# Synthesis and Structural Characterization of Azatitanacyclobutane Derivatives

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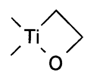
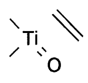
Received August 5, 1997

**Keywords:** Titanium / Vinylidene complexes / [2+2] Cycloaddition / Metallacycles / Azatitanacyclobutanes / Clathrates

The titanocene vinylidene intermediate [$Cp^*{}_2Ti=C=CH_2$] (**9**) reacted with the carbodiimides R−N=C=N−R [R = $p$-$CH_3C_6H_4$ (**19a**), $C_6H_{11}$ (**19b**)] to give the N=C-cycloaddition products [$Cp^*{}_2Ti\{-NR-C(=NR)-(C=CH_2)-\}$] [(R = $p$-$CH_3C_6H_4$ (**20a**), $C_6H_{11}$ (**20b**)]. The X-ray structure of **20a** in form of a surprisingly stable $n$-hexane clathrate is presented. The azatitanacyclobutane [$Cp^*{}_2Ti\{-NPh-C(Ph)(H)-(C=CH_2)-\}$] (**22**) was formed from the reaction between **9** and benzylidene aniline [PhN=C(Ph)H (**21**)]. Reactivity studies showed that azatitanacyclobutanes are unreactive upon typical ring-enlargement reactions as observed for other four-membered titanacycles.

Oxatitanacyclobutanes (**1**) and azatitanacyclobutenes (**3**) are under discussion as intermediates in reactions of Ti=$CR_2$ with carbonyl compounds or nitriles. The high electrophilicity of the metal centre has generally prevented the isolation and characterization of oxa- and azatitanacyclobutenes: spontaneous ring opening reactions afford carbonyl olefination (**1**→**2**), or products of vinylimido intermediates (**3**→**4**).[1] The present paper deals with the formation of azatitanacyclobutane complexes (**5**) prepared by [2+2] cycloaddition of a Ti=C and N=C units.


**1**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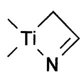
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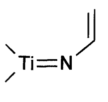
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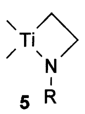
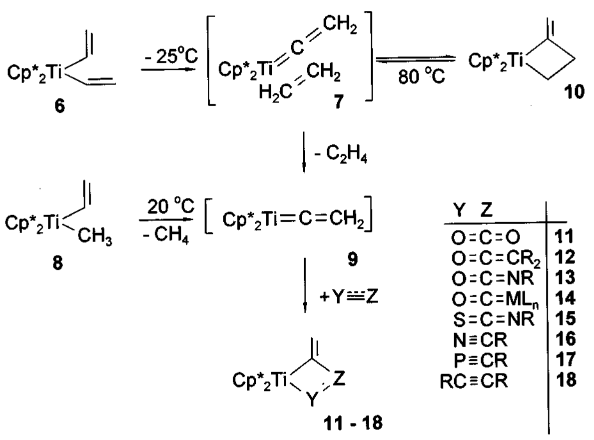
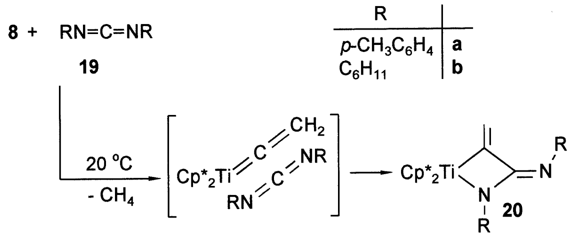

**5**

From the thermally generated titana-allene intermediate $Cp^*{}_2Ti=C=CH_2$ (**9**), formed by ethane or methane elimination from $Cp^*{}_2Ti[-CH_2CH_2(C=CH_2)-]$ (**10**) or $Cp^*{}_2Ti(CH=CH_2)(CH_3)$ (**8**), a wide range of four-membered titanacycles (**11**−**18**) can be produced.[2][3][4][5][6][7][8] The high thermal stability of these titanacycles is the major advantage of using **9** instead of titanium methylene intermediates.[2a]



## Results and Discussion

The vinylmethyl derivative **8** reacts with one equivalent of the carbodiimide RN=C=NR (R = $p$-$CH_3C_6H_5$ **19a**, R = $C_6H_{11}$ **19b**) at room temperature in $n$-hexane as solvent with evolution of methane to give a dark green solution, from which the azatitanacyclobutane complexes **20** are obtained as green crystals (**20a**) or as a green oil (**20b**). These compounds are formed nearly quantitatively (NMR) and can be isolated in 92% (**20a**) and 88% (**20b**) yield. The mass spectra show the expected molecular peaks. For **20b**, a cycloreversion with formation of **9** can be detected from the fragmentation pattern, whereas for **20a**, the liberation of a $C_5Me_5$ ligand is the main fragmentation step, indicating a higher stability of the azatitanacyclobutane unit.



The two chemical shift signals in the $^1H$-NMR spectra for the protons of the $exo$-methylene group in **20** (**20a** δ = 4.13, 5.87; **20b** δ = 4.52, 6.32) appear to be a distinguishing feature of the new complexes and similar metallacycles. In addition, the chemical shifts of the ring carbon atoms in the $^{13}C$-NMR spectra are in accordance with a σ titanium-bonded $sp^2$ carbon atom (**20a** δ = 202.5; **20b** δ = 202.0). The eight ring proton signals of the two $p$-tolyl substituents in **20a** are detectable upon cooling to −80°C [ring A: (C11−C16, assignment according to Figure 1) δ = 4.63 (d, 1 H), 9.81 (d, 1 H), 6.68 (d, 1 H), 7.10 (d, 1 H); ring B: (C21−C26) 7.26 (m, 4 H)]. The low field shift of one proton signal in ring A (δ = 9.81) is attributed to a hydrogen bridge between the N2 and the H atom at C12, as concluded from

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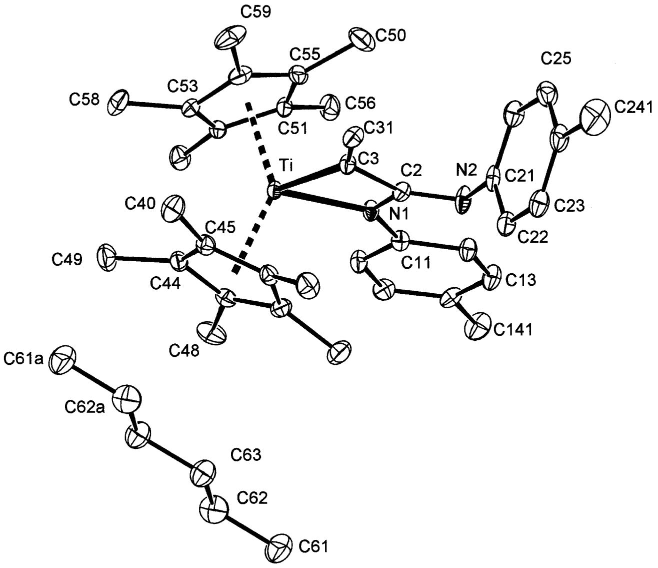
comparison of δ values in NH compounds.[9] Indeed, in the X-ray structure the distance C12−N2 (2.875 Å) was found to be short. The rotation of ring A is probably blocked in solution at lower temperatures, as indicated by $^{13}C$ NMR: three *ortho* C signals (δ = 120.1, 121.6, 123.3) of the two aromatic rings are detectable, whereas at room temperature, only two ortho carbon resonances (δ = 121.6, 122.1) are present. Surprisingly, only six of the eight expected protons are detectable at room temperature [δ = 7.09 (m, 4 H), 6.85 (d, 2 H)], similar to the observation of other *N*-phenyl ligands in samarium complexes.[10]

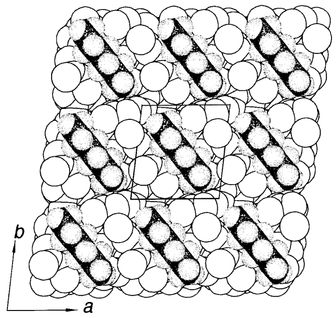
The structure of **20a** was confirmed by X-ray structure determination. The PLATON plot[11a] is shown in Figure 1, and relevant bond lengths and angles are given in Table 1. The azatitanacyclobutane is obtained as a surprisingly stable clathrate $2[Cp^*_2Ti\{-N(p\text{-}CH_3C_6H_4)C(=N-p\text{-}CH_3C_6H_4)(C=CH_2)-\}] \cdot n\text{-}C_6H_{14}$. It crystallizes in space group $P\bar{1}$ with complex molecules in general position (2*i*) and *n*-hexane on the crystallographic inversion centers (1*e*) (s. Figure 2). The atoms of the aliphatic chain exhibit small displacement parameters, and all hydrogen atoms of the *n*-hexane molecule could be located in a Fourier difference synthesis. Bond length and angles are in good agreement with a previous report.[11c] The cocrystallization of the *n*-hexane molecule illustrates in an excellent manner the highly organophilic character of permethylated metallocene complexes of the type $Cp^*_2TiX_2$.

Figure 1. PLATON drawing[11a] of $2\ [Cp^*_2Ti\{-N(p\text{-}CH_3C_6H_4)C(=N-p\text{-}CH_3C_6H_4)C(=CH_2)-\} \cdot n\text{-}C_6H_{14}]$ (**20a** · 0.5 $C_6H_{14}$) (30% ellipsoids) (two titanocene molecules and one molecule *n*-hexane are present in the unit cell)



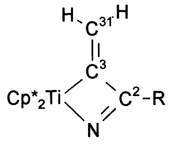
The azatitanacyclobutane ring is planar. The *p*-tolyl ring A (C11−C16) is localized in the plane of the four-membered ring, whereas ring B (C21−C26) is orientated perpendicular to the equatorial plane. The sum of the angles at N1 is approximately 358°, which means that the nitrogen ring atom must be $sp^2$ hybridized with the lone pair located in a vacant p-orbital perpendicular to the ring plane.

Figure 2. SCHAKAL drawing[11b] of molecular packing of $2\ [Cp^*_2Ti\{-N(p\text{-}CH_3C_6H_4)C(=N-p\text{-}CH_3C_6H_4)C(=CH_2)-\} \cdot C_6H_{14}]$ (**20a**· 0.5 $C_6H_{14}$) view on *ab*-plane; hydrogen atoms of **20a** omitted, hexane molecules shaded



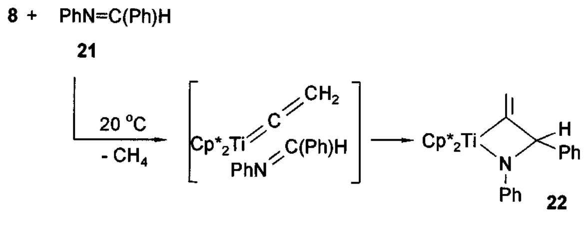
Compared to the azatitanacyclobutene **16** (R = *t*Bu) the Ti−N1 distance in **20a** was found to be significantly longer, resulting from the hybridization of the nitrogen atom. In contrast with **16**, in **20** a p*ϕ*−d*ϕ* interaction is no longer possible, due to the perpendicular orientation of the lone pair at the titanium-bonded nitrogen to the $Cp^*_2Ti$-acceptor orbitals in **20**.[12] This behaviour is in accordance with the general observation that reactivity of bent titanocene complexes is determined by the electron-deficient character of the metal centre, in combination with the orientation of the acceptor orbitals in the equatorial plane of the metallocene fragment.[13] The N1−C2 distance in **20** is in accordance with a N−C single bond, as expected.[12] To summarize, the structural data suggest that the reactivity of **20a** should differ from that of **16**. The short C3−C2 distance in **16** [1.485(3) Å] indicates a stronger C−C bond than that found in **20a** [1.505(4) Å]. Electrocyclic ring-opening reactions are indeed observed for **16**, whereas cycloreversion reactions are expected for azametallacyclobutanes, and are observed in the mass spectrometric fragmentation behaviour of **20b**, and the dynamic properties of other azametallacyclobutanes derived from $[Cp_2Zr=NR]$[15] or $[(tBu_3SiO)_2Ti=NR]$[16] intermediates and olefins.

Table 1. Selected bond lenghts [Å] and angles [deg] in $2\ [Cp^*_2Ti\{-N(p\text{-}CH_3C_6H_4)C(=N-p\text{-}CH_3C_6H_4)C(=CH_2)-\} \cdot n\ C_6H_{14}]$ (**20a**·0.5 *n* $C_6H_{14}$) and the azatitanacyclobutene $[Cp^*_2TiN=C(tBu)C=CH_2]$ (**16**)[6], assignment according the figure



| distances [Å] | | | angles [°] | | |
|---|---|---|---|---|---|
| | **20a** | **16** | | **20a** | **16.00** |
| Ti−C3 | 2.129(3) | 2.134(2) | C3−Ti−N1 | 65.8(1) | 67.8(1) |
| Ti−N1 | 2.084(2) | 2.017(2) | Ti−N1−C2 | 97.4(2) | 94.5(1) |
| Ti−C2 | 2.64 | 2.48 | Ti−C3−C31 | 140.6(2) | 145.4(2) |
| N1−C2 | 1.374(4) | 1.290(3) | Ti−N1−C11 | 135.5(2) | − |
| C2−N2 | 1.287(4) | − | C11−N1−C2 | 124.6(3) | − |
| C2−C3 | 1.505(4) | 1.485(3) | N1−C2−C3 | 105.1(2) | 113.2(2) |
| C3−C31 | 1.329(4) | 1.337(3) | C2−C3−Ti | 91.5(2) | 84.4(1) |

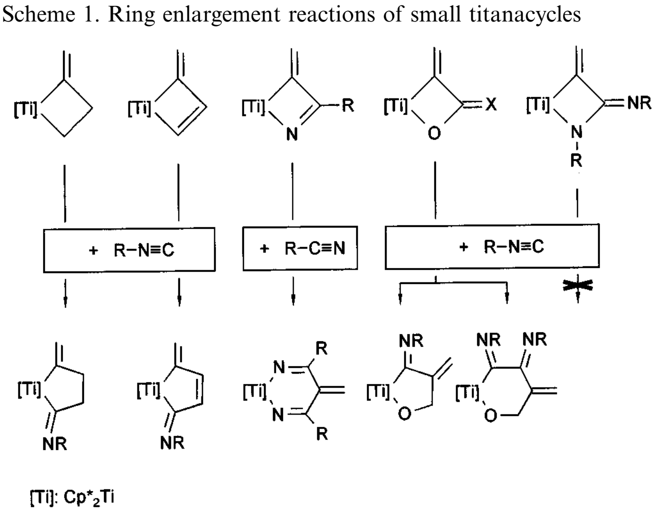
When **8** reacts with *N*-benzylidene aniline, the azatitanacyclobutane derivative **22** is formed by cycloaddition of **9** with **21**. Compound **22** was isolated in 30% yield as thermally stable (mp 158 °C, dec.) red crystals. The expected molecular peak is found in the mass spectrum, and fragmentation occurs mainly with formation of a $Cp^*_2Ti{=}NR$ fragment (40.7%). Attempts to use this reactivity pattern for preparative purposes, e. g. in reaction with acetone, have until now been unsuccessful.



Proton transfer reactions leading to azavinylidene derivatives $Cp^*_2Ti(N{=}CPh_2)CH{=}CH_2$ occur when Schiff bases with nitrogen bearing an acidic hydrogen atom are used.[17] In the case of *N*-benzylidenemethylamine, the fulvene complex $Cp^*(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)TiCH{=}CH_2$ is formed instead of the metallacyclic cycloaddition product.

To compare the reactivity of **20** to that of the other four-membered titanacycles **10−18**, different reactions were carried out. With isonitriles, a fast and selective insertion into the Ti−C σ-bond is observed for **10**[18] and **18**[7a] (Ti−C bond opposite to the *exo*-$CH_2$ group) as well as for the oxetanes **11−14**,[8a][19]. The azatitanacyclobutanes **20** are however inert to ring enlargements with small molecules (RNC, R = *t*Bu, $C_6H_{11}$). Especially fast reactions take place between **16** and nitriles to form six-membered rings.[6] However, in the case of **20** no reactions are detectable. These reactions are summarized in Scheme 1. The azatitanacyclobutane **20** also appears to be inert in the presence of protic agents (PhC≡CH, PhOH, MeOH). Only with HCl/$Et_2O$ the formation of $Cp^*_2TiCl_2$ is observed.

Scheme 1. Ring enlargement reactions of small titanacycles



This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie.*

## Experimental Section

*General:* The preparation and handling of compounds were performed with rigorous exclusion of air and moisture under a nitrogen atmosphere, using a standard vacuum line and Schlenk techniques. All solvents were dried with the appropriate drying agents and distilled under a nitrogen atmosphere. Deuterated solvents were degassed by freeze-pump-thaw cycles and dried over molecular sieves (3 or 4 Å) prior to use. − $^1H$- and $^{13}C$-NMR spectra were recorded on a Varian Unity 500 spectrometer. Chemical shifts are reported in ppm with reference to residual protons in deuterated solvents ([$D_6$]benzene, δ = 7.15 for $^1H$-NMR spectroscopy; [$D_6$]benzene, δ = 127.96 for $^{13}C$-NMR spectroscopy). − Mass spectroscopic analyses were performed on a Finnigan MAT 95 mass spectrometer. − Infrared spectra were recorded as KBr pellets on a Perkin−Elmer 1720X FT-IR spectrometer. − Elemental analyses were carried out at the Analytische Laboratorien in Lindlar, Germany. − The titanocene complex $[Cp^*_2Ti(CH{=}CH_2)CH_3]$ (**8**) was prepared by literature procedures.[4] The Schiff bases were purchased from Aldrich.

*Preparation of* **20a**: To a solution of **8** (200 mg, 0.55 mmol) in 30 ml of *n*-hexane was added di-*p*-tolylcarbodiimide (**19a**) (0.12 g, 0.55 mmol) at −20 °C. The mixture was stirred and warmed to 25 °C over 4 h, forming a dark green solution, from which **20a** precipitates. Recrystallization from *n*-hexane at −20 °C, yields **20a** as dark green crystals (210 mg, 67%) − mp 150−153 °C (dec.) − $^1H$ NMR ($C_7D_8$, 500 MHz, −80 °C): δ = 1.56 [s, 30 H, $C_5(CH_3)_5$], 2.19 (s, 3 H, $CH_3$), 2.32 (s, 3 H, $CH_3$), 4.06 (s, 1 H, =CH*H*), 5.79 (s, 1 H, =C*H*H), 4.63 (d, 1 H, *J* = 7.9 Hz), 6.68 (d, 1 H, *J* = 7.6 Hz), 7.10 (d, 1 H, *J* = 7.3 Hz), 7.26 (m, 4 H), 9.81 (d, 1 H, *J* = 7.9 Hz). − $^1H$ NMR ($C_7D_8$, 500 MHz, 25 °C): δ = 1.68 [s, 30 H, $C_5(CH_3)_5$], 2.19 (s, 3 H, $CH_3$), 2.30 (s, 3 H, $CH_3$), 4.08 (s, 1 H, = CH*H*), 5.76 (s, 1 H, =C*H*H), 6.85 (d, 2 H, *J* = 6.4 Hz), 7.09 (m, 4 H). − $^{13}C\{^1H\}$ NMR ($C_7D_8$, 125 MHz, −80 °C) δ = 12.7 [$C_5(CH_3)_5$], 21.2 ($CH_3$), 21.2 ($CH_3$), 118.7 (=$CH_2$), 120.1, 121.6, 123.3, 128.6, 128.7, 130.2, 146.0, 152.1 (Ph, 2 signals hidden), 140.5 (N-C=N). 201.5 (TiC), 125.4 [$C_5(CH_3)_5$]. − $^{13}C\{^1H\}$ NMR ($C_7D_8$, 125 MHz, 25 °C) δ = 12.7 [$C_5(CH_3)_5$], 21.0 ($CH_3$), 21.1 ($CH_3$), 118.4 (=$CH_2$), 121.6, 122.1, 128.3, 128.4, 129.9, 146.1, 151.8 (Ph, 1 signal hidden), 140.3 (N-C=N), 202.5 (TiC), 125.7 [$C_5(CH_3)_5$]. − IR (KBr): ṽ = 2909 (m), 2854 (m), 1608 (w), 1590 (w), 1541 (s), 1504 (s), 1497 (s), 1453 (m), 1434 (m), 1335 (s), 1303 (s), 819 (s) $cm^{-1}$. − EI-MS (70 eV) *m/e* (*I*rel) 566 (57) [$M^+$], 459 (19), 461 (2), 432 (60), 384 (19), 318 (26). − $C_{37}H_{46}N_2Ti$ (566.67): calcd. C 78.42, H 8.18, N 4.94; found C 78.69, H 8.10, N 4.89.

*Preparation of* **20b**: To a solution of **8** (200 mg, 0.55 mmol) in 30 ml of *n*-hexane was added dicyclohexylcarbodiimid (**19b**) (110 mg, 0.55 mmol) at −20 °C. The mixture was stirred and warmed to 25 °C over 12 h. The solvent was removed to dryness, yielding **20b** as a dark green oil. (220 mg, 73%) − $^1H$ NMR (300 MHz, $C_6D_6$) δ = 0.88−2.14 (m, 20 H, $C_6H_{11}$), 1.75 [s, 30 H, $C_5(CH_3)_5$], 4.04 (tt, $J_{HH}$ = 4.0 and 5.4 Hz, 1 H, N−CH), 4.44 (tt, $J_{HH}$ = 3.4 and 11.4 Hz, 1 H, N−CH), 4.52 (s, 1 H, =$CH_2$), 6.32 (s, 1 H, = $CH_2$). − $^{13}C$ NMR ($C_6D_6$, 75 MHz): δ = 12.7 [$C_5(CH_3)_5$], 25.9, 26.9, 27.3, 27.5, 33.6, 37.7, 55.7, 56.2 ($C_6H_{11}$), 112.0 (=$CH_2$), 124.3 [$C_5(CH_3)_5$], 139.6 (N−*C*=N), 202.0 (Ti−C). − EI-MS (70 eV) *m/e* (%): 550 (10) [$M^+$], 453 (5) [$M^+$ − N − $C_6H_{11}$], 416 (14) [$M^+$ + H − $C_5(CH_3)_5$], 344 (91) [$M^+$ − $C_{13}H_{22}N_2$], 318 (100) [$M^+$ − $C_{15}H_{24}N_2$]. − $C_{35}H_{54}N_2Ti$ (550.8): calcd. C 76.32, H 9.90, N 5,09; found C 73.65, H 10.22, N 5.09.

*Preparation of* **22**: To a solution of **8** (300 mg, 0.83 mmol) in 30 ml of *n*-hexane was added N-benzylideneaniline (**21**) (150 mg) at −20 °C. The mixture was stirred and warmed to 25 °C over 12 h.

After filtration, the solvent was concentrated to 50%. After cooling to −78°C **22** was formed as red crystals (130 mg, 30%): − mp 158°C, dec. − $^1$H NMR (300 MHz, $C_6D_6$, TMS): δ = 1.67, 1.80 [each 15 H, $C_5(CH_3)_5$], 3.89 (1 H, C*H*Ph), 4.69 (d, 1 H, $=CH_2$, $J$ = 3.0 Hz); 6.05 (d, 1 H, $=CH_2$, $J$ = 2.4 Hz); 5.84, 6.15, 6.58, 6.86 (each 1 H, PhH); 7.09, 7.26, 7.37 (each 2 H, PhH). − $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, TMS): δ = 12.7, 13.0 [$C_5(\mathit{C}H_3)_5$]; 47.9 (CHPh); 107.7 ($=CH_2$); 114.8, 116.5, 118.7 (arom. C); 123.9, 124.2 [$\mathit{C}_5(CH_3)_5$]; 125.8, 128.2, 129.1 (arom. C); 139.2 (C−*C*ipso); 154.1 (N−Cipso); 217.8 (Ti−C). MS: *m/z* (%): 525.5 (9.5) [$M^+$], 343.3 (5.8) [$M^+ - C_{13}H_{12}N$], 318.2 (9.1) [$M^+ - C_{15}H_{13}N$], 274.3 (40.7) [$M^+ - C_{19}H_{23}$], 115.0 (100). − $C_{35}H_{43}NTi$ (525.67): C 79.96, H 8.26, N 2.67; found: C 79.58, H 8.17, N 2.70.

*Structure Determination and Refinement of* **20a**: Geometry and intensity data were collected on a ENRAF-Nonius CAD4 diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation. Crystal data, data collection parameters, and convergence results are compiled in Table 2. After Lorentz and polarization corrections, an empirical absorption correction based on azimuthal scans[20] was applied, before averaging symmetry related intensity data. **20a** was crystallized from *n*-hexane in the composition 2 [$Cp^*_2Ti\{-N(p\text{-}CH_3C_6H_4)-C(=N\text{-}p\text{-}CH_3C_6H_4)-C(=CH_2)-\}]\cdot n\text{-}C_6H_{14}$. The structure was solved by direct methods,[21] refined with the SDP program system.[22] In the final refinement cycles, hydrogen atoms were included in riding geometry with fixed isotropic displacement parameters [$d_{C-H}$ = 0.98 Å, $U_{iso}(H) = 1.30\ U_{eq}(C)$]. Further details of the crystal structure investigations are available on request from the Cambridge Crystallographic Data Centre, on quoting the depository number CCDC-100571.

Table 2. Crystal data, data collection parameters, and convergence results of **20a**

| | | | |
|---|---|---|---|
| Formula | $C_{40}H_{53}N_2Ti$ | *Data collection* | |
| Formula weight | 609.78 | Wavelength λ [Å] | 0.71073 |
| Crystal size [mm$^3$] | 0.28×0.32×0.36 | Temperature [K] | 203 |
| Space group (no) | $P\bar{1}$(2) | Scan range θ [°] | 3.0−26.0 |
| | | Scan type | |
| ω-2θ | | | |
| *Crystal data* | | Absorption correction (min./max) | empirical (0.851/0.996) |
| *a* [Å] | 9.756(5) | Reflection measured | 12085 |
| *b* [Å] | 10.445(1) | Independent reflections | 6709 |
| *c* [Å] | 17.604(2) | | |
| α [deg] | 79.57(1) | *Refinement results* | |
| β [deg] | 79.53(2) | Obeserved reflections | 4453, $I>1.0\sigma(I)$ |
| γ [deg] | 81.14(2) | Variables refined | 388 |
| *V* (Å$^3$) | 1721(1) | *R*, *Rw*[a] | 0.059, 0.061 |
| *Z* | 2 | *GOF* | 1.339 |
| μ [cm$^{-1}$] | 2.73 | Max. residual electron density [eÅ$^{-3}$] | 0.547 |
| *D*calc [gcm$^{-3}$] | 1.177 | | |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_W = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F_o)$; GOF = $[\Sigma w(|F_o| - |F_c|)^2/n_{obs} - n_{var}]^{1/2}$; $n_{obs}$: no of observations; $n_{var}$: no of varibales refined.

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