Reactivity of Bimetallic Compounds Containing Planar Tetracoordinate Carbon toward Unsaturated Organic Substrates

Paul Binger,* Frank Sandmeyer, and Carl Krüger

Max Planck Institut für Kohlenforschung, Kaiser Wilhelm Platz 1, 45466 Mülheim an der Ruhr, Germany

Received February 6, 1995[∞]

Anti van't Hoff/le Bel compound 1 consisting of titanocene tolan and diethylborane units reacts with ethene, acetylenes, phosphaacetylenes, and acetone to give metallacycles 2, 3, 6, and 7, and in most cases the corresponding diethylorganylboranes are formed by hydroboration of the carbon-carbon or carbon-heteroatom multiple bond in the substrate. With nitriles the new bimetallic systems 9a-c (X-ray structure available for 9a) with titanium and boron centers and 12 containing zirconium and aluminium centers are generated by the formal insertion of the nitrile into the $B-C_{planar}$ bond of 1 or the $Al-C_{planar}$ bond of 11.

Introduction

The synthetic and structural aspects of bimetallic complexes containing a planar tetracoordinate carbon atom bridging between a group 4 transition metal and a main group element are of current interest and have been treated extensively in recent publications.¹ For example we have successfully synthesized and characterized such anti van't Hoff/le Bel compounds that contain a zirconium or titanium atom with a boron atom.² Besides their structural characterization, the reactivity of these systems has been of great interest to use. Here we wish to report our results obtained by allowing two complexes of the type, 1 and 11, to react with selected unsaturated organic substrates.

The X-ray crystallographic studies of 1 and 11 have revealed that the bonding situation can be approximated by the two mesomeric structures \mathbf{A} (Figure 1). Since the reactivity characteristics of these complexes cannot satisfactory be given by A alone, two alternative descriptions, **B** and **C**, are shown in Figure 1 which help explain how these compounds could react with suitable substrates.

Form **B** emphasizes the fact that the transition metal-carbon interaction, M-C2, is weaker than a conventional metal-carbon σ -bond by suggesting the bonding to be an agostic interaction. This formalism is reasonable in light of the results obtained by electron deformation density measurements made on Zr/Al bimetallic systems.³ A B-C2 bond activation might result. Cleavage of this bonding interaction is equivalent to the loss of the transition metal σ -acceptor effect which has been found to be essential for the stability of these molecules.⁴ Form C is a much better description for the electronic situation than A; this form emphasizes that the anti van't Hoff/le Bel compounds contain two three-center, two-electron bonds between the transition metal M, the square planar carbon C2, the boron atom, and the hydridic hydrogen. Boranes which are connected by means of this bonding type show their typical reactions, e.g. hydroboration, after cleavage of the twoelectron, three-center bond, which results in the fragmentation of the diborane structure. The analogous chemical behavior could occur when allowing the anti van't Hoff/le Bel compounds to react with appropriate substrates.

Results and Discussion

When ethene is added to a suspension of complex 1 in pentane at ambient temperatures, a spontaneous reaction occurs to produce the titanacyclopentene 2 and triethylborane, as already reported in a preliminary communication.^{2a,5} We have now extended our studies of the reactivity of 1 to various acetylenes, to acetone as a representative of the ketone family, and to various nitriles. Complex 1 does not react with bis(trimethylsilyl)acetylene possibly due to steric factors which would exist in the expected titanacyclopentadiene. With less bulky substituted acetylenes such as tolan, phenylacetylene, and 2-butyne, metallacyclopentadienyl complexes 3a,b,d are formed in high yields at ambient temperatures.⁶ The asymmetric phenylacetylene gives only one regioisomer **3d** with the aromatic group located

^{*} Abstract published in Advance ACS Abstracts, May 15, 1995.

<sup>Abstract published in Advance ACS Abstracts, May 15, 1995.
(1) (a) Erker, G. Comments Inorg. Chem. 1992, 13, 111. (b) Erker, G. Nachr. Chem. Tech. Lab. 1992, 40, 1099. (c) Albrecht, M.; Erker, G.; Krüger, C. Synlett 1993, 441. (d) Erker, G.; Albrecht, M.; Krüger, C.; Nolte, M.; Werner, S. Organometallics 1993, 12, 4979. (e) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S. J. Am. Chem. Soc. 1992, 114, 8531. (f) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S.; Binger, P.; Landbauser, F. Organometallics 1993, 12, 3517. (g) Erker, G.</sup> Langhauser, F. Organometallics 1992, 11, 3517. (g) Erker, G.;
 Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. Chem. Ber. 1992, 125, 1953. (h) Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. J.
 Am. Chem. Soc. 1990, 112, 9620.

^{(2) (}a) Binger, P.; Sandmeyer, F.; Krüger, C.; Kuhnigk, J.; Goddard, R.; Erker, G. Angew. Chem. 1994, 106, 213; Angew. Chem., Int. Ed. Engl. 1994, 33, 197. (b) Binger, P.; Sandmeyer, F.; Krüger, C.; Erker, G. Tetrahedron 1995, 51, 4277.

^{(3) (}a) Werner, S. Dissertation, Universität Münster, **1992**. (b) Krüger, C.; Werner, S. In *Transition Metal Carbyne Complexes*; Kreissl, F. R., Ed.; NATO ASI Series C; Plenum: New York, 1993; Vol. 392, p 131.

⁽⁴⁾ Gleiter, R.; Kryspin, I. H.; Niu, S.; Erker, G. Angew. Chem. 1993, 105, 753; Angew. Chem., Int. Ed. Engl. 1993, 32, 754.

 ⁽⁶⁾ Alt, H. G.; Herrmann, G. S. J. Organomet. Chem. 1990, 390, 159.
 (6) Shur, V. B.; Burlakov, V. V.; Vol'pin, M. E. Bul. Acad. Sci. USSR 1983, 32, 1753.



Figure 1.

Scheme 1. Reactions of 1 with Ethene and Acetylenes



on the α -carbon to the metal. With tolan and phenylacetylene the corresponding hydroborated acetylenes are obtained. Phenylacetylene produced both the Markovnikov and the anti-Markovnikov vinylboranes in a ratio of 2:3, estimated by ¹H NMR spectroscopy. 2-Butyne formed one product which has not yet been isolated or identified. From ¹¹B NMR spectroscopy, however, it can be concluded that this boron organic product is not the expected vinylborane (Scheme 1). A δ ⁽¹¹B) value of 75.7 ppm should be observed for the latter. The new boron organic compound exhibits a resonance at δ = -10.6 ppm, which is in the region for borates or for carboranes.

The zirconocene complex $Cp_2Zr(PhCCPh)(\mu-H)(BEt_2)$ (5), which is structurally analogous to 1, does not react with acetylenes at ambient temperatures. When heated to 80 °C, the reactants undergo some as yet unknown transformation. No identifiable products could be observed.

The titanocene complex 1 reacts with acetone within a few minutes at ambient temperatures to give the red titanadihydrofuran 6, which has been previously described by Vol'pin.⁷ The only organoboron product formed in this reaction is diethylisopropoxyborane, which has been identified by the ¹¹B resonance at $\delta =$ 52.8 ppm.⁸ With phosphaalkynes 1 reacts readily to give the dark red titanophospholes **7a**⁹ and **7b**, bearing either a *tert*-butyl or an adamantyl substituent. Complex **7a** has been synthesized recently by the reaction of $(\eta^2$ -*tert*-butylphosphaalkyne)(trimethylphosphine)titanocene with tolan in the presence of triethylborane at ambient temperatures.⁹ The regioselectivity of this





cycloaddition as depicted in Scheme 2 is corroborated proved by the ¹³C NMR spectra of **7a** and **7b**. Both C atoms directly bonded to the transition metal exhibit resonances at considerably lower field than the β -C atoms (e.g. in **7a**: $\delta = 303.8 \text{ Ti}-\underline{C}tBu = P$, ¹ $J_{P,C} = 67.2$ Hz; 196.4 Ti- $\underline{C}Ph=C$, 118.9 Ti- $C=\underline{C}Ph$, ¹ $J_{P,C} = 30.2$ Hz). No specific boron organic product can be identified, nor could any evidence for a hydroboration of the P-C triple bond be obtained.

The reactions described so far can be explained on the basis of the reactivity patterns implicit in structure **C** as discussed above. The starting complex can be considered to undergo fragmentation to give the two components, titanocene-tolan¹⁰ and diethylborane, which then show their characteristic chemical behavior. In certain cases the diethylborane performs hydroboration reactions (where the reaction products could be identified), while the metallocene-tolan component oxidatively couples with the unsaturated organic substrate to give the corresponding five-membered ring system. Therefore diethylborane can be considered as a reversible protecting group for the titanocene-tolan complex.

A remarkably different and absolutely new reaction product is observed when acetonitrile, propionitrile, or benzonitrile is used as substrate for conversions with the titanocene anti van't Hoff/le Bel compound 1 (Scheme 3). In less than 1 h the reactions are completed in pentane at ambient temperatures. Instead of the hydroborated products and titanaazoles only complexes 9 are detected containing the borane unit as well as the titanocene-tolan fragment. The same complex type (9a) is obtained by reaction of the titanaazole 8^{11} with tetraethyldiborane at room temperature. Mass spec-

⁽⁷⁾ Shur, V. B.; Burlakov, V. V.; Yanovsky, AS.I.; Petrovsky, P. V.;
Struchkov, Yu. T.; Vol'pin, M. E. J. Organomet. Chem. 1985, 297, 51.
(8) Wrackmeyer, B; Köster, R. In Houben Weyl, Methoden der

⁽⁸⁾ Wrackmeyer, B.; Köster, R. In Houben Weyl, Methoden der organischen Chemie, Organobor-Verbindungen, Band XIII/3c; Köster, R., Ed.; G. Thieme-Verlag: Stuttgart, New York, 1984; S 440 and references cited therein.

⁽⁹⁾ Herrmann, A. T. Dissertation, University of Kaiserslautern, 1990.

⁽¹⁰⁾ Shur, V. B.; Burlakov, V. V.; Vol'pin, M. E. J. Organomet. Chem. 1988, 347, 77.

⁽¹¹⁾ Preparation as discribed for zirconium analogous: (a) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. J. Am. Chem. Soc. 1987, 109, 7137. (b) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C. Tetrahedron Lett. 1987, 28, 3245. (c) Buchwald, S. L.; Huffman, J. C.; Watson, B. T. J. Am. Chem. Soc. 1987, 109, 2544. (d) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. Tetrahedron Lett. 1993, 34, 687.

Bimetallic Compounds Containing Tetracoordinate C



Figure 2.

Scheme 3. Reaction of Nitriles with Anti-van't Hoffle Bel Complexes



trometry and the elemental analysis prove that this new compound is a 1:1 adduct of the corresponding nitrile and 1. On the basis of the NMR-spectroscopic results it is not possible to distinguish between a monocyclic and a bicyclic structure. An X-ray investigation performed with a single crystal of compound **9a** proves these complexes to contain a bicyclo[3.2.0] skeleton as shown for **9a-c** (Scheme 3) thus ruling out the monocyclic alternative **9A** (Figure 2).

The presence of hydride bridges in 9a-c can be corroborated by IR and NMR data. The proton resonances are located at high field ($\delta \approx -3.2$ ppm) in the range expected for a hydrogen atom bridging the boron and the transition metal center.¹² A nonbridging B-H hydrogen atom features proton resonance signals at δ = 3.76 - 4.40 ppm.⁸ The IR absorptions of the B-H-Ti units in 9-11 are located in the spectral range of 1675-1680 cm⁻¹, a region typical for a bridging hydride.⁸ Signals around 2340 cm⁻¹ usually belong to B-H bonds of amine adducts of dialkylboranes in which the hydrogen atoms are nonbridging.¹³ Therefore structures of the type **9B**,**C** can be excluded (Figure 2). Further IR absorptions of analytical importance can be assigned to the C=N units. Their wavenumbers appear in the region from 1585 to 1595 cm^{-1} due to the fact that the C-N double bond is part of a conjugated system.²³

Splitting of the ¹H NMR signals of the ethyl groups attached to boron into two signals with the methyl groups located at lower field as the methylene groups as well as the $\delta^{(11B)}$ values indicates that the boron atom is tetracoordinate.⁸ The boron atoms give rise to ¹¹B resonances in the region from -9.8 to -12.0 ppm, which amounts to an upfield shift of about 30 ppm compared to the absorptions of the starting complexes. The boron atoms of free imino boranes show absorptions



Figure 3. ORTEP plot of **9a** showing the atom-numbering scheme. The hydrogen atoms except the bridging hydride are omitted for clarity.

in the region of about $\delta = 30$ ppm, while their dimers feature resonances in the region of -2.3 to 11.3 ppm.⁸ As the two Cp signals give rise to only one signal in the ¹H and the ¹³C spectra, the complex must be planar. As it is difficult to imagine that a monocycloheptadiene framework is perfectly planar, this observation strongly speaks in favor of the bicyclic structures of 9a-c. Further valuable information is provided by ¹³C NMR spectroscopy. The carbon atoms C1 give rise to resonances above $\delta = 220$ ppm which is in the typical region for sp²-carbon atoms bonded to metals. Because of this feature a competing insertion of the nitrile into the metal-C1 bond can be excluded. The further question concerning the regioselectivity of the insertion remains to be answered. Of the two possibilities to be taken into consideration, Scheme 3 suggests an imino borane structure which is the result of B-N and C-C bond formation. The other possibility would be B-C and C–N bond formation to yield a vinyl borane. The $\delta^{(13)}$ C) value of the nitrile carbon atom and the boron resonance provide the information necessary to solve this problem. The C=N carbon features a sharp singlet at $\delta \simeq 180$ ppm. If this carbon atom were bonded to the boron atom, the signal would have to show a striking line broadening as a result of the quadrupole coupling with the boron nucleus. From the spectroscopic data it can be unequivocally deduced that the insertion as shown in Scheme 3 is obtained. Another question however cannot be answered by NMR or IR spectroscopy: namely whether there is a bonding interaction between the transition metal and the nitrogen atom. Whether 9a-cor 9A is the correct structure can only be answered on the basis of the interatomic distances which were obtained for 9a from the results of an X-ray investigation. Single crystals of 9a where obtained by crystallization from a pentane-toluene solution (2:1; -20 °C). The ORTEP plot of **9a** is presented in Figure 3.

Complex **9a** exhibits a planar seven-membered framework consisting of the transition metal, the carbon atoms C1, C2, and C3, the nitrogen atom, and the B-Hunit with the hydrogen atom bridging the transition and

^{(12) (}a) Kot, W. K.; Edelstein, N. M.; Zalkin, A. Inorg. Chem. **1987**, 26, 1339. (b) Erker, G.; Hoffmann, U.; Zwettler, R.; Krüger, C. J. Organomet. Chem. **1989**, 367, C15. (c) Erker, G.; Noe, R.; Wingberg-mühle, D.; Petersen, J. L. Angew. Chem. **1993**, 105, 1216; Angew. Chem., Int. Ed. Engl. **1993**, 32, 1213.

⁽¹³⁾ Köster, R.; Griasnow, G.; Larbig, W.; Binger, P. Liebigs Ann. Chem. **1964**, 672, 1.





the main group element. The skeleton is located in the plane bisecting the Cp(centroid)-Ti-Cp(centroid) angle. As the phenyl groups attached to C1 and C2 are twisted out of this plane, a stabilizing interaction of the aromatic ring systems with the C1-C2 double bond can be excluded. The boron atom is tetrahedrally coordinated with a bonding interaction to the nitrogen atom. Up to this point the routine spectroscopic results are fully confirmed. The vexing question as to whether there is a Ti-N interaction or not can now be answered by examining the most interesting datum, namely the distance between the Ti and the N atom. A separation of 2.075(2) Å is found for this pair of atoms. This value is within the range expected for a Ti-N bond with the nitrogen atom bonded to a sp²-hybridized carbon atom¹⁴ and indicates unequivocally the existence of a strong Ti-N interaction. This finding permits one to designate **9a-c** as the correct structures for these new complexes. Ti-N bonds in dialkylamides and bis(trimethylsilyl)amides are considerably shorter, e.g. 1.88 Å in CpTiCl₂- $[N(SiMe_3)_2]^{15}$ and 1.89 Å in $Fe[C_5H_4Ti(NEt_2)_3]$.¹⁶

Pure Ti-N donor interactions are long by comparison, 2.293Å in complex e.g. \mathbf{the} pyridine

 $Ti(OC_6H_3^tBuMe_2CH_2)(OC_6H_3^tBu_2)(CH_2SiMe_3)(py)^{14b}$ or

the pyridine-2,6-dicarboxylato compound Cp₂Ti[C₅H₃N-

 $2,6-(CO_2)_2$] (2.160 Å).¹⁷ **9a** can very well be compared to the complex $[Ti(salen)(BH_4)_2]\cdot 2thf^{18}$ (10) (salen = N,N'-ethylenebis(salicylideniminate), $C_{16}H_{16}N_2O_2$), which also exhibits a four-membered system consisting of Ti, B, N, and H. An averaged transition metal-nitrogen bond distance of 2.14 Å is found in this compound. Further bond distances and angles are listed in Table 1. The B–N distance of 9a (1.515(4) Å) and those found in the Ti-salen complex (average 1.54 Å) are almost identical. Furthermore B-N distances in the range from 1.4 to 1.6 Å are rather common for organic boron compounds.¹⁹ This result clearly support a strong boron nitrogen interaction in 9a. The B-H bond length in **9a** (1.37(3) Å) is comparable to the corresponding value determined for 10 (averaged value: $d_{av}(B-H) = 1.3(1)$ Å) whereas the Ti–H bond is remarkably longer in **9a** (2.01(3) Å) than in 10 $(d_{av}(\text{Ti}-\text{H}) = 1.8(1) \text{ Å})$.

Formally the new compounds can be considered as insertion products of the corresponding nitrile into the boron $-C_{planar}$ bond, but this is quite unlikely, because

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 9a

Distances						
Ti-C1	2.289(2)	C1-C2	1.362(3)			
Ti–N	2.075(2)	C2-C3	1.475(4)			
Ti-H	2.01(3)	N-C3	1.276(3)			
Ti-B	2.688(3)	B-H	1.37(3)			
B-N	1.515(4)					
Angles						
H-Ti-C1	135.8(8)	B-N-Ti	95.7(2)			
H–Ti–N	63.7(8)	C3-C2-C1	114.6(2)			
C1-Ti-N	72.3(1)	C1-C2-Ti	43.0(1)			
B–H–Ti	103(2)	C2-C1-Ti	113.0(2)			
C3-N-B	139.4(2)	H-B-N	96.7(1)			

in numerous insertion reactions of nitriles into Ti- or Zr-cyclic systems reported usually the nitriles insert into the bond of the group 4 transition metal to the carbon atom but not into a metal-heteroatom bond.²⁰

As the titanaazole 8 can be converted with tetraethyldiborane to give 9a as well, we assume as an more likely alternative a fragmentation mechanism which could satisfactorily explain the formation of 9a-c. As outlined in Scheme 4, this mechanistic concept designates three reaction steps starting with the fragmentation of 1 to give titanocene-tolan and diethylborane fragments. The subsequent oxidative coupling of the nitrile with the tolan in the coordination sphere of the transition metal leads to the titanaazole intermediate. Up to this point the reaction would be identical to what has been observed when allowing 1 to react with carbon-carbon multiple bonds or with acetone. The deviation from the pattern shown in these reactions is to be seen in the third reaction step, namely the adduct formation leading to 9a-c instead of leading to the hydroboration of the nitrile.

This reaction type resulting from the interaction between a titanacycle and a boron hydride is yet unknown in literature. Erker and co-workers observed an insertion of 9-bis(borabicyclononane) (9-BBN) and diisobutylaluminum hydride²¹ into the zirconiumcarbon bond of the dimeric zirconocene η^2 -formaldehyde complex. In the course of these reactions the original ring system is enlarged by incorporation of the B-H or the Al-H unit.

On the basis of the above mentioned analytical data. the bonding properties of the complexes 9a-c can be described as follows: The four-membered ring consisting of Ti, N, B, and H represents an electron-deficient unit with only six electrons available to form four bonds.

^{(14) (}a) Bochmann, M.; Wilson, M. L. Organometallics 1987, 6, 2556. (b) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. J. Am. Chem. Soc. **1987**, 109, 390.
(15) Bochmann, M.; Wilson, M. L. Organometallics **1987**, 6, 2556

and literature cited therein.

⁽¹⁶⁾ Thewalt, U.; Schomburg, D. Z. Naturforsch. 1975, 30B, 636.

⁽¹⁷⁾ Leik, R.; Zsolnai, L.; Huttner, G.; Neuse, E. W.; Brintzinger,

H. H. J. Organomet. Chem. 1986, 312, 177. (18) Dell'Amico, G.; Marchetti, F.; Floriani, C. J. Chem. Soc., Dalton Trans. 1982, 2197.

⁽¹⁹⁾ Allen, F. H.; Kennard, O.; Watson, G. D.; Brammer, L.; Orpen, A. G.; Taylor, R. J. Chem. Soc., Perkin Trans. 2 1987, 1.

^{(20) (}a) Reviews: Doxsee, K. M.; Mouser, J. K. M.; Farahi, J. B. Synlett 1992, 13. Buchwald, S. L.; Nielsen, R. B. Chem. Rev. 1988, 88, 1047. (b) Doxsee, K. M.; Mouser, J. K. M. Organometallics 1990, 60, 1041. (d) Douber, I. M., House, J. H. M. Organometaria, 100, 9, 3012. (e) Meinhard, J. D.; Grubbs, R. H. Bull. Chem. Soc. Jpn. 1988, 61, 171. (d) Erker, G.; Humphrey, M. G. J. Organomet. Chem. 1989, 378, 163. (e) Fisher, R. A.; Buchwald, S. L. Organometallics 1990, 9, 871

^{(21) (}a) Bendix, M.; Grehl, M.; Fröhlich, R.; Erker, G. Organometallics 1994, 13, 3366. (b) Erker, G.; Sosna, F.; Hoffmann, U. J. Organomet. Chem. 1989, 372, 41. (c) Erker, G.; Hoffmann, U.; Zwettler, R.; Krüger, C. J. Organomet. Chem. 1989, 367, C15.

Bimetallic Compounds Containing Tetracoordinate C



Figure 4.



We suggest that the bond between Ti, H, and B be considered as a three-center, two-electron bond. The bonding interaction between the nitrogen atom and the titanium should be a normal σ -bond as in the titanaazole 8, on the basis of crystallographic data. The nitrogen lone pair should provide the electrons for the bond between N and B, thus forming a donor-acceptor bond. The latter conclusion is drawn by analogy with the bonding situation found in the dimeric zirconaazole complex $Cp_2Zr(C_6H_4)(RCN)$,²² derived from the reaction of an in situ-generated zirconocene-benzyne complex and a nitrile. This complex is dimeric due to the interactions of the nitrogen lone pairs with the zirconium atoms. Furthermore, the high-field position of the boron resonance can be explained by assuming that the nitrogen lone pair compensates for the electron deficiency of the boron atom.

The results obtained by allowing 1 to react with nitriles were not reflected in the reactions of the analogous zirconium-boron compounds. These complexes decompose slowly in the presence of the nitrile. In contrast to this, the zirconium aluminum compound $Cp_2Zr(PhCCPh)(\mu-Cl)(AlMe_2)$ (11) reacts readily with acetonitrile to give the expected bicyclic ring system 12 (Scheme 5).

The reaction takes 2 days at ambient temperature for completion. The product was found to be analogous to the boron-containing complexes 9a-c by comparison of the appropriate spectroscopic data.

The framework carbon atoms C1, C2, and C3 give rise to ¹³C resonances at 222.5, 148.4, and 190.2 ppm which are located in the expected spectral regions. The methyl carbon atoms of the dimethylaluminum unit show a δ -(¹³C) value at -6.8 ppm and the anticipated high-field resonance at $\delta = -0.65$ ppm in the corresponding proton spectrum. The stretching frequency of the conjugated C=N unit is identified at 1585 cm⁻¹ in the IR spectrum. Compared with the values found for isolated C-N double bonds, this amounts to a shift of about 100 cm⁻¹ to lower wavenumbers.

By means of X-ray crystallographic studies, the Zr-Nbond length has been determined to be 2.228 Å which is the usual range for a zirconium-nitrogen bond. For comparison Zr-N distances of 2.229 and 2.236 Å have been found for the 1-zirconabicyclo[3.2.0^{1.5}]hepta-3.6-

(22) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C. Tetrahedron Lett. 1987, 28, 3245.



Figure 5. ORTEP plot of 12 showing the atom-numbering scheme. The hydrogen atoms are omitted for clarity.

diene system Cp₂Zr(^tBu)CPNNC(^tBu)P(Me₂)²³ and the 1-zirconabicyclo[$4.2.0^{1.6}$]heteroocta-4.7-diene Cp₂Zr(^tBu)CPNNC(H)C(OMe)O²³ for which the Zr-N bonds are considered to be σ -bonds. A slightly shorter Zr-N bond length of 2.142 Å has been found in the ketenimine complex Cp₂Zr(η^2 -Ph₂CCNPh)(PMe₃).²⁴ On the basis of interatom separations, the transition metalnitrogen interaction is found to be rather strong. For the atom pair Al and N a bond distance of 1.888(2) Å is found which corresponds very nicely to the corresponding value already discussed for the analogous titaniumnitrogen bond in compound **9a** when taking the larger atomic radius of aluminum into account.

12 can also be prepared by reacting the zirconaazole

 $Cp_2Zr(PhCCPh)(MeCN)$ (13)¹¹ with dimethylaluminum chloride. When equimolar amounts of these two reagents are heated in toluene to 60 °C for 2 days, the complex 12 is obtained in 44% yield. Besides 12 the new compound 14 (ratio 12:14 = 10:3 as judged by the ¹H NMR intensities) is formed in the course of this reaction. 14 is analogous to 12 containing a methylaluminum dichloride fragment instead of dimethylaluminum chloride. The formation of 14 may be the result of the disproportionation of the aluminum organic reagent to give trimethylaluminum and methylaluminum dichloride during the reaction.

Experimental Section

General Considerations. The preparations and handling of organometallic compounds were carried out in an inert argon atmosphere using Schlenk-type glassware. Solvents (pentane, toluene) were dried with sodium/potassium and distilled prior to use. Product characterization was performed by use of routine spectroscopic and physical methods. TMS serves as the standard for carbon and proton spectroscopy and

⁽²³⁾ Binger, P.; Herrmann, A. T. Unpublished results. Herrmann, A. T. Dissertation, University Kaiserslautern, 1990.

⁽²⁴⁾ Binger, P.; Langhauser, F. Unpublished results. Langhauser, F. Dissertation, University Kaiserslautern, 1991.



Table 2.Selected Bond Lengths (Å) and Angles(deg) for 12

Distances						
Zr-C1	2.363(3)	Al-N	1.888(2)			
Zr–N	2.228(2)	C1-C2	1.359(4)			
Zr-Cl	2.928(1)	C2-C3	1.479(4)			
Al-Cl	2.247(1)	N-C3	1.285(3)			
Angles						
Al-Cl-Zr	83.8(1)	Cl-Zr-N	72.0(1)			
N-Al-Cl	91.3(1)	N-Zr-Cl	68.7(1)			
C3–N–Zr	119.5(2)	C3-N-Al	124.7(2)			
C2-C1-Zr	113.6(2)	Al-N-Zr	115.8(1)			
C2-C3-N	118.9(2)	C3-C2-C1	116.1(2)			

Table 3. Details of the Data Collection and
Structure Solution of 9a and 12

	9a ^{<i>a</i>}	12	
mol formula	C ₃₀ H ₃₄ TiBN	C ₂₈ H ₂₉ AlClNZr	
mol wt	467.3	533.2	
cryst color	yellow	light yellow	
cryst syst	monoclinic	monoclinic	
space group [no.]	$P2_{1}/c$ [14]	$P2_1/n$ [14]	
a, Å	16.493(3)	15.568(2)	
b, Å	8.100(1)	11.066(1)	
<i>c</i> , Å	19.086(2)	15.840(3)	
β , deg	101.78(1)	113.42(1)	
V, Å ³	2496.0	2504.1	
Ζ	4	4	
$D_{\rm calcd}, {\rm g}~{\rm cm}^{-3}$	1.24	1.41	
μ , cm ⁻¹	3.55	5.89	
λ (K α radiation), Å	0.710 69	0.710 69	
<i>F</i> (000), e	992	1096	
diffractometer	Enraf-Nonius CAD4		
scan mode	$\omega - 2\theta$	$\omega - 2\theta$	
$[(\sin \theta)/\lambda]_{\rm max}, {\rm \AA}^{-1}$	0.65	0.65	
T, °C	20	-173	
no. of measd rflns	$6276(\pm h,+k,+l)$	$6240(\pm h,\pm k,\pm l)$	
no. of indep reflns	5687	5722	
no. of obsd rflns $(I \ge 2\sigma(I))$	4240	5285	
no. of refined params	302	289	
R	0.055	0.035	
$R_{\rm w} \left(w = 1/\sigma^2(F_{\rm o}) \right)$	0.064	0.063	
resid electron dens, e Å ⁻³	0.97	1.02	
structure solution	heavy-atom method		

^a The H1 atom position has been found and included in the final refinement stages. The other H atom positions were calculated and kept fixed in the final refinement stages.

 H_3PO_4 for ³¹P NMR spectroscopy. The starting complexes 1 and 11 were prepared according to literature procedures.² Details of the X-ray crystallographic analysis (data collection and the structure solution) of **9a** and **12** are given in Table 3.

Reaction of 1 with Ethylene. Ethylene is passed through a solution of 0.5 g (1.2 mmol) of 1 in 15 mL of toluene at ambient temperatures for 5 min. The color changes almost immediately from orange to dark red. The solvent is removed in vacuo, the residue is suspended in 10 mL of pentane, and the red precipitate of 2 is filtered off. Yield: 0.44 g (95%). Triethylborane is obtained as the only organoboron product. When the reaction is performed in an NMR tube, no products other than the titanacycle and triethylborane can be detected. Anal. Calcd for $C_{26}H_{24}Ti$ (384.4): C, 81.25; H, 6.25. Found: C, 81.66; H, 6.30. ¹H NMR ([D₈]-THF, 29 °C, 300.1 MHz) (δ): 1.57, 2.81 (t, 4H, CH₂, ³J_{HH} = 6.7 Hz), 6.27 (s, 10H, Cp), 6.92– 6.42 (m, 10H, Ph). ¹³C NMR ([D₈]-THF, 29 °C, 75.5 MHz) (δ -

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) with Standard Deviations in Parentheses of Complex 9a^a

atom	x	у	z	$U_{ m eq}$
Ti1	0.8313(1)	0.0206(1)	0.3036(1)	0.041(1)
N1	0.7626(1)	-0.1327(3)	0.3563(1)	0.044(1)
B1	0.8202(2)	-0.1199(4)	0.4288(2)	0.053(2)
C1	0.7166(1)	-0.0617(3)	0.2223(1)	0.038(1)
C2	0.6728(1)	-0.1820(3)	0.2479(1)	0.039(1)
C3	0.7010(2)	-0.2183(3)	0.3247(1)	0.042(1)
C4	0.8688(2)	-0.2867(4)	0.4583(2)	0.063(2)
C5	0.9459(2)	-0.2692(5)	0.5168(2)	0.098(3)
C6	0.7768(3)	-0.0271(6)	0.4885(2)	0.111(3)
C7	0.8211(4)	0.0354(8)	0.5516(3)	0.169(6)
C11	0.6850(2)	0.0044(3)	0.1486(1)	0.042(1)
C12	0.7329(2)	0.0288(4)	0.0977(1)	0.054(2)
C13	0.6994(2)	0.0905(4)	0.0300(2)	0.067(2)
C14	0.6175(2)	0.1323(4)	0.0126(2)	0.070(2)
C15	0.5689(2)	0.1145(4)	0.0627(2)	0.065(2)
C16	0.6025(2)	0.0517(3)	0.1300(1)	0.051(2)
C21	0.6051(2)	-0.2815(3)	0.2037(1)	0.045(2)
C22	0.6211(2)	-0.3696(4)	0.1462(2)	0.061(2)
C23	0.5603(3)	-0.4633(4)	0.1035(2)	0.083(3)
C24	0.4832(3)	-0.4716(5)	0.1172(2)	0.089(3)
C25	0.4656(2)	-0.3874(5)	0.1739(2)	0.080(3)
C26	0.5257(2)	-0.2902(4)	0.2170(2)	0.062(2)
C31	0.6621(2)	-0.3476(4)	0.3627(2)	0.060(2)
C81	0.8725(2)	-0.1635(4)	0.2185(2)	0.054(2)
C82	0.8938(2)	-0.2391(4)	0.2856(2)	0.056(2)
C83	0.9562(2)	-0.1434(4)	0.3281(2)	0.064(2)
C84	0.9718(2)	-0.0072(4)	0.2886(2)	0.068(2)
C85	0.9197(2)	-0.0184(4)	0.2202(2)	0.062(2)
C91	0.7452(2)	0.2576(4)	0.2706(2)	0.076(2)
C92	0.7588(2)	0.2421(4)	0.3449(2)	0.064(2)
C93	0.8431(2)	0.2700(4)	0.3714(2)	0.067(2)
C94	0.8806(2)	0.2989(4)	0.3155(2)	0.078(3)
C95	0.8200(3)	0.2904(4)	0.2520(2)	0.082(3)
H1	0.873(2)	-0.006(3)	0.410(1)	0.065(9)

^a $U_{eq} = \frac{1}{3} ij Uij a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$.

Reaction of 1 with Diphenylacetylene. To a suspension of 1.0 g (2.3 mmol) of 1 in 30 mL of pentane is added a solution of 1.0 g (5.6 mmol) of diphenylacetylene in 10 mL of diethyl ether at room temperature. The suspension slowly changes its color from yellowish green to dark green. The reaction mixture is stirred for 21 h. The green product **3a** is filtered off. To complete the isolation the mother liquor is cooled to -78 °C and a further crop of **3a** is obtained: yield 0.8 (65%); dec 134 °C; identification by comparison with the data of an authentic sample.²⁵ The residue is dried in vacuo. A green viscous oil is obtained which contains as the organoboron product the hydroborated tolan **4a**. Furthermore, stilbene, tolan, and small amounts of the titanacycle **3a** could be identified (¹H NMR).

Reaction of 1 with 2-Butyne. To a solution of 1.2 g (2.8 mmol) of 1 in 35 mL of toluene is added by syringe 0.4 g (0.6 mL, 7.4 mmol) of 2-butyne. After 5 min of stirring at room temperature, the color of the reaction mixture has changed from orange to dark green. Suspended particles are filtered off, the solvent is removed in vacuo, and the residue is suspended in pentane. The green precipitate of 3d is filtered off. Upon cooling of the mother liquor to -78 °C, another crop of the product 3d is obtained: yield 1.1 g (93%); dec 126 °C. No organoboron product can be isolated in the pure state or be identified unequivocally (¹H NMR ([D₈]-THF, 27 °C, 200.1 MHz) (δ): 5.37 (q, J_{HH} = 6.0 Hz), 1.15 (s), 1.10 (s), 0.77 (t, J_{HH} = 7.8 Hz), 0.50 (t, 7.5 Hz), 1.59 (d, J_{HH} = 6.4 Hz), 1.54 (s). ¹¹B

⁽²⁵⁾ Alt, H.; Rausch, M. D. J. Am. Chem. Soc. 1974, 96, 5936.

NMR ([D₈]-THF, 27 °C, 64.2 MHz) (δ): 10.6 ($H_{1/2} = 115$ Hz). Anal. Calcd for C₂₈H₂₆Ti (410.4): C, 81.95; H, 6.34. Found: C, 81.78; H, 6.46. ¹H NMR ([D₈]-THF, 29 °C, 300.1 MHz) (δ): 1.25, 1.42 (s, 6H, Me), 6.21 (s, 10H, Cp), 6.98–6.56 (m, 10H, Ph). ¹³C NMR ([D₈]-THF, 29 °C, 75.5 MHz) (δ [¹J_{C,H}]): 198.4 (s, Ti-C(Ph)=), 137.5 (s, =C(Ph)), 197.2 (s, Ti-C(Me)=), 127.1 (s, =C(Me)), 16.4, 20.9 (q, Me [125, 124 Hz]), Ph 148.8 (s), 143.2 (s), 130.8 (d), 127.6 (d), 125.1 (d), 123.1 (d), 127.7 (d), 127.3 (d). MS (70 eV): the sample decomposes in the temperature range 50–350 °C without giving identifiable fragments.

Reaction of 1 with Phenylacetylene. To a suspension of 1.2 g (2.8 mmol) of 1 in 45 mL of pentane is added by syringe 0.6 g (5.9 mmol) of phenylacetylene. After 30 min of stirring at ambient temperatures, the suspension has become dark green. The product 3b is filtered off. Another crop of 3b is obtained upon reducing the filtrate to two-thirds of its volume and cooling to -78 °C: yield 1.2 g (93%); dec 132 °C. The solvent is removed in vacuo. A green viscous residue is obtained which contains the Markovnikov and the anti-Markovnikov hydroboration products of phenylacetylene (1H, ¹¹B NMR). ¹H NMR ([D₈]-THF, 29 °C, 300.1 MHz) (δ): 6.25 (s, 10H, Cp), 6.35 (s, 1H, =CH), 7.19–6.41 (m, 15H, Ph) $^{13}\text{C-}$ NMR ([D₈]-THF, 29 °C, 75.5 MHz) (δ [$^{1}J_{\text{C,H}}$]): 200.3 (s, Ti-C(Ph)=), 130.8 (s, =C(Ph)), 199.4 (s, Ti-C(Ph)=C(H)), 133.5 (d, =C(H) [158 Hz]), Ph 143.7 (s), 145.5 (s), 149.8 (s), 127.8 (d), 127.9 (d), 129.8 (d), 125.5 (d), 125.7 (d), 124.1 (d), 128.3 (d), 128.5(d), 128.1 (d).

Reaction of 1 with Acetone. To 1.1 g (2.6 mmol) of 1 in 30 mL of pentane is added by syringe 0.6 mL (0.4 g, 6.7 mmol) of acetone. After 2 h of stirring at ambient temperatures, the suspension has changed its color from orange to red. The red precipitate of 6 is filtered off. Further product is obtained upon cooling the mother liquor to -78 °C: yield 1.0 g (93%); dec 122 °C. Anal. Calcd for C₂₇H₂₆TiO (414.4): C, 78.26; H, 6.28. Found: C, 77.98; H, 6.20. ¹H NMR ([D₈]-THF, 29 °C, 300.1 MHz) (d): 1.27 (s, 6H, Me), 6.27 (s, 10H, Cp), 7.04-6.68 (m, 10H, Ph). ¹³C-NMR ([D₈]-THF, 29 °C, 75.5 MHz) (δ [¹J_{C,H}]): 192.4 (s, Ti–C(Ph)=), 159.4 (s, =C(Ph)), 91.3 (s, O–C), 27.9 (q, CH₃ [126 Hz]), 116.5 (d, Cp, [173 Hz]), Ph 150.8 (s), 143.9 (s), 130.3 (d), 127.7 (d), 127.3 (d), 123.7 (d), 125.9 (d), 127.4 (d). MS (70 eV, 125 °C) (m/z (intensity [%])): 178 (Cp₂Ti [100], 236 (M - PhCCPh [12]), 113 (CpTi [10]), 414 (M [4]). IR (KBr): $\bar{\nu} = 1150, 965 \text{ cm}^{-1} (\text{C-O})$. From the mother liquor of 6 the solvent is removed in vacuo. A viscous red oil is obtained which contains the hydroborated acetone as the only boron organic compound (identified by its proton and ¹¹B NMR properties)⁸ besides small amounts of **6** and minor amounts of impurities.

Reaction of 1 with *tert*-Butylphosphaalkyne. To a suspension of 1.0 g (2.3 mmol) of 1 in 30 mL of pentane is added by syringe 0.5 g (5.0 mmol) of ^tBuCP.²⁶ After 2 h the reaction is complete. The suspended red product **7a** is filtered off: yield 1.0 g (95%); dec 112 °C. Anal. Calcd for C₂₉H₂₉TiP (456.4): C, 76.31; H, 6.40. Found: C, 75.40; H, 6.26. ¹H NMR ([D₈]-THF, -30 °C, 200.1 MHz) (δ): 1.46 (d, 9H, ^tBu; ⁴J_{P,H} = 0.7 Hz), 6.01 (s, 10H, Cp), 7.18-6.87 (m, 10H, Ph). ¹³C NMR ([D₈]-THF, -30 °C, 50.3 MHz) (δ [¹J_{C,H}]): 196.4 (s, Ti-C(Ph), ²J_{P,C} = 63.5 Hz), 118.9 (s, =C(Ph), ¹J_{P,C} = 30.2 Hz), 303.8 (s, C=P, ¹J_{P,C} = 67.2 Hz), 49.9 (s, Me₃C, ²J_{P,C} = 17.6 Hz), 37.0 (q, CH₃ [125 Hz]), 112.3 (d, Cp [175 Hz]), Ph 147.5 (s), 151.2 (s), 128.5 (d), 127.9 (d), 125.4 (d), 124.8 (d), 130.1 (d). ³¹P NMR ([D₈]-THF, -30 °C, 121.0 MHz) (δ): 121.1 ppm (s). MS (70 eV, 75-250 °C): decomposition of the sample.

Reaction of 1 with 1-Adamantylphosphaalkyne. To a suspension of 1.2 g (2.8 mmol) of 1 in 40 mL of pentane is added 0.75 g (4.2 mmol) of 1-AdCP. After 2 h **7b** is filtered off as a red precipitate: yield 1.4 g (93%); dec 136 °C. Anal. Calcd for $C_{3b}H_{35}$ TiP (534.5): C, 78.65; H, 6.54; P, 5.81. Found: C, 77.82; H, 6.68; P, 5.74. ¹H NMR ([D₈]-THF, 27 °C,

200.1 MHz) (δ): Ad, 2.19, 2.07, 1.90, 1.82, 1.70 (15H), 6.00 (s, 10H, Cp), 7.20–6.79 (m, 10H, Ph). ¹³C NMR ([D₈]-THF, 27 °C, 50.3 MHz) (δ [¹J_{C,H}]): 195.0 (s, Ti–C(Ph=, ²J_{P,C} = 63.8 Hz), 115.2 (s, =C(Ph), ¹J_{P,C} = 31.2 Hz), 338.9 (s, C=P, ¹J_{P,C} = 67.7 Hz), Ad 50.1 (s), 49.8 (t [126 Hz]), 31.2 (d [129 Hz]), 37.9 (t [126 Hz]), 112.1 (d, Cp [173 Hz]), Ph 148.3 (s), 148.1 (s), 130.9 (d), 128.8 (d), 127.9 (d), 127.4 (d), 125.4 (d), 124.7 (d). ³¹P NMR ([D₈]-THF, 27 °C, 81.0 MHz) (δ): 113.8 ppm (s). MS (70 eV, 100–300 °C) (*m*/*z* (intensity [1%])): 178 (Cp₂Ti, PhCCPh, AdCP [100]).

Upon removal of the solvent, a red oil is obtained in which no product could be identified.

Reaction of 1 with Acetonitrile. To 1.3 g (3.1 mmol) of 1 in 45 mL of toluene is added by syringe 0.4 mL (0.3 g, 7.3 mmol) of acetonitrile. After 5 min the suspension becomes clear and the color changes from orange to red. Suspended particles are filtered off, the toluene is removed in vacuo, and the residue is suspended in pentane. The yellow precipitate of 9a is filtered off and the mother liquor cooled to -20 °C to crystallize further product: yield 1.2 g (83%); dec 142 °C. The filtrate is evaporated to dryness. No further product was identified. Anal. Calcd for C₃₀H₃₄TiBN (467.3): C, 77.09; H, 7.28; N, 3.00; B, 2.36. Found: C, 76.89; H, 7.01; N, 2.95; B, 2.39. ¹H NMR ([D₈]-THF, 29 °C, 300.1 MHz) (δ): -3.22 (s, $H_{1/2} = 75$ Hz, 1H, μ -H), 1.94 (s, 3H, NC-CH₃), 1.06 (t, 6H, CH_3 , ${}^{3}J_{H,H} = 7.7 Hz$, 0.66, 0.38 (ddq, 4H, B- CH_2 , ${}^{2}J_{H,H} = 14.1$ Hz, ${}^{3}J_{H,H} = 7.7$ Hz, ${}^{3}J_{H,u-H} = 1.6$ Hz), 6.80-7.15 (m, 10H, Ph); 5.66 (s, 10H, Cp). ¹³C NMR ([D₈]-THF, 29 °C, 75.5 MHz) (δ [${}^{1}J_{C,H}$]): 223.4 (s, Ti–C(Ph)=), 147.5 (s, =C(Ph)), 179.6 (s, C=N), 23.8 (q, NC-CH₃ [127 Hz]), 15.0 (t, B-CH₂), 12.8 (q, $B-CH_2-CH_3\;[124\;Hz]),\;107.0\;(d,\;Cp\;[175\;Hz]),\;Ph\;153.1\;(s),$ 142.3 (s), 131.4 (d), 127.4 (d), 128.0 (d), 128.1 (d), 126.1 (d), 124.7 (d). ¹¹H B NMR ([D₈]-THF, 27 °C, 64.2 MHz) (δ): -12.0 ppm ($H_{1/2} = 167 \text{ Hz}$). MS (70 eV, 135 °C) (m/z (intensity [%])): 178 (Cp₂Ti, PhCCPh [100]), 219 (Cp₂Ti(MeCN) [14]), 41 (MeCN $\label{eq:main_second} \hbox{\tt [12]), 438} \ (M-Et \ \hbox{\tt [7]), 401} \ (M-Ph \ \hbox{\tt [7]), 398} \ (M-BEt_2 \ \hbox{\tt [3]), 467}$ (M, [2]). IR (KBr): $\bar{\nu} = 1675 \text{ cm}^{-1} (B-H-Ti); 1590 \text{ cm}^{-1}$ (C=N)

Reaction of 8 with Tetraethyldiborane. A mixture of 1.3 g (3.3 mmol) of the titanaazole **8** in 45 mL of toluene and 0.4 mL (0.3 g, 2.3 mmol) of tetraethyldiborane is stirred for 4 days at room temperature. The color changes from brown to green. Suspended particles are filtered off, the toluene is removed in vacuo, and the residue is suspended in pentane. The yellow precipitate of **9a** is filtered off. The isolation is completed upon cooling of the mother liquor to -20 °C. Yield: 1.0 g (65%).

Reaction of 1 with Propionitrile. To a solution of 1.4 g (3.3 mmol) of 1 in 35 mL of toluene is added by syringe 0.4 g (0.5 mL, 7.3 mmol) of propionitrile. After 15 min the suspension has become clear and dark red. Suspended particles are filtered off, the solvent is removed in vacuo, and the residue is suspended in pentane. The yellow precipitate of $\mathbf{9b}$ is filtered off, half of the pentane is removed in vacuo, and the mother liquor is cooled to -78 °C for further product crystallization: yield 1.4 g (97%); dec 204 °C. Anal. Calcd for C₃₁H₃₆TiBN (481.4): C, 77.33; H, 7.48; N, 2.91; B, 2.29. Found: C, 75.24; H, 7.65; N, 2.96; B, 2.45. ¹H-NMR ([D₈]-THF, 27 °C, 200.1 MHz) (δ): -3.24 (s, $H_{1/2} = 24$ Hz, 1H, μ -H), 2.41 (q, 2H, NC-CH₂, ${}^{3}J_{H,H} = 7.4$ Hz), 0.67 (t, 3H, NC-CH₂- CH_{3} , ${}^{3}J_{H,H} = 7.4 Hz$), 0.44, 1.08 (m, 4H, B– CH_{2}), 1.12 (t, 6H, $\begin{array}{l} \mathrm{B-CH_2-CH_3,\ ^3J_{\mathrm{H,H}}=7.5\ Hz),\ 7.12-6.80\ (m,\ 10\mathrm{H},\ \mathrm{Ph}),\ 5.62\\ \mathrm{(s,\ 10\mathrm{H},\ Cp).\ ^{13}\mathrm{C}\ NMR\ ([\mathrm{D_8]-THF,\ 27\ ^{\circ}\mathrm{C},\ 50.3\ MHz)\ (\delta\ [^{1}J_{\mathrm{C,H}}]):} \end{array}$ 224.4 (s, Ti-C(Ph)=), 146.6 (s, =C(Ph)), 184.5 (s, C=N), 107.0 (d, Cp [175 Hz]), Ph 153.0 (s), 142.1 (s), 131.4 (d), 128.1 (d), 127.3 (d), 126.2 (d), 124.8 (d), 30.6 (t, NC -CH2 [129 Hz]), 15.7 (t, $B-CH_2$, ${}^{1}_{JC,H}$ superposed), 11.9 (q, $NC-CH_2-CH_3$ [123 Hz]), 13.0 (q, B-CH₂-CH₃ [127 Hz]). ¹¹B NMR ([D₈]-THF, 27 °C, 64.2 MHz) (δ): 11.2 ppm ($H_{1/2} = 542$ Hz). MS (70 eV, 210 °C) (m/z (intensity [%])): 178 (Cp₂Ti, PhCCPh [100]), 233 $(Cp_2Ti(EtCN) [12]), 113 (CpTi [11]), 452 (M - Et [11]), 481$ (M [3]). IR (KBr): $\bar{\nu} = 1680 \text{ cm}^{-1} (B-H-Ti); 1595 \text{ cm}^{-1} (C=N).$

⁽²⁶⁾ Rösch, W.; Vogelbacher, U.; Allspach, T.; Regitz, M. J. Organomet. Chem. 1986, 306, 39.

Reaction of 1 with Benzonitrile. A 1.0 g (2.3 mmol) amount of the titanocene complex 1 and 0.5 g (0.5 mL, 4.9 mmol) of benzonitrile are mixed in 35 mL of toluene. After 45 min the color has changed from orange to red and a solution was formed. Suspended particles are filtered off, the solvent is removed in vacuo, and the residue is suspended in pentane. Filtration yields the first crop of 9c as a yellow precipitate. Further product can be crystallized upon cooling the mother liquor to -20 °C: yield 1.1 g (90%); dec 224 °C. Anal. Calcd for C₃₅H₃₆TiBN (529.5): C, 79.40; H, 6.81; N, 2.65; B, 2.08. Found: C, 79.63; H, 6.76; N, 2.50; B, 2.00. ¹H NMR ([D₈]-THF, 27 °C, 200.1 MHz) (δ): -3.22 (s, $H_{1/2} = 22$ Hz, 1H, μ -H), 7.04-6.73 (m, 15H, Ph), 5.69 (s, 10H, Cp), 0.38 (m, 4H, B-CH₂), 0.77 (t, 6H, B-CH₂-CH₃, ${}^{3}J_{H,H} = 6.9$ Hz). ${}^{13}C$ NMR $([D_8]-THF, 27 \text{ °C}, 50.3 \text{ MHz}) (\delta [{}^1J_{C,H}]): 227.9 (s, Ti-C(Ph)=),$ 153.2 (s, =C(Ph)), 181.2 (s, C=N), 107.0 (d, Cp [175 Hz]), Ph 146.8 (s), 141.5 (s), 141.5 (s), 131.8 (d), 128.5 (d), 128.3 (d), 128.1 (d), 127.9 (d), 127.4 (d), 125.4 (d), 124.8 (d), 17.6 (t, $B-CH_2$ [114 Hz]), 12.7 (q, CH_3 [123 Hz]). ¹¹B NMR ([D₈]-THF, 27 °C, 64.2 MHz) (δ): 9.8 ppm ($H_{1/2} = 542$ Hz). MS (70 eV, 175 °C) (m/z (intensity [%])): 178 (Cp₂Ti, PhCCPh [100]), 500 $(M - Et [53]), 529 (M [2]). IR (KBr): \bar{\nu} = 1685 \text{ cm}^{-1} (B-H-$ Ti); 1595 cm⁻¹ (C=N).

Reaction of 11 with Acetonitrile. To a suspension of 1.2 g (2.4 mmol) of 11 in 35 mL of toluene is added by syringe 0.3 mL (0.2 g, 5.6 mmol) of acetonitrile. The reaction mixture is stirred for 27 h. Suspended particles are filtered off, the

solvent is removed in vacuo, and the residue is suspended in pentane. A 1.1 g (2.1 mmol) amount of the pale yellow product **12** can be isolated from this mixture by filtration. Upon crystallization at -20 °C further product can be obtained: yield 1.2 g (96%); dec 198 °C. Anal. Calcd for C₂₈H₂₉ZrAlClN (533.2): C, 63.01; H, 5.48; N, 2.63. Found: C, 63.13; H, 5.41; N, 2.34. ¹H NMR ([D₈]-THF, 29 °C, 300.1 MHz) (δ): -0.65 (s, 6H, Al-CH₃), 1.91 (s, 3H, CH₃), 7.10-6.78 (m, 10H, Ph), 6.18 (s, 10H, Cp). ¹³C NMR ([D₈]-THF, 29 °C, 75.5 MHz) (δ [¹J_{C,H}]): 222.5 (s, Zr-C(Ph)=), 148.4 (s, =C(Ph)), 190.2 (s, C=N), 112.6 (d, Cp [174 Hz]), Ph 152.0 (s), 142.4 (s), 130.7 (d), 126.4 (d), 125.7 (d), 124.4 (d), 128.1 (d), 128.0 (d), 28.3 (q, CH₃ [127 Hz]), -6.8 (q, Al-CH₃ [126 Hz]). MS (70 eV, 130 °C) (m/z (intensity [%])): 516 (M - Me [100]), 220 (Cp₂Zr [79]); 261 (Cp₂Zr(MeCN) [20]), 338 (M - PhCCPh [20]), 178 (PhCCPh [17]).

Acknowledgment. F.S. thanks the "Fonds des Verbandes der Chemischen Industrie" for a stipendium.

Supplementary Material Available: Tables giving details of the X-ray structure analyses of **9a** and **12**, complete listings of bond lengths and angles and positional and thermal parameters, and an ORTEP diagram (14 pages). Ordering information is given on any current masthead page.

OM950094Z