azavinylidene complexes is therefore best explained by the sequence of reaction steps of path A (Scheme I). The mechanism has certain features that reflect on the insertion mechanism of alkenes into titanium alkyl bonds, with nitrile acting as an ethylene surrogate. Hoffmann et al. have calculated the two lowest unoccupied molecular orbitals of a $[Cp_2Ti-X]^+$ fragment; they are designated d_σ and d_π because of their symmetry with respect to the bond between Ti and incoming ligand L in the *xy* plane[32] (Figure 4).

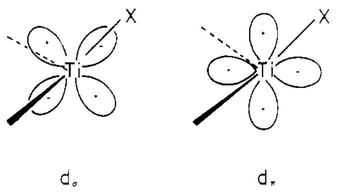
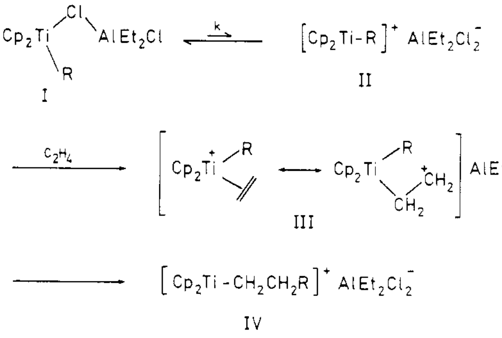


Figure 4. Schematic representation of the two vacant frontier orbitals d_σ and d_π of a $[Cp_2TiX]^+$ fragment.[32] The orbitals lie in the *xy* plane.

Scheme II



A donor ligand, e.g. nitrile or ethylene, coordinates to $[Cp_2Ti-R]^+$ by interacting with the d_σ orbital.[33] In the case of nitrile this leads to a complex stable enough to be isolated, and it is the next step, the 1,3-alkyl shift, which experiences an activation barrier high enough to become rate-determining in the formation of the azavinylidene product. The weaker donor ethylene is similarly able to donate electron density to the d_σ orbital; stabilization of the resulting complex by a metal-to-ligand back-bonding interaction as in ethylene complexes of electron-rich metals is, however, not possible since the appropriate orbital, d_π, is vacant. A species $[Cp_2TiMe(C_2H_4)]^+$ can therefore be expected to be highly unstable and not isolable and is unlikely to experience a significant activation barrier toward insertion. (An ethylene "slippage" as discussed to explain the activation of coordinated alkenes toward nucleophilic attack[34] may be envisaged and may assist the 1,3-alkyl migration step.) The importance of the instability of the titanium–ethylene complex for the success of the ethylene insertion step in the catalytic system is further underlined by the behavior of complexes with occupied d_π orbitals, e.g. the Nb(III) complexes $Cp_2NbEt(C_2H_4)$,[35] $Cp_2NbMe(CO)$,[36] and their Cp* analogues[37] and the W(IV)

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[30] Den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509.

[31] (a) The electron-donating or -withdrawing character of substituted cyclopentadienyl ligands and their influence on catalyst activity has been demonstrated by ^{59}Co NMR spectroscopy on $Cp'CoL_2$ complexes: Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. Bönnemann, H.; Brijoux, W. *Bull. Soc. Chim. Belg.* **1985**, *94*, 635. (b) The olefin polymerization activity of indenyl zirconium complexes also exceeds that of cyclopentadienyl analogues: Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. Kaminsky, W. *Angew. Makromol. Chem.* **1986**, *145/6*, 149.

[32] Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

[33] In complexes where the $d\sigma$ orbital is occupied, as in $Cp_2TiMeCl$ or Cp_2ZrR_2, the d_π orbital is the LUMO and should be available to interact with donor ligands but is apparently only accessible to small molecules such as CO to give, eventually, metal acyl complexes: (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605.

[34] (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148. (b) *Ibid.* **1981**, *103*, 4308.

[35] (a) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793. (b) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *Ibid.* **1974**, *96*, 5420.

[36] Otto, E. E. H.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *170*, 209.

cation $[Cp_2WMe(C_2H_4)]^+$;[34b,38] in none of these can an insertion into the metal–alkyl bond be induced, in spite of the structural resemblance to the titanium ethylene complex, because of extensive metal–π-ligand back-donation from energetically high-lying d orbitals.[34b]

A mechanism of the insertion of ethylene into the titanium–alkyl bond based on this discussion is outlined in Scheme II.[39,40]

In contrast to the reactions with nitriles, the rate-determining step is in this case the removal of a chloride ligand from the Ti center, i.e. the formation of $[Cp_2TiR]^+[AlCl_2R_2]^-$ (II), which is followed by the formation of the ethylene precoordination complex III. Neither II nor III is likely ever to be present in the reaction mixture in measurable quantities, in agreement with spectroscopic results.[1d,4] The insertion product IV can either react with further ethylene or be stabilized by recoordinating $AlCl_2R_2^-$ to give a complex of type I. We believe that the nitrile complexes **1** and **3** and the insertion products **2** and **4** provide useful models for the unstable (and as yet unobserved) intermediates III and IV and illustrate the ligand–metal interactions required to bring about the insertion of unsaturated substrates into titanium–alkyl bonds.

Experimental Section

All experiments were carried out under argon by using standard vacuum-line (Schlenk) techniques. Solvents were distilled under nitrogen from sodium–benzophenone (diethyl ether, THF), sodium (toluene), or calcium hydride (dichloromethane, acetonitrile). NMR solvents (CD_2Cl_2, CD_3CN), PhCN, *t*-BuCN, and *n*-PrCN were stored over activated 4A molecular sieve under nitrogen, Me_3SiCN was used as supplied. Infrared spectra were recorded as CCl_4 (4000–800 cm^{-1}) or Nujol mulls between KBr plates on Perkin-Elmer 297 and 684 spectrometers. NMR spectra were measured on JEOL PMX-60 (^1H) and JEOL FX-100 (^{13}C) instruments. Melting points were determined in sealed capillaries under argon and are uncorrected. The complexes **1a–d**,[9] **3a–c**,[9] and $CpCp^*TiCl_2$ ($Cp = C_5Me_5$)[41] were prepared as described.

$[Cp_2Ti(NCMe_2)(NCMe)]BPh_4$ (2a). A solution of 1.0 g (1.81 mmol) of $[Cp_2TiMe(NCMe)]BPh_4$ (**1a**) in 20 mL of acetonitrile was stirred at room temperature for 2 weeks. The solvent was then removed and the product extracted with dichloromethane (3 × 15 mL). The filtrate was concentrated to the point of crystallization and cooled to give **2a** as light brown crystals (750 mg, 1.27 mmol, 70%): decomp pt 153–155 °C; IR (cm^{-1}) 3120 (w), 3060 (m), 2310 (m), 2280 (w), 1700 (m), 1685 (m), 1580 (m), 1480 (m), 1430 (m), 1370 (m), 1250 (w), 1020 (m), 820 (s), 740 (s), 710 (s), 705 (m), 610 (m). Anal. Calcd for $C_{39}H_{39}BN_2Ti$: C, 78.8; H, 6.56; N, 4.7. Found: C, 78.6; H, 6.50; N, 4.68.

Table V. Fractional Atomic Coordinates ($\times10^4$ for $[(Indenyl)_2Ti(NCMePh)(NCPh)]BPh_4$

	x	*y*	*z*
Ti(1)	6909 (2)	3353 (2)	6618 (2)
N(1)	7706 (5)	1759 (5)	6111 (5)
N(2)	7850 (5)	3243 (5)	8622 (5)
C(1)	8078 (6)	694 (6)	5629 (6)
C(2)	7555 (7)	279 (6)	4204 (6)
C(3)	8443 (6)	3106 (5)	9638 (5)
C(4)	9029 (4)	−200 (4)	6429 (4)
C(5)	9733 (4)	234 (4)	7709 (4)
C(6)	10577 (4)	−590 (4)	8495 (4)
C(7)	10717 (4)	−1849 (4)	8002 (4)
C(8)	10013 (4)	−2283 (4)	6723 (4)
C(9)	9169 (4)	−1458 (4)	5936 (4)
C(10)	9150 (4)	2884 (4)	10887 (4)
C(11)	9128 (4)	1744 (4)	11197 (4)
C(12)	9855 (4)	1532 (4)	12430 (4)
C(13)	10603 (4)	2459 (4)	13353 (4)
C(14)	10624 (4)	3598 (4)	13043 (4)
C(15)	9898 (4)	3811 (4)	11810 (4)
C(16)	7501 (7)	5372 (6)	6854 (7)
C(17)	7076 (7)	4833 (6)	5556 (6)
C(18)	8103 (7)	3862 (6)	5345 (6)
C(19)	9255 (6)	3819 (6)	6508 (6)
C(20)	10586 (6)	3058 (6)	6843 (6)
C(21)	11540 (7)	3269 (7)	8013 (7)
C(22)	11241 (7)	4241 (7)	8927 (7)
C(23)	9957 (8)	4984 (6)	8674 (6)
C(24)	8911 (7)	4788 (6)	7430 (6)
C(25)	4528 (7)	3271 (7)	5221 (6)
C(26)	4795 (7)	2253 (7)	5737 (7)
C(27)	5004 (6)	2597 (6)	7017 (6)
C(28)	4724 (6)	3899 (5)	7323 (5)
C(29)	4693 (7)	4722 (7)	8438 (7)
C(30)	4278 (8)	5997 (7)	8370 (7)
C(31)	3927 (8)	6377 (7)	7221 (8)
C(32)	3942 (7)	5611 (7)	6136 (8)
C(33)	4393 (6)	4365 (6)	6182 (6)
B(1)	3286 (6)	7895 (6)	3050 (6)
C(111)	3687 (4)	8882 (3)	2311 (3)
C(112)	4206 (4)	8475 (3)	1272 (3)
C(113)	4437 (4)	9329 (3)	641 (3)
C(114)	4149 (4)	10591 (3)	1049 (3)
C(115)	3630 (4)	10998 (3)	2088 (3)
C(116)	3399 (4)	10143 (3)	2719 (3)
C(211)	4177 (4)	6474 (3)	2736 (3)
C(212)	5644 (4)	6375 (3)	2783 (3)
C(213)	6353 (4)	5223 (3)	2454 (3)
C(214)	5595 (4)	4169 (3)	2078 (3)
C(215)	4129 (4)	4267 (3)	2031 (3)
C(216)	3420 (4)	5420 (3)	2360 (3)
C(311)	1467 (4)	7777 (4)	2498 (4)
C(312)	634 (4)	8130 (4)	1342 (4)
C(313)	−863 (4)	7979 (4)	858 (4)
C(314)	−1527 (4)	7474 (4)	1529 (4)
C(315)	−695 (4)	7121 (4)	2685 (4)
C(316)	802 (4)	7273 (4)	3169 (4)
C(411)	3823 (4)	8457 (3)	4638 (3)
C(412)	5285 (4)	8263 (3)	5371 (3)
C(413)	5733 (4)	8783 (3)	6658 (3)
C(414)	4720 (4)	9498 (3)	7212 (3)
C(415)	3259 (4)	9692 (3)	6479 (3)
C(416)	2810 (4)	9172 (3)	5192 (3)

Other azavinylidene complexes were prepared by analogous procedures using the appropriate nitrile but were stirred for only 24 h (cyclopentadienyl complexes) or 2–6 h (indenyl complexes).

$[Cp_2Ti(NCMePh)(NCPh)]BPh_4$ (2b): 870 mg (1.32 mmol, 78%); mp 126–128 °C; IR (cm^{-1}) 3100 (w), 3060 (m), 2262 (m), 1660 (s), 1592 (w), 1580 (m), 1480 (m), 1450 (m), 1380 (m), 1250 (w), 1180 (w), 1130 (w), 1070 (w), 1025 (m), 1010 (m), 830 (s), 820 (s), 750 (m), 730 (s), 705 (s), 680 (m), 610 (m). Anal. Calcd for

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(37) (a) Bell, R. A.; Cohen, S. A.; Doherty, N. M.; Threlkel, R. S.; Bercaw, J. E. *Organometallics* **1986**, *5*, 972. (b) Coordinated olefins are able to insert reversibly into the Nb–H bond of $Cp^*_2NbH(CH_2CHR)$ by an unimolecular pathway and the insertion product can be trapped by L = CO or MeNC as $Cp^*_2NbCH_2CH_2R(L)$ without insertion of L into the Nb–C bond: Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

(38) (a) Benfield, F. W. S.; Cooper, N. J.; Green, M. L. H. *J. Organomet. Chem.* **1974**, *76*, 49. (b) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761. (c) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27.

(39) A closely related mechanism is likely to operate in the carbometalation of alkynes catalyzed by Cp_2MCl_2 (M = Ti, Zr): (a) Van Horn, D. E.; Valente, L. F.; Idacavage, M. J.; Negishi, E. *J. Organomet. Chem.* **1978**, *156*, C20. Negishi, E.; van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, *107*, 6639 and cited references.

(40) For recent accounts of olefin polymerizations catalyzed by related complexes of trivalent metals see: (a) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (c) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (e) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *Ibid.* 8103. (f) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *Ibid.* **1987**, *109*, 203. (g) Den Haan, K. H.; Wielstra, Y.,; Eshuis, J. J. W.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *323*, 181 and cited references. (h) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(41) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.

$C_{49}H_{43}BN_2Ti$: C, 80.7; H, 5.9; N, 3.85. Found: C, 80.5; H, 5.9; N, 3.8.

[Cp$_2$Ti(NCMe-*t*-Bu)(NC-*t*-Bu)]BPh$_4$ (2c): 750 mg (1.21 mmol, 69%); mp 114–116 °C; IR (cm^{-1}) 3120 (w), 3060 (m), 2270 (m), 1679 (s), 1585 (m), 1485 (m), 1430 (m), 1370 (w), 1240 (w), 1190 (w), 1020 (m), 820 (s), 740 (s), 715 (s), 705 (m), 610 (m). Anal. Calcd for $C_{45}H_{51}BN_2Ti$: C, 79.6; H, 7.5; N, 4.1. Found: C, 79.0; H; 7.5; N, 4.0.

[Cp$_2$Ti(NCMe-*n*-Pr)(NC-*n*-Pr)]BPh$_4$ (2d): 860 mg (1.32 mmol, 77%); decomp pt 106–108 °C; IR (cm^{-1}) 3120 (w), 3060 (m), 2282 (m), 1682 (s), 1585 (m), 1485 (m), 1430 (m), 1360 (w), 1270 (m), 1185 (w), 1020 (m), 820 (s), 735 (s), 710 (s), 610 (m). Anal. Calcd for $C_{43}H_{47}BN_2Ti$: C, 79.4; H, 7.2; N, 4.3. Found: C, 79.3; H, 7.1; N, 4.3.

[Ind$_2$Ti(NCMe$_2$)(NCMe)]BPh$_4$ (4a): 620 mg (0.89 mmol, 58%); decomp pt 102–104 °C; IR (cm^{-1}) 3100 (w), 3060 (m), 2310 (w), 2282 (w), 1678 (m), 1585 (w), 1482 (m), 1430 (m), 1350 (m), 1220 (m), 830 (s), 740 (s), 710 (s), 610 (m). Anal. Calcd for $C_{48}H_{43}BN_2Ti$: C, 81.3; H, 6.2, N, 4.0. Found: C, 81.0; H, 6.2; N, 4.0.

[Ind$_2$Ti(NCMePh)(NCPh)]BPh$_4$ (4b): 740 mg (0.91 mmol, 65%); mp 106–108 °C; IR (cm^{-1}) 3100 (w), 3060 (m), 2270 (m), 1645 (s), 1590 (w), 1580 (w), 1485 (m), 1430 (m), 1380 (m), 1240 (m), 1180 (w), 830 (s), 750 (m), 730 (s), 705 (s), 610 (m). Anal. Calcd for $C_{57}H_{47}BN_2Ti$: C, 82.6; H, 5.7; N, 3.4. Found: C, 82.4; H, 5.7; N, 3.3.

[Ind$_2$Ti(NC-*t*-Bu)(NC-*t*-Bu)]BPh$_4$ (4c): 690 mg (0.89 mmol, 62%): mp 124–126 °C; IR (cm^{-1}) 3100 (w), 3060 (m), 2270 (m), 1665 (s), 1582 (m), 1480 (m), 1430 (m), 1380 (m), 1350 (w), 1235 (w), 1150 (w), 830 (s), 750 (m), 735 (s), 705 (s), 610 (m). Anal. Calcd for $C_{53}H_{55}BN_2Ti$: C, 81.7; H, 7.1; N, 3.6. Found: C, 81.2; H, 7.1; N, 3.4.

[CpCp*Ti(NCMePh)(NCPh)]BPh$_4$ (5): 260 mg (0.33 mmol, 47%); mp 88–89 °C; IR (cm^{-1}) 3160 (w), 3130 (w), 3060 (s), 2260 (m), 1658 (w), 1652 (m), 1585 (m), 1485 (s), 1452 (m), 1432 (m), 1383 (m), 1260 (s), 1190 (m), 1180 (w), 1155 (m), 1035 (m). The compound was identified by NMR and contained ca. 12% **2b** as an impurity which could not be removed satisfactorily by recrystallization.

[Cp$_2$Ti(η^2-Me$_3$SiNCMe)(CNSiMe$_3$)]BPh$_4$ (6). A mixture of 2.0 g (8.8 mmol) of Cp_2TiCl_2 and 3.0 g (8.8 mmol) of $NaBPh_4$ in 15 mL of THF was treated with 2.81 g (28 mmol) of Me_3SiCN and stirred for 1 h at room temperature. Removal of THF and extraction of the residue with CH_2Cl_2 gave a pale filtrate which was concentrated and cooled to yield **6** as colorless crystals (4.74 g, 6.6 mmol, 76%): decomp pt 98–100 °C; IR (cm^{-1}) 3120 (w), 3060 (m), 2910 (w), 2140 (s), 1715 (s), 1585 (w), 1485 (m), 1430 (m), 1270 (m), 1260 (m), 1090 (m), 1020 (m), 860 (s), 820 (s), 750 (m), 740 (s), 675 (w), 650 (w), 610 (m). Anal. Calcd for $C_{43}H_{51}BN_2Ti$: C, 72.6; H, 7.2; N, 3.9. Found: C, 71.9; H, 7.2; N, 3.9.

Kinetic Studies. Solutions of different concentrations of **1b–d** and **3a–c** in CD_2Cl_2 were prepared under argon in NMR tubes, and various amounts of nitriles were then added, at nitrile:titanium ratios ranging from 0 to 105. The reactions could be conveniently followed in the NMR spectrometer at 35 ± 0.1 °C by recording the changes in the integration of the titanium–methyl peak and the appearance of the azaalkenylidene–methyl signal. Complex **1a** is poorly soluble in CD_2Cl_2, and the reaction was monitored in neat CD_3CN. A full list of the concentrations employed is given in the supplementary material.

X-ray Structure Determination of 4b. Crystals of **4b** were grown from dichloromethane at −15 °C and obtained as light brown prisms. The specimen used for X-ray work had the dimensions 0.15 × 0.2 × 0.35 mm. The orientation matrix and cell dimensions were obtained by using standard SEARCH and INDEX routines on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 295 ± 2 K and refined by using setting angles for 25 well-spaced reflections with $9.9 \leqslant \theta \leqslant 13.9°$. The crystal system was found to be triclinic, with space group $P1$ and cell dimensions a = 9.713 (1) Å, b = 11.143 (2) Å, c = 11.363 (2) Å, α = 102.63 (1)°, β = 109.57 (1)°, γ = 80.91 (1)°, V = 1125.87 Å^3, Z = 1, and D_{calcd} = 1.21 g cm^{-3}, μ(Mo Kα) = 2.25 cm^{-1}.

Intensity data were recorded by using an $\omega/2\theta$ scan technique with $1.5 \leqslant \theta \leqslant 25°$, $\pm h,\pm k,+l$, ω scan width $\omega = (0.85 + 0.35 \tan \theta)°$, and variable scan speed between 1.2 and 6.6 deg min^{-1}, to achieve $I \geqslant 33\sigma(I)$ subject to $t_{\max}$ = 60 s. A total of 4128 data were measured, of which 3963 were unique and 2655 observed $[I > 1.5\sigma(I)]$. The data were corrected for absorption empirically; relative maximum and minimum transmission factors were 1.0 and 0.96, respectively. The structure was solved by the application of direct methods (SHELXS 86),[42] the first E map giving the positions of all non-hydrogen atoms. Refinement was by full-matrix least squares; phenyl rings of the BPh_4 anion were refined as idealized hexagons. All non-hydrogen atoms were assigned anisotropic displacement factor coefficients; hydrogen atoms were included in idealized positions with group isotropic dfc's. The final R and R_w values were 0.056 and 0.061, respectively, with 478 parameters and weights $= 1/[\sigma^2(F_o) + g(F_o)^2$ with g = 0.0006, giving acceptable agreement analysis. The maximum and minimum values on the final difference electron density map were 0.26 and −0.20 e Å^{-3}, respectively. The non-hydrogen atom coordinates are listed in Table V.

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Registry No. **1a**, 109630-95-7; **1b**, 109631-03-0; **1c**, 109631-01-8; **1d**, 110613-17-7; **2a**, 113647-07-7; **2b**, 113668-30-7; **2c**, 113647-09-9; **2d**, 113647-11-3; **3a**, 110589-70-3; **3b**, 109631-37-0; **3c**, 109631-09-6; **4a**, 113647-13-5; **4b**, 109630-91-3; **4c**, 109630-89-9; **5**, 113668-32-9; **6**, 113647-15-7; CpCp*TiMeCl, 113110-29-5; Cp_2TiCl_2, 1271-19-8; MeCN, 75-05-8; PhCN, 100-47-0; *t*-BuCN, 630-18-2; *n*-PrCN, 109-74-0; Me_3SiCN, 7677-24-9.

Supplementary Material Available: Tables of nitrile insertion rates at different nitrile:titanium ratios, fractional coordinates of hydrogen atoms, and U_{ij} values for non-hydrogen atoms (4 pages); a listing of F_o/F_c values (16 pages). Ordering information is given on any current masthead page.

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(42) Sheldrick, G. M. SHELXS86, University of Göttingen, Göttingen, FRG, 1986.