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Synthesis of Carbodiimidotitanium Complexes by the Reaction of (Trimethylstannyl)carbodiimides with Titanium Chlorides

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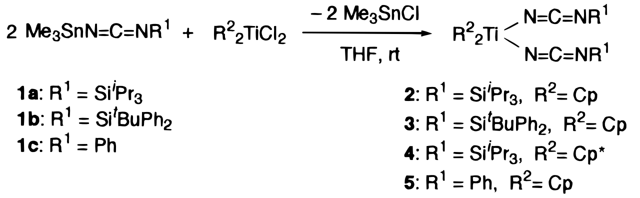
Summary: $Me_3Sn-N{=}C{=}N-R^1$ ($R^1 = Si^iPr_3$, $SiPh_2{}^tBu$, Ph) *reacts with* Cp_2TiCl_2 ($Cp = \eta^5\text{-}C_5H_5$) *or* $Cp^*{}_2TiCl_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) *selectively at the Sn−N bond to give the corresponding bis(carbodiimido)titanium complexes* ($Cp_2Ti(N{=}C{=}N-SiR_3)_2$, $Cp^*{}_2Ti(N{=}C{=}N-SiR_3)_2$, *and* $Cp_2Ti(N{=}C{=}N-Ph)_2$) *in moderate to high yields. The structure of* $Cp_2Ti(N{=}C{=}N-Ph)_2$ *was determined by X-ray crystallography. Oligomeric complexes were formed by the reaction of* $Me_3Sn-N{=}C{=}N-X-N{=}C{=}N-SnMe_3$ ($X = -C_6H_3Cl-CH_2-C_6H_3Cl-$) *with* $Cp^*{}_2TiCl_2$.

Introduction

Titanium complexes having amido-type nitrogen ligands are attracting much interest because of their potential use as new catalysts for polymerization and organic reactions[1] and as pyrolytic precursors for titanium nitride and titanium carbonitride.[2] Accordingly, a number of amidotitanium complexes have been synthesized.[1−3] Among amido-type nitrogen ligands, carbodiimido ligands with their linear N=C=N moiety are sterically less demanding and can retain larger space around the metal center than the usual amido ligands and a variety of substituents can be introduced onto the terminal nitrogen. However, no useful method for the preparation of carbodiimidotitanium complexes has been reported. A paper by Plenio and Roesky disclosed the synthesis of $Cp_2Ti(N{=}C{=}O)(N{=}C{=}N-SiMe_3)$ ($Cp = \eta^5\text{-}C_5H_5$) and $Cp_2Ti(N{=}C{=}N-SiMe_3)_2$ by the reaction of $Cp_2Ti(N{=}C{=}O)_2$ with $LiN(SiMe_3)_2$,[4] but the product yields were low (<15%). Here, we report a general and high-yield synthesis of carbodiimidotitanium complexes and the X-ray crystal structure determination of $Cp_2Ti(N{=}C{=}N-Ph)_2$.

Scheme 1



Results and Discussion

Transmetalation reactions between $R_3Si-N{=}C{=}N-X$ and L_nM-Cl (M = B, Sb, Ta, Mo, W) have been used to synthesize (carbodiimido)metal species $L_nM-N{=}C{=}N-X$ with elimination of R_3SiCl.[5] The use of trialkylstannylcarbodiimides seems more attractive because they have higher reactivities toward transmetalation reactions.[6] For example, selective monosubstitution proceeds at the Sn−N bond in the reaction of $R_3Sn-N{=}C{=}N-SiR'_3$ with $(^iPr_2N)_2PCl$.[7] This procedure proved to work nicely for the synthesis of carbodiimidotitanium complexes. Thus, (silyl)(stannyl)carbodiimides **1a**,**b** reacted selectively at the Sn−N bond with $R^2{}_2TiCl_2$ (R^2 = Cp or Cp* (= $\eta^5\text{-}C_5Me_5$)) in THF at room temperature to form bis[(trialkylsilyl)carbodiimido]titanium complexes **2**−**4** nearly quantitatively (by ^{13}C NMR spectroscopy). These complexes were readily purified by recrystallization to give thin orange or red plates (**2**, 85%; **3**, 94%; **4**, 45%), Scheme 1.[8] Phenyl(stannyl)carbodiimide **1c** reacted similarly with Cp_2TiCl_2 to give **5** nearly quantitatively. The color of the resulting THF solution of **5** was very strongly purple-violet, but **5** crystallized to form shiny metallic thin green plates.

Complexes **2**−**4** are air- and light-stable in the crystalline state, while in solution they gradually de-

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[1] (a) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 1906. (b) Scollard, J.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (c) Scollard, J.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (d) Fuhrmann, H.; Brenner, S.; Arndt, P.; Kempe, R. *Inorg. Chem.* **1996**, *35*, 6742.

[2] For recent examples, see: (a) Seyferth, D.; Mignani, G. *J. Mater. Sci. Lett.* **1988**, *7*, 487. (b) Brown, G. M. *Inorg. Chem.* **1989**, *28*, 3028. (c) Gross, M. E.; Siegrist, T. *Inorg. Chem.* **1992**, *31*, 4898. (d) Laurent, F.; Zhao, J. S.; Valade, L.; Choukroun, R.; Cassoux, P. *J. Anal. Appl. Pyrolysis* **1992**, *24*, 39. (e) Laurent, F.; Cyr-Athis, O.; Legros, J. P.; Choukroun, R.; Valade, L. *New J. Chem.* **1994**, *18*, 575. (f) Narula, C. K.; Demczyk, B. G.; Czubarow, P.; Seyferth, D. *J. Am. Ceram. Soc.* **1995**, *78*, 1247. (g) Weiller, B. H. *J. Am. Chem. Soc.* **1996**, *118*, 4975.

[3] For recent examples, see: (a) Visciglio, V. M.; Fanwick, P. E.; Rothwell, I. P. *Acta Crystallogr.* **1994**, *C50*, 896. (b) Irigoyen, A. M.; Martín, A.; Mena, M.; Palacios, F.; Yélamos, C. *J. Organomet. Chem.* **1995**, *494*, 255. (c) Bowen, D. E.; Jordan, R. F. *Organometallics* **1995**, *14*, 3630. (d) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562. (e) Minhas, R. K.; Scoles, L.; Wong, S.; Gambarotta, S. *Organometallics* **1996**, *15*, 1113. (f) Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825. (g) Friedrich, S.; Memmler, H.; Gade, L. H.; Li, W.-S.; Scowen, I. J.; McPartlin, M.; Housecroft, C. E. *Inorg. Chem.* **1996**, *35*, 2433. (h) Kempe, R.; Arndt, P. *Inorg. Chem.* **1996**, *35*, 2644. (i) Guérin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085. (j) Tsuie, B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 1392. (k) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 1491. (l) Guzei, I. A.; Baboul, A. G.; Yap, G. P. A.; Rheingold, A. L.; Schlegel H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1997**, *119*, 3387.

[4] Plenio, H.; Roesky, H. W. *Z. Naturforsch.* **1989**, *44b*, 94.

[5] (a) Rajca, G.; Schwarz, W.; Weidlein, J. *Z. Naturforsch.* **1984**, *39b*, 1219. (b) Rajca, G.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1986**, *538*, 36. (c) Einholz, W.; Haubold, W. *Z. Naturforsch.* **1986**, *41b*, 1367.

[6] Réau, R.; Bertrand, G. *Rev. Heteroat. Chem.* **1996**, *14*, 137.

[7] Veneziani, G.; Réau, R.; Bertrand, G. *Organometallics* **1993**, *12*, 4289.

[8] The lower isolated yield of **4** was due to its high solubility in the recrystallization solvents. Most of the products described in this paper were reluctant to burn in combustion analysis. Use of a larger quantity of combustion promoter (V_2O_5) proved to improve elemental analyses but was not sufficiently helpful to obtain satisfactory data.

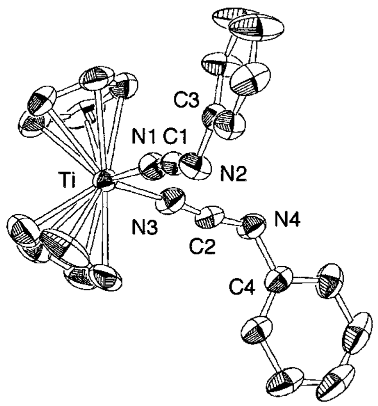


Figure 1. A view of the molecular structure of **5**.

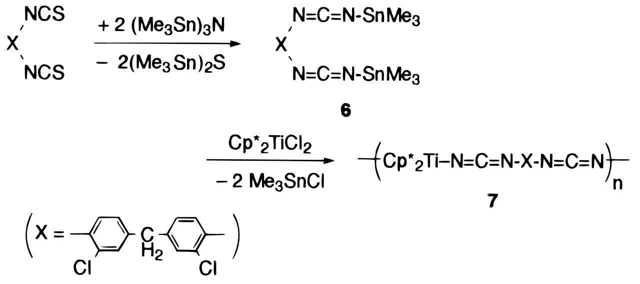
Table 1. Crystallographic Data for 5

formula	$C_{24}H_{20}N_4Ti$
fw	412.35
cryst size, mm	0.40 × 0.20 × 0.03
a, Å	11.674(2)
b, Å	21.154(2)
c, Å	9.226(2)
β, deg	112.82(1)
V, Å^3	2100.0(1)
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
Z	4
D_{calc}, g cm^{-3}	1.304
μ (Cu Kα), cm^{-1}	35.75
λ, Å	1.541 78
$2\theta_{max}$, deg	120.1
no. of rflns measd	3454
no. of unique rflns	3234
no. of rflns $I_o > 3.0\sigma(I_o)$	1876
R, R_w	0.047, 0.062
GoF	1.53

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Ti–N1	2.002(4)	N2–C3	1.404(6)
Ti–N3	1.985(5)	N3–C2	1.177(6)
N1–C1	1.187(7)	N4–C2	1.247(7)
N2–C1	1.260(7)	N4–C4	1.399(6)
N1–Ti1–N3	95.4(2)	C2–N4–C4	125.4(5)
Ti1–N1–C1	168.1(4)	N1–C1–N2	173.8(6)
Ti1–N3–C2	174.5(4)	N3–C2–N4	171.3(5)
C1–N2–C3	123.3(5)		

Scheme 2



compose under sunlight, even under a nitrogen atmosphere to give insoluble materials. In the decomposition of **2** and **4**, the major soluble product was $^{i}Pr_3Si{-}N{=}C{=}N{-}Si^{i}Pr_3$, as characterized by comparison of its spectral data with those of an authentic sample. On the other hand, the insoluble products did not show N=C=N nor C=O absorptions in the IR spectra. In a patent it was reported that a polymer containing $-SiPh_2{-}N{=}C{=}N-$ repeat units underwent cross-linking upon exposure to an electron beam.[9] In our photodegradation process, not only the metathesis reaction leading to the formation of $^{i}Pr_3Si{-}N{=}C{=}N{-}Si^{i}Pr_3$ but also a cross-linking process may have been involved. However, further characterization of the insoluble products was not undertaken. On the other hand, complex **5** is air stable in the solid state and insensitive to the light. When a THF solution of **5** was exposed to air, slow decomposition occurred to precipitate a light orange powder. The IR spectrum of the latter showed several new bands assignable to C=O stretching vibrations, formed at the expense of the N=C=N bands. This suggests the formation of urea-type products, as in the case of the usual organic carbodiimides. Such hydrolytic degradation has never been observed for complexes **2**–**4**.

The molecular structure of complex **5** was determined by X-ray diffraction, and the ORTEP drawing[10] is shown in Figure 1. Crystallographic data and selected bond lengths and angles for **5** are given in Tables 1 and 2, respectively. The structure of M–N=C=N–M′ is known to be highly dependent on the nature of M and M′. For example, even in the case of symmetric $R_3Si{-}N{=}C{=}N{-}SiR_3$, the Si–N–C angle can vary between 180° (R = Ph) and 142.0(11)° (R = Me).[11] Complex **5** has asymmetric N=C=N linkages; the N1–C1 and N3–C2 bond lengths are 1.187(7) and 1.177(6) Å, respectively, which are close to the N–C triple bond length. On the other hand, the N2–C1 and N4–C2 bond lengths are 1.260(7) and 1.247(7) Å, respectively, suggesting a double-bond character of these bonds. The bond angles distinctly reflect the difference in these N–C bond lengths; Ti–N1–C1 (168.1(4)°) and Ti–N3–C2 (174.5(4)°) are almost linear, while C1–N2–C3 (123.3(5)°) and C2–N4–C4 (125.4(5)°) are those of usual trigonal nitrogens.

The present method should be applicable to the synthesis of polymeric complexes. The reaction of $Me_3Sn{-}N{=}C{=}N{-}SnMe_3$ with $Cp^*{}_2TiCl_2$, $Cp^*{}_2TiCl_2$, and $TiCl_4$ gave red or reddish-brown materials. However, high air and/or light sensitivity and insolubility prevented characterization of the products. To ensure the characterization of possible polymeric complexes by improving the air- and light-stability and solubility, bis(stannylcarbodiimido) compound **6**, having an organic spacer, was synthesized by the procedure of Hänssgen and Hajduga.[12] The reaction of **6** with $Cp^*{}_2TiCl_2$ gave a deep violet solid **7**, which indeed was more stable to air and light than the products derived from $Me_3Sn{-}N{=}C{=}N{-}SnMe_3$, Scheme 2. Product **7** was soluble in $CHCl_3$ and THF. Its IR spectrum showed a typical N=C=N absorption band at 2130 cm^{-1}. GPC (gel permeation chromatography; THF, polystyrene standards) analysis of the crude mixture revealed that the molecular weight of the product ranged from 300 to 3000, indicative of the formation of low molecular weight

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(9) Klebe, J. F.; Murray, J. G. U.S. Patent 3352799 (to General Electric Co.), 1967; *Chem. Abstr.* **1968**, *68*, 14164x.

(10) Johnson, C. K. *Ortep, a FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1970.

(11) Sheldrick, G. M.; Taylor, R. *J. Organomet. Chem.* **1975**, *101*, 19. Hammel, A.; Volden, H. V.; Haaland, A.; Weidlein, J.; Reischmann, R. *J. Organomet. Chem.* **1991**, *408*, 35. Obermeyer, A.; Kienzle, A.; Weidlein, J.; Riedel, R.; Simon, A. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1357.

(12) Hänssgen, D.; Hajduga, D. *Chem. Ber.* **1977**, *110*, 3961.

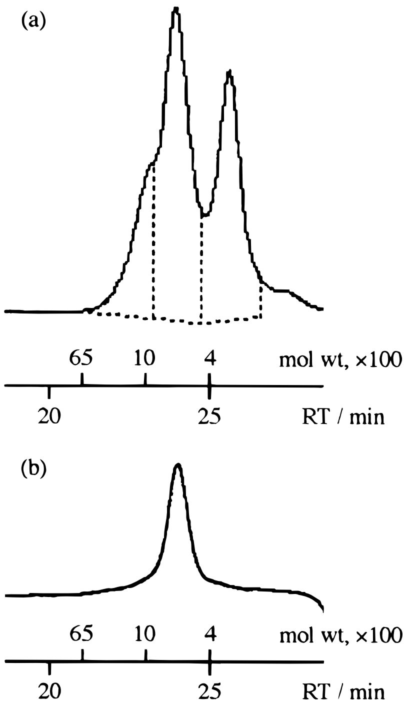

Figure 2. GPC profiles of (a) a crude mixture of **7** and (b) an isolated needle of **7**.

oligomers (Figure 2a; the formula weight of the repeat unit of **7** is 633). The ^{1}H NMR spectrum of crude **7** displayed signals arising from $C_5(CH_3)_5$ and aromatic hydrogens as well as a small amount of $Sn(CH_3)_3$, which was assignable to the unreacted $-NCN-SnMe_3$ terminus. A small amount of purer **7** could be isolated by recrystallization as fine needles[13] and showed the same retention time in the GPC analysis (Figure 2a; M_w (polystyrene standard) = 631, M_w/M_n = 1.08) as that of the major fraction of the crude material. Although the M_w estimated by GPC corresponds to the formula weight of one repeat unit, the absolute value is meaningless since the polystyrene standards are used. Indeed, the FAB mass spectrum of the needle showed a signal at *m/z* 1267 (with the expected isotope pattern), which corresponds to the molecular ion peak of a cyclic dimer $(-Cp^*_2Ti-N=C=N-C_6H_3Cl-CH_2-C_6H_3Cl-N=C=N-)_2$. This result suggests that GPC analysis using the standards underestimates the molecular weight of **7**. Similar underestimations are reported for dendrimers and organometallic oligomers and polymers.[14] The ^{1}H and ^{13}C NMR spectra of the needle verified the presence of Cp* and $C_6H_3Cl-CH_2-C_6H_3Cl$ groups and the absence of Me_3Sn. These spectra also are consistent with the cyclic structure.

Experimental Section

General Procedures. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk tube techniques. $Me_3Sn-N=C=N-SnMe_3$,[15] $Me_3Sn-N=C=N-Si^iPr_3$,[7] and $Me_3Sn-N=C=N-Ph$[12] were prepared according to the literature procedures. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker AC200 and ARX300 spectrometers.

Preparation of $Me_3Sn-N=C=N-SiPh_2{}^tBu$ (1b). To a THF solution (10 mL) of $Me_3SnNCNSnMe_3$ (0.55 g, 1.5 mmol) was added dropwise $^tBuPh_2SiCl$ (0.41 g, 1.5 mmol) at room temperature. After 2 h, the solvent and Me_3SnCl were removed under vacuum to give **1b** as a colorless oil, which was used in the following reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.47 (s, 9H, $J_{H^{119}Sn}$ = 58.7 Hz, $J_{H^{117}Sn}$ = 56.6 Hz, $SnCH_3$), 1.06 (s, 9H, ^{t}Bu), 7.33−7.39 (m, 6H), 7.72−7.76 (m, 4H). ^{13}C NMR ($CDCl_3$): δ − 4.14 ($J_{C^{119}Sn}$ = 401 Hz, $J_{C^{117}Sn}$ = 381 Hz, $SnMe_3$), 19.55 (CMe_3), 26.27 (CMe_3), 127.10, 128.84, 130.41 (NCN), 134.51, 134.76 (*ipso*). ^{29}Si NMR ($CDCl_3$): δ − 15.96. IR (neat, cm^{-1}): 2148 (NCN). HRMS calcd for $C_{16}H_{19}N_2SiSn$ ($M^+ - {}^tBu$): 386.0328. Found: 386.0323.

General Procedure for the Synthesis of Compounds 2−4. To a THF solution (8 mL) of $R^2{}_2TiCl_2$ (0.3 mmol) was added dropwise a THF solution (8 mL) of $R^1-N=C=N-SnMe_3$ (0.6 mmol) at room temperature. After the mixture was stirred overnight, the solvent and Me_3SnCl were removed under vacuum (3 h, 10^{-2} mmHg) to give **2**−**4**, which were recrystallized from pentane (**2**, 85%), hexane (**3**, 94%), or a THF/acetonitrile mixture (3/7, **4**, 45%).

$Cp_2Ti(N=C=N-Si^iPr_3)_2$ (2). Orange thin plates (85% yield), mp 112 °C. ^{1}H NMR ($CDCl_3$): δ 1.07 (m, 42H, ^{i}Pr), 6.24 (s, 10H, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 12.89 ($CHMe_2$), 18.19 ($CHMe_2$), 115.68 (C_5H_5), NCN was not observed. ^{29}Si NMR ($CDCl_3$): δ 2.39. IR (KBr, cm^{-1}): 2146, 2112 (NCN). MS (EI, relative intensity): *m/z* 572 (M^+, 8), 529 ($M^+ - {}^iPr$, 100), 507 ($M^+ - C_5H_5$, 100), 486 (56). HRMS Calcd for $C_{30}H_{52}N_4Si_2Ti$: 572.3210. Found: 572.3176. Anal. Calcd for $C_{30}H_{52}N_4Si_2Ti$: C, 62.90; H, 9.15; N, 9.18. Found: C, 62.34; H, 9.19; N, 9.14.

$Cp_2Ti(N=C=N-SiPh_2{}^tBu)_2$ (3). Orange-red thin plates (94% yield), mp 105 °C. ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 18H, CMe_3), 6.14 (s, 10H, C_5H_5), 7.38−7.78 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 19.84 (CMe_3), 26.77 (CMe_3), 116.12 (C_5H_5), 127.60, 129.27, 135.19, 135.88 (*ipso*), 138,63 (NCN). ^{29}Si NMR ($CDCl_3$): δ−15.53. IR (KBr, cm^{-1}): 2156, 2094 (NCN). MS (EI, relative intensity): *m/z* 679 ($M^+ - {}^tBu$, 63), 223 (100), 178 (42). Anal. Calcd for $C_{44}H_{48}N_4Si_2Ti$: C, 71.71; H, 6.57; N, 7.60. Found: C, 72.04; H, 6.67; N, 7.60.

$Cp^*_2Ti(N=C=N-Si^iPr_3)_2$ (4). Red plates (45% yield), mp 182 °C. ^{1}H NMR ($CDCl_3$): δ 1.04 (m, 42H, ^{i}Pr), 1.95 (s, 30H, C_5Me_5). ^{13}C NMR ($CDCl_3$): δ 11.99, 13.06, 18.32, 124.74 (C_5Me_5), NCN was not observed. ^{29}Si NMR ($CDCl_3$): δ −1.66. IR (KBr, cm^{-1}): 2166, 2102 (NCN). MS (EI, relative intensity): *m/z* 712 (M^+, 0.4), 669 ($M^+ - {}^iPr$, 0.59), 578 ($M^+ - C_5Me_5$, 100). HRMS Calcd for $C_{40}H_{72}N_4Si_2Ti$: 712.4775. Found: 712.4786.

$Cp_2Ti(N=C=N-Ph)_2$ (5). To a THF solution (3 mL) of Cp_2TiCl_2 (0.075 g; 0.3 mmol) was added dropwise a THF solution (3 mL) of $PhNCNSnMe_3$ (0.168 g; 0.6 mmol) at room temperature. After the mixture was stirred overnight, the solution was poured into pentane (20 mL). Filtration followed by drying in vacuo gave metallic green crystals **5** (95% yield), mp: 123 °C. ^{1}H NMR ($CDCl_3$): δ 6.41 (s, 10H, C_5H_5), 6.98−7.24 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 116.33 (C_5H_5), 122.01, 122.26, 129.37, 143.72 (NCN), 145.53 (*ipso*). IR (KBr, cm^{-1}): 2132, 2092 (NCN). MS (EI, relative intensity): *m/z* 412 (M^+, 21), 295 (M^+ − PhNCN, 100), 178 (Cp_2Ti, 87). HRMS Calcd for $C_{24}H_{20}N_4Ti$: 412.1167. Found: 412.1185. Anal. Calcd for $C_{24}H_{20}N_4Ti$: C, 69.91; H, 4.89; N, 13.59. Found: C, 69.29; H, 4.90; N, 13.29.

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(13) We tried the reaction of **6** with $Cp^*_2TiCl_2$ several times. In all cases, GPC profiles of the resulting mixtures of oligomers were almost the same. However, we succeeded only once to obtain a small amount of a purer compound as needles by cooling a saturated THF solution of a mixture of oligomers. FAB mass analyses of the crude products also always showed the signal corresponding to the cyclic dimer $(-Cp^*_2-Ti-N=C=N-C_6H_3Cl-CH_2-C_6H_3Cl-N=C=N-)_2$ at *m/z* 1267, 1131, and 633.

(14) For recent examples, see: Hawker, C. J.; Frechet, J. M. J.; Wooley, K. L. *Pure Appl. Chem.* **1994**, *A31*, 1627. Foucher, D.; Ziembinski, R.; Petersen, R.; Pudelski, J.; Edwards, M.; Ni, Y.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1994**, *27*, 3992. Achar, S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 43. Liano, Y.-H.; Moss, J. R. *Organometallics* **1996**, *15*, 4307.

(15) Forder, R. A.; Sheldrick, G. M. *J. Chem. Soc. A* **1971**, 1107.

Preparation of 6. To a hexane solution (8 mL) of $(Me_3Sn)_3N$ (0.505 g; 1.0 mmol) stirred at room temperature was added dropwise an EtOH solution (3 mL) of 1,1′-methylenebis(3-chloro-4-isothiocyanatobenzene) (0.175 g; 0.50 mmol). After the mixture was stirred overnight, the solvent and $(Me_3Sn)_2S$ were removed by a syringe. The residue was then dissolved in THF (5 mL) and poured into pentane (20 mL) under vigorous stirring. The solvent was again removed by a syringe, and the remaining product was dried under vacuum, affording a pale yellow solid (89% yield), which was used in subsequent reactions without further purification. ^{1}H NMR ($CDCl_3$): δ 0.55 (s, 18H, $J_{H^{119}Sn} = 58.4$ Hz, $J_{H^{117}Sn} = 53.5$ Hz, Sn*Me*$_3$), 3.76 (s, 2H, CH_2), 6.91−7.05 (m, 6H). ^{13}C NMR ($CDCl_3$): $\delta - 1.98$ ($J_{C^{119}Sn} = 402$ Hz, $J_{C^{117}Sn} = 384$ Hz, Sn*Me*$_3$), 40.85 (*C*H_2), 124.59, 127.79, 128.81, 130.95, 133.14 (N*C*N), 136.36, 140.02. IR (neat, cm^{-1}): 2128 (NCN). HRMS Calcd for $C_{20}H_{23}N_4{}^{119}Sn_2{}^{35}Cl_2$ ($M^+ - Me$): 628.9342. Found: 628.9360.

Synthesis of 7. To a THF solution (5 mL) of $Cp^*{}_2TiCl_2$ (0.233 g, 0.60 mmol) stirred at room temperature was added dropwise a THF solution (4 mL) of **6** (0.386 g; 0.60 mmol). After the mixture was refluxed for 2 h, the solution was poured into pentane (20 mL). The precipitate was filtered, redissolved in THF (5 mL), and poured again in pentane (15 mL). Filtration and drying under vacuum afforded the oligomers **7** (0.285 g). ^{1}H NMR ($CDCl_3$): δ 1.95 (s), 2.01 (s), 3.7−3.8 (m), 6.7−7.2 (m). IR (KBr, cm^{-1}): 2130 (NCN).

A small amount (ca. 5 mg) of deep brown needles was obtained from a saturated THF solution of crude **7**. ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 30H, C_5*Me*$_5$), 3.73 (s, 2H, *C*H_2), 6.83−7.13 (m, 6H, C_6*H*$_3$Cl). ^{13}C NMR ($CDCl_3$): δ 12.35 (C_5*Me*$_5$), 40.03 (*C*H_2), 123.05, 125.91, 126.52, 127.63, 129.98, 134.16, 139.64 (N*C*N), 141.63. IR (KBr, cm^{-1}): 2136, 2102 (NCN). MS (FAB): *m*/*z* 1267, 1131, 633.

X-ray Structure Determination of 5. A red plate crystal was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Cu Kα radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 22 carefully centered reflections in the range $50.04° < 2\theta < 58.38°$. The data were collected at 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 120.1°. Of the 3454 reflections which were collected, 3234 were unique ($R_{int} = 0.025$). The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 28.7%. A linear correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient, μ, for Cu Kα radiation was 35.8 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied, resulting in transmission factors ranging from 0.69 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[16] and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1876 observed reflections ($I > 3.00\sigma(I)$) and 262 variable parameters and converged (largest parameter was 1.31 times its esd) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.047$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2} = 0.062$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.26 and − 0.26 e$^-$/Å^3, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

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Supporting Information Available: Details of X-ray analysis and tables of crystal data and structure refinement, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (14 pages). Ordering information is given on any current masthead page.

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[16] Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: New York, 1985; p 175.

[17] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.