

Reactions of the Titanaallene Intermediate [Cp*₂Ti=C=CH₂] with Isonitriles: An Approach to the Chemistry of Radialene Type Molecules[†]

Cristina Santamaría, Rüdiger Beckhaus,* Detlev Haase, Rainer Koch, Wolfgang Saak, and Isabelle Strauss

Inorganic Chemistry Department, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany

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The titanaallene intermediate [Cp*₂Ti=C=CH₂] (**2**), obtained via methane elimination from Cp*₂Ti(CH=CH₂)Me (**1**), reacts with an excess of cyclohexylisocyanide (CyNC), to give the five-membered metallacycle Cp*₂TiC(=NCy)C(=NCy)C(=CH₂)C=NCy (**4**), which exhibits a radialene substructure. This reaction occurs by a [2+1] addition followed by subsequent insertion of two molecules of isocyanide. A [2+1] addition product is isolated from the reaction of **1** with 2,6-dimethylphenylisocyanide (ArNC) in 1:2 ratio in the form of the azabutatriene complex [Cp*₂Ti(CNAr)(η²-H₂CC=C=NAr) (**5**). The X-ray structure analysis of **5** reveals a pentacoordinated geometry consisting of a η²-C,C-azabutatriene moiety stabilized by a further ArNC ligand. Whereas **5** is stable in the solid state (dec 102–105 °C), in solution (20 °C) one molecule of isocyanide is released. Subsequent intramolecular C–H bond activation and C–C bond formation afford product **7**. The latter can be directly isolated from reaction of **2** with 1 equiv of ArNC. The treatment of the titanaallene species **2** with 3 equiv of ArNC leads, through the insertion of two isocyanide molecules into the Ti–CH₂ bond in complex **5**, to the five-membered ring complex **8**, Cp*₂TiC(=NAr)C(=NAr)CH₂C=C=NAr. The molecular structure of **8** shows a planar titanacyclopentane. Density functional theory calculations confirm the terminal C,C-coordination mode as found in **5** as the preferred arrangement against the C,N- or internal C,C-coordination modes.

Introduction

Cumulated bond systems, particularly butatrienes and derivatives thereof, in the coordination sphere of transition metals^{1,2} are of fascinating interest due to the variety of possible coordination modes, dynamic behavior, and synthetic applications (Scheme 1).³ Particularly, migration processes of metal centers along hydrocarbon backbones are of current interest in organometallic chemistry.^{4–6} On the other hand, cumulene complexes can also serve as an alternative sources of radialenes.^{7,8}

Free radialenes (polymethylenecycloalkanes (Scheme 2))⁷ have received considerable attention by both theoretical and experimental chemists because of their π-electronic arrangement and in order to understand their potential as electron donors and acceptors.⁷ Due to the generally high reactivity exhibited by these species, the syntheses are limited to a few selected examples, often highly substituted.⁹ Heteroradialenes of type **II**, prepared from 3,4-dithiohexadienes¹⁰ or

[†] Dedicated to Professor Dr. Peter Köll on the occasion of his 60th birthday.

* Corresponding author. Tel: +49 441 798 3656. Fax: +49 441 798 3581. E-mail: ruediger.beckhaus@uni-oldenburg.de.

(1) For selected butatriene complexes see M = Ir,^{1a} M = Rh,^{1b,c,d} M = Pt,^{1e} M = Cr,^{1f} and M = Ti.² (a) Ohmura, T.; Yorozuya, S.-I.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2000**, *19*, 365–367. (b) Werner, H.; Laubender, M.; Wiedemann, R.; Windmüller, B. *Angew. Chem.* **1996**, *108*, 1330–1332; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1237–1239. (c) Song, L.; Arif, A. M.; Stang, P. J. *J. Organomet. Chem.* **1990**, *395*, 219–226. (d) Stang, P. J.; White, M. R.; Maas, G. *Organometallics* **1983**, *2*, 720–725. (e) White, M. R.; Stang, P. J. *Organometallics* **1983**, *2*, 1654–1658. (f) Schubert, U.; Grönen, J. *Chem. Ber.* **1989**, *122*, 1237–1245.

(2) Maercker, A.; Groos, A. *Angew. Chem.* **1996**, *108*, 216–217; *Angew. Chem., Int. Ed. Engl.* **1995**, *35*, 210–212.

(3) (a) Wentrup, C.; Flammang, R. *J. Phys. Org. Chem.* **1998**, *11*, 350–355. (b) Bunz, U. H. F. *Angew. Chem.* **1994**, *106*, 1127–1131; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1073–1076. (c) Lange, T.; Gramlich, V.; Amrein, W.; Diederich, F.; Gross, M.; Boudon, C.; Gisselbrecht, J.-P. *Angew. Chem.* **1995**, *107*, 898–901; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 805–809.

(4) For an example of dynamic properties: sliding processes of Cp*₂M (Ti, Zr),^{4a} Cp₂V^{4b} fragments along a polyene chain; for CpCo₃ chain-walking in polymerization reactions.⁶ (a) Pellny, P.-M.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **2000**, *122*, 6317–6318. (b) Choukroun, R.; Donnadiet, B.; Lorber, C.; Pellny, P.-M.; Baumann, W.; Rosenthal, U. *Chem. Eur. J.* **2000**, *6*, 4505–4509.

(5) Fritch, J. R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1978**, *100*, 3643–3644.

(6) Möhring, V. M.; Fink, G. *Angew. Chem.* **1985**, *97*, 982–984; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1001–1003.

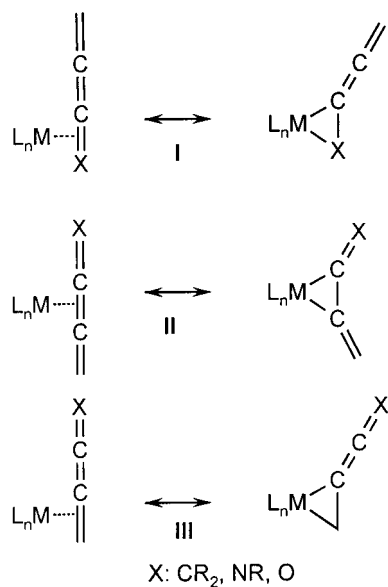
(7) Hopf, H.; Maas, G. *Angew. Chem.* **1992**, *104*, 953–977; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 931–955.

(8) (a) Iyoda, M.; Kuwatani, Y.; Oda, M. *J. Am. Chem. Soc.* **1989**, *111*, 3761–3762. (b) Iyoda, M.; Tanaka, S.; Otani, H.; Nose, M.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8494–8500.

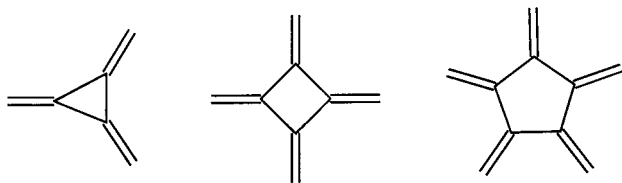
(9) [5]-Radialenes as substructures are found in bowl-shaped corannulenes;^{9a,b} dynamic Li complexes of [4]-radialenes.^{9c} (a) Sastry, G. N.; Rao, H. S. P.; Bednarek, P.; Priyakumar, U. D. *Chem. Commun.* **2000**, 843–844. (b) Mehta, G.; Sarma, P. V. S. *Chem. Commun.* **2000**, 19–20. (c) Sekiguchi, A.; Matsuo, T.; Sakurai, H. *Angew. Chem.* **1998**, *110*, 1751–1754; *Angew. Chem., Int. Ed.* **1998**, *37*, 1661–1664.

(10) Maercker, A.; Dujardin, R. *Angew. Chem.* **1985**, *97*, 612–613; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 571–572.

Scheme 1



Scheme 2

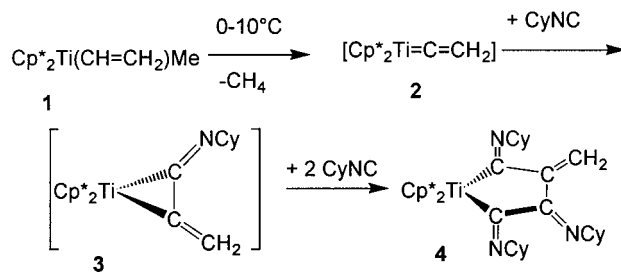


directly from butatrienes, are known.¹¹ The strained structure of type **II** molecules leads often to rearrangements.^{2,11c} For five-membered titanacyclocumulenes a dimerization to [4]-radialenes complexes has been extensively investigated.¹² In continuation of our investigations on the highly reactive titanaallene intermediate [Cp*₂Ti=C=CH₂] (**2**),^{13,14} preferentially generated by methane elimination from [Cp*₂Ti(CH=CH₂)CH₃] (**1**), we report several trapping experiments of **2** with isonitriles to give heteroradialene type molecules.

Results and Discussion

The C_α-nucleophilic titanallene species [Cp*₂Ti=C=CH₂] (**2**)¹⁵ undergoes facile reactions with isonitriles. If diethyl ether solutions of **1** are added to an excess of cyclohexylisonitrile, CyNC (Cy = C₆H₁₁) at -40 °C, and the solution is then allowed to slowly warm to room

Scheme 3



temperature, the five-membered metallacycle **4** is isolated in the form of black crystals (Scheme 3). Alternative insertion reactions of the isonitrile into the Ti-C σ -bond of **1**, as a general way to iminoacyl complexes,^{16,17} are not observed.

The ¹H NMR spectrum of **4** shows as a remarkable feature the chemical shifts of the exo-methylene protons at δ 4.80 and 4.54 ppm. The ¹³C NMR spectrum reveals resonances at δ 228.0 and 226.1 ppm, corresponding to the σ -Ti-iminoacyl carbons, and the absorptions at δ 166.5 ppm (C=N) and 149.0 ppm (C=C) are assigned to the ring carbon atoms in β -position. The mass spectrum shows the expected molecular peak (m/z 671) and the consecutive losses of three isonitrile molecules. In the IR spectrum appear four bands at ν 1630 (m), 1596 (m), 1583 (m), and 1543 (s) cm⁻¹, corresponding to the C=N and C=C stretching vibration. An exact assignment to clarify not only the C=X (X = N, C) vibrations but also the hapticity (η^1 or η^2) of the iminoacyl groups¹⁶ is not possible due to the wide interval found for conjugated systems with double carbon-nitrogen (1660–1480 cm⁻¹) and carbon-carbon bonds ($\nu \leq 1620$ cm⁻¹).¹⁸ All these data are in agreement with the proposed heteroradialene structure of **4** shown in Scheme 3. The primary [2+1] cycloaddition product **3** was not detectable, even if understoichiometric amounts of isonitrile are used. However, the formation of **3** is in accordance with the known reactivity of isonitriles with transition metal carbene complexes.¹⁹ Formation of **4** can be explained in terms of symmetric or asymmetric insertion in **3** of two further isonitrile molecules.

A more detailed insight into these processes becomes available by using 2,6-dimethylphenylisonitrile (ArNC, Ar = 2,6-Me₂C₆H₃). Treatment of **1** with ArNC in 1:2 molar ratio in *n*-hexane, within the temperature range 0–20 °C to eliminate methane, gives a dark orange solution from which the complex **5** was isolated in 65% yield as orange crystals (see Scheme 4) suitable for an X-ray diffraction analysis.

Molecular Structure of Complex 5. Dark orange crystals of **5** were obtained from a diluted hexane solution at 5 °C. The molecular structure is shown in Figure 1, and the relevant geometrical parameters are summarized in Table 1. The complex **5** possesses a pentacoordinated geometry consisting of an isonitrile

(11) Derivatives of B,^{11a} Si,^{11b,c} and Sn.^{11d} (a) Maercker, A.; Brieden, W.; Schmidt, T.; Lutz, H. D. *Angew. Chem.* **1989**, *101*, 477–479; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 477–479. (b) Maercker, A.; Brieden, W.; Kastner, F. and Mannschreck, A. *Chem. Ber.* **1991**, *124*, 2033–2036. (c) Yamamoto, T.; Kabe, Y.; Ando, W. *Organometallics* **1993**, *12*, 1996–1997. (d) Maercker, A.; Bauers, F.; Brieden, W.; Jung, M.; Lutz, H. D. *Angew. Chem.* **1988**, *100*, 413–414; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 404–405.

(12) Pellny, P.-M.; Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Francke, V.; Rosenthal, U. *J. Organomet. Chem.* **1999**, *578*, 125–132.

(13) Beckhaus, R.; Santamaria, C. *J. Organomet. Chem.* **2000**, in press.

(14) (a) Beckhaus, R. *Angew. Chem.* **1997**, *109*, 694–722; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686–713. (b) Beckhaus, R.; Oster, J.; Sang, J.; Strauss, I.; Wagner, M. *Synlett* **1997**, 241–249. (c) Beckhaus, R. *J. Chem. Soc., Dalton Trans.* **1997**, 1991–2001.

(15) (a) Beckhaus, R.; Flatau, S.; Troyanov, S. I.; Hofmann, P. *Chem. Ber.* **1992**, *125*, 291–299. (b) Beckhaus, R.; Thiele, K.-H.; Ströhl, D. *J. Organomet. Chem.* **1989**, *369*, 43–54.

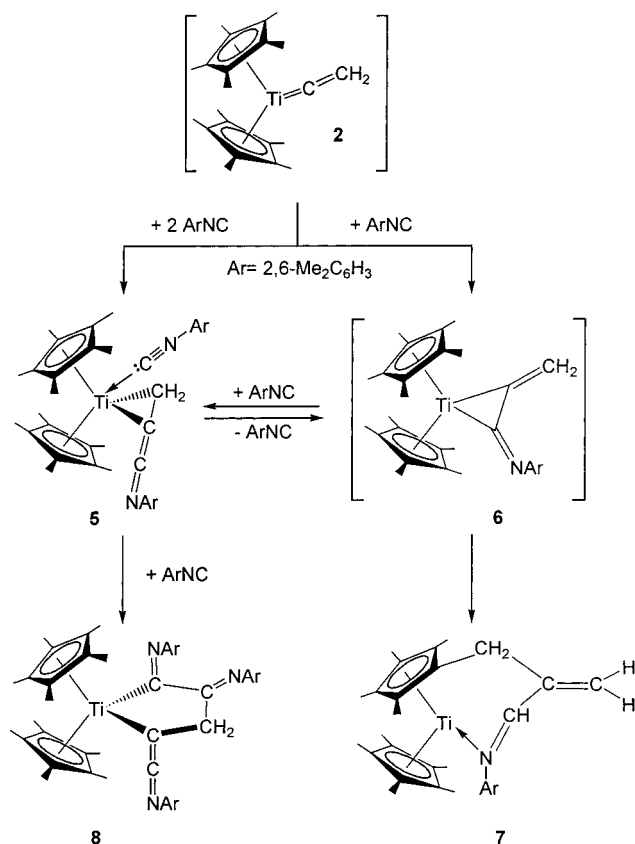
(16) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079.

(17) Starting from methylenetitanacyclobutanes insertion reactions in the Ti-Csp³ become dominant over the addition to **2**. Beckhaus, R.; Zimmermann, C.; Wagner, T.; Herdtweck, E. *J. Organomet. Chem.* **1993**, *460*, 181–189.

(18) Socrates, G. *Infrared Characteristic Group Frequencies*; J. Wiley & Sons Ltd.: Chichester, 1980.

(19) Aumann, R. *Angew. Chem.* **1988**, *100*, 1512–1524; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456–1467.

Scheme 4



molecule and a η^2 -azabutatriene moiety in the equatorial plane of a Cp*₂ fragment.

The coordination of the azabutatriene ligand to the decamethyltitanocene fragment leads to an increase in the C(1)–C(2) bond length, from 1.337(2) Å for free ethylene²⁰ to 1.424(3) Å. This feature compares to those found for (C₅Me₅R)₂Ti(η -C₂H₄) (R = Me, 1.438(5) Å,²¹ R = SiMe₃, 1.442(9) Å²²) and other ethylene complexes.²³ As a consequence of the isonitrile coordination as additional π -acceptor ligand, the Ti(3)–C(1) and Ti(3)–C(2) bond lengths of 2.249(2) and 2.200(2) Å, respectively, are significantly longer than those in (η -C₅Me₅R)₂Ti(η -C₂H₄) (R = Me, 2.160(4) Å,²¹ R = SiMe₃, 2.167(4) Å²²). Moreover, it is found that the Ti–Cp*(centroid) distances of 2.149 and 2.135 Å are also longer than the corresponding bond lengths in the titanium–ethylene complexes (R = Me, 2.092(4) Å,²¹ R = SiMe₃, 2.129 Å²²), reflecting the previous fact. The N(1)–C(3) distance in the azabutatriene fragment is close to that reported for a carbon–nitrogen double bond (1.28 Å).^{16,24} The N(2)–C(12) bond length of 1.167(3) Å in the coordinated isonitrile is elongated compared with C–N distances in pure σ -donor complexes (TiCl₄·2RNC, R = ^tBu 1.145(10), 1.137(10) Å;^{25a} R = *o*-Me₃SiOPh 1.142(5) Å^{25b}). This fact is also reflected in the low ν C≡N absorption at 2066 cm⁻¹ (TiCl₄·2RNC, R = ^tBu 2210, 2226 cm⁻¹,^{25a}

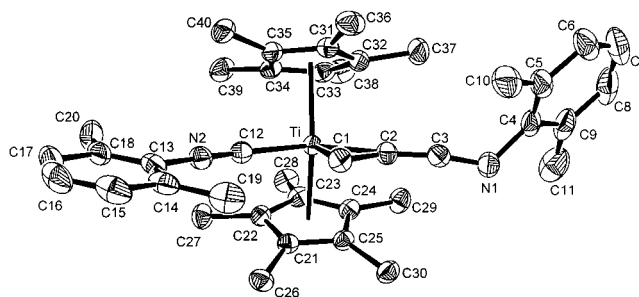


Figure 1. ORTEP plot of **5** at 50% probability ellipsoids.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **5**

Ti–C(1)	2.249(2)	C(2)–C(3)	1.264(3)
Ti–C(2)	2.200(2)	N(1)–C(3)	1.262(3)
Ti–C(12)	2.098(2)	N(2)–C(12)	1.167(3)
C(1)–C(2)	1.424(3)	N(1)–C(4)	1.418(3)
Ti–Cp*(3)(Cen)	2.149	N(2)–C(13)	1.405(3)
Ti–Cp*(2)(Cen)	2.135		
C(12)–Ti–C(2)	108.66(8)	C(3)–C(2)–Ti	138.23(19)
C(12)–Ti–C(1)	71.37(8)	C(3)–C(2)–C(1)	148.1(2)
C(2)–Ti–C(1)	37.31(8)	C(2)–C(1)–Ti	69.46(12)
N(2)–C(12)–Ti	178.24(18)	C(12)–N(2)–C(13)	173.7(2)
C(1)–C(2)–Ti	73.24(12)	C(3)–N(1)–C(4)	123.5(2)
N(1)–C(3)–C(2)	170.7(3)	Cp*(3)–Ti–Cp*(2)	140.2

R = *o*-Me₃SiOPh 2200 cm⁻¹;^{25b} free isonitriles ArNC 2110 cm⁻¹ (KBr)²⁶). In the π -acceptor derivatives (Cp₂Ti(CNAr)₂ 2038, 1937 cm⁻¹)²⁶ low values are also found.

On the basis of the structural data, the C–C coordination in **5** could be best described as a titanacyclopropane with a higher π -content in the C–C bond, consistent with a lower back-donation from titanium to the olefinic unit.

The NMR spectrum of **5** shows a signal for the Cp* ligands, in accordance with C_{2v} symmetry in solution, and the characteristic signals for azabutatriene and isonitrile ligands. The ¹³C NMR spectrum reveals the resonances of the heterocumulene (Ar–N=C_α=C_β=C_γH₂) which exhibit absorptions at δ 231.4 ppm for the α -carbon, while the β -carbon appears at δ 66.9 ppm. These values are more or less in agreement with those found for free ketenimines (RN=C_α=C_βR₂, C_α: δ 187–195 ppm, C_β: δ 37–78 ppm).²⁷ The γ -carbon of the heterocumulene shows a resonance at δ 43.5 ppm (¹J_{CH} = 128.5 Hz), following the tendency before. It is also remarkable that in the ¹³C NMR spectrum the singlet at δ 173.6 ppm assigned to the coordinated isonitrile lies in the same region as the free ligand (2,6-Me₂C₆H₃-NC, δ 170.4 ppm).²⁶ Additionally, in the IR spectrum a band at 2000 cm⁻¹ corresponding to the stretching >C=C=N is observed and compares well to that found for organic keteneimines.^{19,27}

Whereas the complex **5** is thermally stable up to 102 °C in the solid state, in solution the dissociation of the coordinated isonitrile is observed (*t*_{1/2} = 12 h, 20 °C). An analogous situation was reported by Rausch et al. for

(20) Bartell, L. S.; Roth, E. A.; Hollowell, C. D.; Kuchitsu, K.; Young, J. E. *J. Chem. Phys.* **1965**, *42*, 2683–2686.

(21) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136–1143.

(22) Horacek, M.; Kupfer, V.; Thewalt, U.; Stepnicka, P.; Polasek, M.; Mach, K. *Organometallics* **1999**, *18*, 3572–3578.

(23) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.

(24) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; pp 1–1495.

(25) (a) Carofiglio, T.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1989**, *28*, 4417–4419. (b) Hahn, F. E.; Lügger, T. *J. Organomet. Chem.* **1995**, *501*, 341–346.

(26) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Engelhardt, H. E.; Herberhold, M. *J. Organomet. Chem.* **1986**, *317*, C38–C40.

(27) Barker, M. W.; McHenry, W. E. Ketene Imines. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; John Wiley and Sons: Chichester, 1980; pp 701–720.

the $\text{Cp}_2\text{M}(\text{CNR})_2$ ($\text{M} = \text{Ti}, \text{Zr}$; $\text{R} = 2,6\text{-Me}_2\text{-dimethylphenyl}$).²⁶ The decomposition process of a benzene- d_6 solution of **5**, followed by ^1H NMR spectroscopy in a sealed tube, leads to free isonitrile and a mixture of products from which compound **7** could be identified. The latter could also be isolated as a green microcrystalline solid as the unique product of the reaction of the titanocenevinylidene intermediate $[\text{Cp}^*_2\text{Ti}=\text{C}=\text{CH}_2]$ (**2**) with $(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NC}$ in 1:1 ratio. Apparently, the $[\text{Cp}^*_2\text{Ti}(\text{H}_2\text{C}=\text{C}=\text{C}=\text{NAr})]$ (**6**) intermediate undergoes an intramolecular rearrangement under C–H bond activation and C–C coupling to give **7** (see Scheme 4). Similar processes of C–C bond formation between Cp^* and π -ligands have been studied in titanacumulene and acetylene complexes.²⁸ The decomposition of **5** via intermediate **6** to yield **7** corresponds effectively to a “sliding” of the titanium center along the azabutatriene chain.

This behavior induced us to carry out DFT calculations on the model system $\text{Cp}_2\text{Ti}\cdots\text{H}_2\text{C}=\text{C}=\text{C}=\text{NH}$ in order to evaluate the stabilities of the three cycloaddition products shown in Scheme 1 ($\text{X} = \text{NH}$). The symmetric structure **II** (or **6** in Scheme 4) is the least favorable product. The titanaazacyclopropane corresponding to **I** is about 25 kJ/mol more stable than **II**. The most stable product compared to type **II** is the one of type **III** (corresponding to **5**), being 30 kJ/mol lower in energy. These findings support the experimental observations of a nonisolable intermediate **6**, which rearranges to either **5** or **7** under the appropriate conditions.

An indicative feature of the proposed structure for **7** is the characteristic “tucked in”²⁹ splitting pattern in the ^1H NMR spectrum, consisting of one Cp^* signal (δ 1.62 ppm, 15H), four nonequivalent methyl groups (δ 1.07, 1.47, 1.70, 2.34 ppm, each 3H), and a diastereotopic methylene group of the fulvene moiety (^1H NMR δ 3.29, 3.92 ppm, $^2J_{\text{HH}} = 14$ Hz; ^{13}C NMR δ 31.2 ppm, $J = 124.8$ Hz). The low-field shift of the fulvene methylene group indicates a nonmetal-coordinated fulvene ligand. Further signals at δ 4.04 ppm ($J_{\text{HH}} = 1.5$ Hz), 4.26 ppm ($J_{\text{HH}} = 1.8$ Hz), and δ 4.34 ppm are attributed to methylene ($>\text{C}=\text{CH}_2$) and methyne ($-\text{CH}=\text{NAr}$) protons, respectively. To determine the correlation between the proton and the carbon resonances of the methylene and methyne groups, a two-dimensional ^1H – ^{13}C NMR spectrum was acquired. An interesting feature in the ^1H NMR spectrum of **7** is the two broad singlets at -0.52 and 2.50 ppm assigned to the methyl substituents of the aromatic ring, indicating a very low rotation of the bulky Ar groups around the $\text{C}_{\text{ipso}}\text{--NAr}$ bond.³⁰ This situation is also observed for the protons in *meta*-position of the aryl group. When heating a d_8 -toluene solution of **7**, coalescence of the aromatic protons occurs

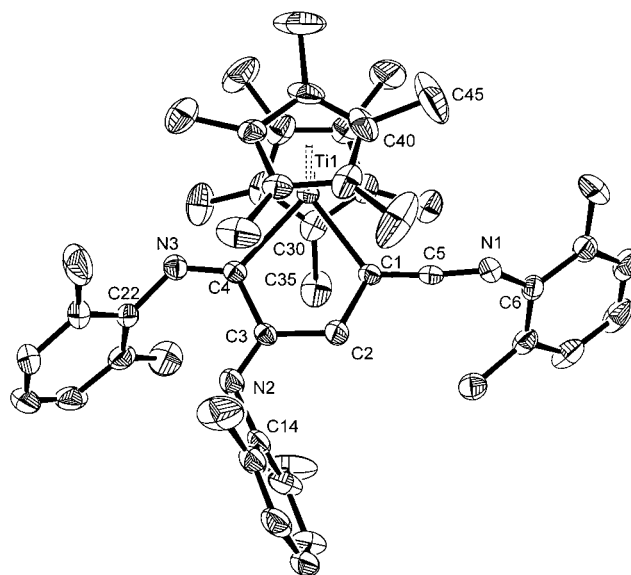


Figure 2. ORTEP plot of **8** at 50% probability ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **8**

Ti(1)–C(1)	2.176(2)	N(1)–C(5)	1.241(3)
Ti(1)–C(4)	2.275(2)	N(1)–C(6)	1.420(4)
C(1)–C(2)	1.520(3)	C(2)–C(3)	1.500(4)
C(1)–C(5)	1.289(4)	N(2)–C(3)	1.258(3)
Ti(1)–Cp*(3)(Cen)	2.114	N(3)–C(4)	1.278(3)
Ti(1)–Cp*(4)(Cen)	2.106		
C(1)–Ti(1)–C(4)	79.39(9)	C(2)–C(1)–Ti(1)	114.15(18)
C(5)–N(1)–C(6)	125.3(3)	C(3)–C(2)–C(1)	114.9(2)
C(3)–N(2)–C(14)	122.5(2)	N(2)–C(3)–C(2)	122.1(2)
C(4)–N(3)–C(22)	129.0(2)	N(2)–C(3)–C(4)	121.2(2)
C(5)–C(1)–C(2)	117.6(2)	C(2)–C(3)–C(4)	116.4(2)
C(5)–C(1)–Ti(1)	127.00(18)	N(3)–C(4)–C(3)	121.5(2)
N(3)–C(4)–Ti(1)	127.17(18)	C(3)–C(4)–Ti(1)	111.20(15)
N(1)–C(5)–C(1)	170.1(3)	Cp*(3)–Ti(1)–Cp*(4)	137.3

at 353 K, but no coalescence of both methyl groups was observed. The resonance of the iminoacyl carbon is observed at 160.8 ppm, and the IR spectrum shows an absorption band at ν 1586 cm^{-1} attributable to the C=N stretching. The molecular ion (m/z 475, 100%) and the fragment $[(\text{M}^+ - \text{C}_5\text{Me}_5), 63\%]$ were observed in the mass spectrum (EI). The spectroscopic and analytical data for complex **7** lead us to the formulation given in the Scheme 4. Unfortunately, all attempts to obtain crystals suitable for X-ray diffraction studies have been unsuccessful.

The vinylmethyl derivative **1** reacts also with $(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NC}$ in a 1:3 ratio in diethyl ether as solvent to afford a dark orange solution, from which the five-membered metallacycle **8** is obtained as black crystals (see Scheme 3). The solid compound is stable under nitrogen atmosphere at room temperature but decomposes slowly (days) in benzene- d_6 solution with formation of **5** and free isonitrile. ^1H and ^{13}C NMR spectra are in full accordance with the proposed structure and also compatible with the solid-state structure determined by single-crystal X-ray diffraction.

Molecular Structure of Complex **8.** The molecular structure in the solid state of compound **8** is shown in Figure 2. Crystallographic parameters and selected geometrical details are listed in Table 2 and Table 3, respectively.

(28) (a) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119–129. (b) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Chem. Eur. J.* **2000**, *6*, 81–90. (c) Horacek, M.; Stepnicka, P.; Gyepes, R.; Cisarova, I.; Polasek, M.; Mach, K.; Pellny, P.-M.; Burlakov, V. V.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **1999**, *121*, 10638–10639. (d) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **1999**, *121*, 8313–8323.

(29) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629–1634.

(30) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 2665–2671.

Table 3. Experimental Crystallographic Data for 5 and 8

	5	8
empirical formula	C ₄₀ H ₅₀ N ₂ Ti	C ₄₉ H ₅₉ N ₃ Ti
fw	606.72	737.89
cryst size (mm)	0.70 × 0.4 × 0.45	0.95 × 0.54 × 0.17
cryst syst.	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.3420(3)	23.1750(16)
<i>b</i> (Å); <i>β</i> (deg)	27.0745(13); 92.576(4)	8.9653(4); 91.069(8)
<i>c</i> (Å)	13.2827(5)	39.855(3)
cell vol <i>V</i> (Å ³)	3356.2(2)	8279.4(9)
<i>Z</i>	4	8
<i>ρ</i> calcd (g cm ⁻³)	1.201	1.184
<i>μ</i> (mm ⁻¹)	0.285	0.243
<i>θ</i> _{range} (deg)	2.65–25.96	2.02–26.06
no. of indep reflns	6139 [<i>R</i> (int) = 0.0347]	7476 [<i>R</i> (int) = 0.0824]
no. of obsd reflns	5035	5700
[<i>I</i> > 2 σ (<i>I</i>)]		
<i>R</i> (<i>F</i>) (%)	4.72	6.16
<i>R</i> _w (<i>F</i>) (%)	5.76	8.06
GOF	1.045	1.055

The X-ray diffraction analysis of **8** shows a planar metallacyclopentane in which the titanium can be considered as pseudotetrahedral with Ti–Cp* distances of 2.106 and 2.114 Å and a Cp*–Ti–Cp* angle of 137.3°. The Ti(1)–C(1) and Ti(1)–C(4) bond distances of 2.176 (2) and 2.275(2) Å, respectively, correspond to a single Ti–Csp² bond and compare well with other five-membered ring compounds.¹⁷ The exocyclic double-bond lengths N(1)–C(5) (1.241(3) Å), N(2)–C(3) (1.258(3) Å), N(3)–C(4) (1.278(3) Å), and C(1)–C(5) (1.289(4) Å) are in the expected range.²⁴

The molecular ion (*m/z* 737) was observed in the EIMS spectrum. The ¹H NMR spectrum reveals a signal for the Cp*-methyl protons indicating the planarity of the titanacyclopentane ring. Instead of the characteristic signals of the exo-methylene group found in **4**, the ¹H and ¹³C NMR spectra of **8** show a metallacycle methylene group (¹H, δ 3.41 (s); ¹³C, δ 42.4 ppm, ¹*J*_{CH} = 128.4 Hz). The ¹³C NMR spectrum shows a signal at 233.0 ppm consistent with a σ -Ti-iminoacyl carbon. The resonances of the α -carbon atom in the ketenimine fragment and the iminoacyl carbon β to the titanium center have similar chemical shifts (δ 169.2 and 169.5 ppm), and we have not attempted to assign them. The IR spectrum shows absorptions at ν 1591 cm⁻¹, assigned to the C=N stretching, and ν 1955 cm⁻¹ due to the >C=C=N stretching in the heterocumulene fragment. In accord with the spectroscopic and structural data the formation mechanism of **8** can be explained by the insertion of two molecules of isonitrile into the Ti–CH₂ bond of the η^2 -C,C-azabutatriene moiety in complex **5**.

Conclusions

Starting from the titanaallene intermediate [Cp*Ti=C=CH₂] (**2**) and isonitriles RNC (R = C₆H₁₁, 2,6-Me₂C₆H₃), the formation of metallacyclic systems with radialene substructures is shown. An azabutatriene complex, formed by [2+1] addition, could be isolated in the form of the isonitrile adduct **5**, which is characterized by a terminal η^2 -C–C bond coordination mode. This fact is in accordance with the general behavior of type **III** molecules, which are found to be thermodynamically more stable than the symmetric coordinated butatriene derivatives (type **II**).^{1b} However, the formation of the

symmetric azabutatriene complexes **3** and **6** can be proposed as intermediates. In such a way, subsequent reactions of **3** with further C₆H₁₁NC leads to **4**, whereas **7** is formed spontaneously by intramolecular rearrangement of **6**. On the other hand, the formation of the metallacycle **8** is understandable by isonitrile insertion in the Ti–CH₂ bond of the asymmetric coordinated complex **5**. Formally, in the formation of **4** and **8** from **1**, three molecules of isonitrile are consumed. Double-insertion products derived from **1** are not observed. Additionally, C,N-coordination modes, as expected for early transition metals (type **I**),³¹ were not found. In summary, these reactions demonstrate the great versatility of **2** as building block in reactions with unsaturated substrates. Particularly, the dynamic behavior of cumulated bond systems in the coordination sphere of transition metals is illustrated.

Experimental Section

General Considerations. All manipulations of the described compounds were carried out under exclusion of air and moisture using Schlenk line or glovebox techniques. Solvents were distilled prior to use. (2,6-Me₂C₆H₃)NC and cyclohexyl-isonitrile were purchased from Aldrich and used without further purification. Cp*₂Ti(CH=CH₂)Me (**1**) was synthesized according to the published procedure.^{32a,b} C, H, and N analyses were performed at the Analytischen Laboratorien in Lindlar (Germany); the C, H, and N analysis of **4** was made in the Institut für Anorganische Chemie der RWTH Aachen. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM 300 or Bruker 500 AVANCE spectrometer, and chemical shifts are referenced to residual protons or carbons of the solvent or to TMS. In the case of the complex **4** a Varian VXR-300 spectrometer was used. Electron impact (IE) mass spectra were recorded on a Finnigan MAT 212 or on a Finnigan MAT CH 5-DF spectrometer for **4**. IR spectra were taken with a BIO-RAD FTS-7 spectrophotometer or, as in the case of the complex **4**, with a Perkin-Elmer 1720X spectrophotometer, using KBr pellets.

Preparation of 4. To a –10 °C cooled solution of cyclohexylisonitrile (0.59 mL, 4.83 mmol) in 30 mL of ether was added a –40 °C cooled solution of Cp*₂Ti(CH=CH₂)Me (**1**) (0.58 g, 1.61 mmol) in 30 mL of diethyl ether. After 1 h at room temperature, the dark brown solution was concentrated to about 20 mL and cooled to 5 °C for 1 day to afford small black crystals of **4** (0.36 g, 33%). Spectral and analytical data for **4**: mp 127–130 °C (dec); IR (KBr, cm⁻¹) (C=X; X = C, N) ν 1630 (m), 1596 (m), 1583 (m), 1543 (s); MS (EI, *m/z*, rel int) 671 ([M⁺], 1%), 562 ([M⁺ – CNCy], 3%), 453 ([M⁺ – 2CNCy], 56%), 344 ([M⁺ – 3CNCy], 23%), 317 ([M⁺ – CNCy – C₂H₅], 100%); ¹H NMR (300 MHz, C₆D₆, 27 °C) δ 1.83 (s, 30H, C₅(CH₃)₅), 2.30–1.20 (m, 30H, H_{Cy}), 4.23, 3.59, 3.52 (tt, ³*J*_{HH} = 4 Hz, 10 Hz, 1H, >N–CH), 4.80, 4.54 (d, ²*J*_{HH} = 2 Hz, 1H, =CH₂); ¹³C-{¹H} NMR (75 MHz, C₆D₆, 27 °C) δ 12.2 (C₅(CH₃)₅), 25.9, 25.4, 24.3 (3-C_{Cy}), 26.7, 26.5, 26.4 (4-C_{Cy}), 35.7 (2-C_{Cy}), 64.5, 63.7, 59.5 (1-C_{Cy}), 107.4 (>C=CH₂), 123.0 (C₅(CH₃)₅), 149.0 (>C=CH₂), 166.5 (>C=N), 228.0, 226.1 (Ti–C). Anal. Calcd for C₄₃H₆₅N₃Ti (M_r = 671.89): C, 76.87; H, 9.75; N, 6.25. Found: C, 77.11; H, 10.11; N, 6.14.

Preparation of 5. (2,6-Me₂C₆H₃)NC (0.31 g, 2.39 mmol) solved in 40 mL of precooled hexane was added to a solution of **1** (0.43 g, 1.19 mmol) in hexane (30 mL) at –78 °C. The reaction mixture was stirred and warmed to room tempera-

(31) Venne-Dunker, S.; Ahlers, W.; Erker, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2000**, 1671–1678.

(32) (a) Beckhaus, R.; Oster, J.; Wagner, T. *Chem. Ber.* **1994**, *127*, 1003–1013. (b) Luinstra, G. A.; Teuben, J. H. *Organometallics* **1992**, *11* (1), 1793–1801.

ture. After that the solution was cooled to 5 °C for one night to afford dark orange crystals suitable for X-ray diffraction analysis (470 mg, 65%). Spectral and analytical data for **5**: mp 102–105 °C (dec); IR (KBr, cm^{-1}) ν 2066 s (C≡NR), 2000 s (RN=C=C), 1589 s (C=NR); MS (EI, m/z , rel int) 606 [M^+], 91%, 486 [$M^+ - \text{NR}$], 44%, 475 [$M^+ - \text{CNR}$], 33%, 340 [$M^+ - \text{CNR} - \text{C}_5\text{Me}_5$], 37%, 318 [$M^+ - \text{CNR} - \text{RNC} = \text{C} = \text{CH}_2$], 10%, 303 [$M^+ - \text{CNR} - \text{RNC} = \text{C} = \text{CH}_2 - \text{Me}$], 100%; ^1H NMR (500 MHz, C_6D_6 , 27 °C) δ 1.49 (s, 2H, =C-CH₂), 1.67 (s, 30H, $\text{C}_5(\text{CH}_3)_5$), 2.29, 2.71 (s, 6H, 2,6-Me₂C₆H₃), 6.74, 7.15 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, *m*-H_{arom.}), 6.81, 6.95 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H, *p*-H_{arom.}); ^{13}C NMR (125 MHz, C_6D_6 , 27 °C) δ 11.7 (q, $J = 125.2$ Hz, $\text{C}_5(\text{CH}_3)_5$), 19.7 (q, $J = 122.7$ Hz, 2,6-Me₂C₆H₃), 43.5 (t, $J \approx 152$ Hz, =C-CH₂), 66.9 (s, =C-CH₂), 110.5 (m, $\text{C}_5(\text{CH}_3)_5$), 122.1 (d, *m*-C_{arom.}), 128.3 (d, *p*-C_{arom.}), 128.4 (d, *p*-C_{arom.}), 128.7 (d, *m*-C_{arom.}), 130.0 (m, *o*-C_{arom.}), 134.6 (m, *o*-C_{arom.}), 148.7 (s, C_{ipso}), 173.6 (s, C≡NR), 231.4 (s, RN=C=C-CH₂). Anal. Calcd for C₄₀H₅₀N₂Ti ($M_r = 606.68$): C, 79.18; H, 8.31; N, 4.61. Found: C, 79.02, H, 8.49; N, 4.50.

Preparation of 7. Preparation is similar to that of **5** from 0.42 g (1.16 mmol) of Cp*₂Ti(CH=CH₂)Me and (2,6-Me₂C₆H₃)-NC (0.15 g, 1.16 mmol) in hexane (60 mL). A green crystalline solid of **7** was obtained with a 78% yield. Spectral and analytical data for **7**: mp 95–100 °C (dec); IR (KBr, cm^{-1}) ν 1672, 1634 (w, C=C), 1586 (s, C=N); MS (EI, m/z , rel int) 475 [M^+], 100%, 340 [$M^+ - \text{C}_5\text{Me}_5$], 63%, 303 [$M^+ - \text{C}_{12}\text{H}_{14}\text{N}$], 11%, 181 [$M^+ - \text{C}_{12}\text{H}_{14}\text{N} - \text{C}_5\text{Me}_5$], 15%; ^1H NMR (500 MHz, C_6D_6 , 27 °C) δ -0.51 (ws, 3H, 2,6-Me₂C₆H₃), 1.07, 1.47, 1.70, 2.34 (s, 3H, $\text{C}_5(\text{CH}_3)_5\text{CH}_2$), 1.62 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 2.50 (ws, 3H, 2,6-Me₂C₆H₃), 3.29, 3.92 (dd, $^2J_{\text{HH}} = 14$ Hz, 1H, $\text{C}_5(\text{CH}_3)_5\text{CH}_2$), 4.04 (m, 1H, $J_{\text{HH}} = 1.5$ Hz, -C=CH₂), 4.26 (m, 1H, $J_{\text{HH}} = 1.8$ Hz, -C=CH₂), 4.34 (s, 1H, -CH=NAr), 6.41, 6.41, 1H, *p*-H_{arom.}), 6.68, 6.84 (ws, 1H, *m*-H_{arom.}); ^{13}C NMR (125 MHz, C_6D_6 , 27 °C) δ 9.9, 10.5, 12.3, 14.8 (q, $J = 125.6$ Hz, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$), 11.8 (q, $J = 125.5$ Hz, $\text{C}_5(\text{CH}_3)_5$), 23.1 (qd, $J = 124.4$ Hz, 2,6-Me₂C₆H₃), 31.2 (t, $J = 124.8$ Hz, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$), 98.5 (t, $J = 155.8$ Hz, -C=CH₂), 116.7 (d, $J = 157.4$ Hz, -CH=NAr), 114.5, 124.1, 128.3, 156.8 (m, $J = 157.1$ Hz, 2,6-Me₂C₆H₃), 114.7, 116.7, 121.6, 129.7, 131.8 (m, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$), 120.9 (m, $\text{C}_5(\text{CH}_3)_5$), 160.8 (s, -C=CH₂). Anal. Calcd for C₃₁H₄₁NTi ($M_r = 475.52$): C, 78.29; H, 8.69; N, 2.94. Found: C, 78.10, H, 8.88; N, 2.80.

Preparation of 8. A 150 mL Schlenk flask was charged with Cp*₂Ti(CH=CH₂)Me (**1**) (1.00 g, 2.77 mmol) in diethyl ether (50 mL) and cooled at -78 °C. A precooled solution of (2,6-Me₂C₆H₃)NC (1.10 g, 2.77 mmol) in 40 mL diethyl ether was added, and the reaction mixture was allowed to warm to room temperature. The solution was filtered and concentrated under reduced pressure. After one night at room temperature, black crystals of **8** (1.79 g, 87%) were isolated. Spectral and analytical data for **8**: mp 137–140 °C (dec); IR (KBr, cm^{-1}) ν 1955 (s, C=C=N), 1591 (m, C=N); MS (EI, m/z , rel int) 737 [M^+], 16%, 607 [$M^+ - \text{CNR}$], 41%, 602 [$M^+ - \text{C}_5\text{Me}_5$], 100%, 475 [$M^+ - 2\text{CNR}$], 19%, 471 [$M^+ - \text{C}_5\text{Me}_5 - \text{CNR}$], 19%, 340 [$M^+ - \text{C}_5\text{Me}_5 - 2\text{CNR}$], 31%; ^1H NMR (500 MHz, C_6D_6 , 27 °C) δ 1.84 (s, 30H, $\text{C}_5(\text{CH}_3)_5$), 2.10, 2.23, 2.44 (s, 6H, 2,6-Me₂C₆H₃), 3.41 (s, 2H, >CH₂), 6.74, 6.81, 6.85 (t, $^3J_{\text{HH}} =$

7.4 Hz, 1H, *p*-H_{arom.}), 6.90, 6.95, 6.96 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H, *m*-H_{arom.}); ^{13}C NMR (125 MHz, C_6D_6 , 27 °C) δ 13.0 (q, $J = 126.1$ Hz, $\text{C}_5(\text{CH}_3)_5$), 19.59, 19.6, 22.5 (qd, $J = 125.3$ Hz, 2,6-Me₂C₆H₃), 42.4 (t, $J = 128.4$ Hz, >CH₂), 86.0 (t, $^2J = 7.2$ Hz, >C=C=NR), 125.7 (m, $\text{C}_5(\text{CH}_3)_5$), 121.3, 123.2, 123.5, 123.8, 126.1, 127.9, 128.3, 128.4, 128.6, 128.7, 130.3 (m, C_{arom.}), 144.4, 147.6, 156.0 (m, C_{ipso}), 169.2, 169.5 (s, >C _{β} =NR, =C=C-NR), 233.0 (s, Ti-C _{α}). Anal. Calcd for C₄₉H₅₉N₃Ti ($M_r = 737.89$): C, 79.76; H, 8.06; N, 5.69. Found: C, 79.67, H, 8.04; N, 5.64.

Crystal Structure Determinations. Data for the structures **5** and **8** were collected on a STOE-IPDS diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$). A summary of crystals data and intensity collection and refinement parameters is reported in Table 3.

Intensity measurements were performed at 193(2) K in sealed glass capillaries. The structure of all complexes was solved by direct phase determination (SHELXL 97)³³ and refined on F^2 (SHELXL 97)³³ with anisotropic thermal parameters for all non-hydrogen atoms.

Computational Details. The DFT calculations have been carried out using the hybrid functional Becke3LYP,³⁴ employing the program package Gaussian 98.³⁵ All structures were optimized and verified as local minima at the B3LYP/6-31G-(d) level of theory.

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Supporting Information Available: Tables giving X-ray crystal structure details for **5** and **8** are available free of charge via the Internet at <http://pubs.acs.org>. Additionally crystallographic data (excluding structure factors) for the structures **5** and **8** have been deposited with the Cambridge Data Centre as supplementary publications nos. CCDC 151666 (**5**) and 151665 (**8**). Copies of the data can be obtained free of charges on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax (+44) 1223-336-033; e-mail deposit@aadc.cam.ac.uk).

OM000929S

(33) Sheldrick, G. M. *SHELXS97, Programm for Structure Solutions*, University of Göttingen, 1997.

(34) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785–789. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.