

Linked amido–indenyl complexes of titanium¹

Francisco Amor, Jun Okuda *

Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, J.-J.-Becher-Weg 24, D-55099 Mainz, Germany

Received 21 March 1996

Abstract

Titanium complexes $\text{Ti}(\eta^5\text{-C}_9\text{H}_6\text{SiMe}_2\text{NCMe}_3)_2\text{X}_2$ ($\text{X} = \text{Cl, Me, CH}_2\text{SiMe}_3, \text{CH}_2\text{Ph}$) containing the *tert*-amido-functionalized indenyl ligand $\text{C}_9\text{H}_6\text{SiMe}_2\text{NCMe}_3$ have been synthesized by the reaction of the dilithium derivative $\text{Li}_2[\text{C}_9\text{H}_6\text{SiMe}_2\text{NCMe}_3]$ with $\text{TiCl}_3(\text{THF})_3$ followed by oxidation or by the alkylation of the dichloro derivative. Unexpectedly, the reaction of $\text{C}_9\text{H}_6(\text{SiMe}_3)(\text{SiMe}_2\text{Cl})$ with TiCl_4 does not give $\text{Ti}(\eta^5\text{-C}_9\text{H}_6\text{SiMe}_2\text{Cl})\text{Cl}_3$.

Keywords: Titanium; Amido–indenyl ligand; Alkyl derivatives

1. Introduction

Titanium complexes with one amido-functionalized cyclopentadienyl ligand are currently attracting considerable attention as components of novel single-site polymerization catalysts [1–3]. In particular, they have been shown to promote the efficient copolymerization of ethene with 1-alkenes, such as 1-octene, to give new types of elastomeric polyolefin [4]. While preliminary studies on the structure–activity relationship of these novel catalysts have appeared [5], thorough understanding of the various effects caused by the ligand periphery remains unachieved. Based on the significant difference of indenyl ligands [6], we have attempted to prepare linked amido–indenyl ligands and their titanium complexes. The limited stability of mono(indenyl)titanium complexes was expected to be improved by the introduction of the linked amido-functionality.

2. Results and discussion

In an attempt to carry out the synthesis of titanium complexes with an indenyl ligand with an additional amido-function, we tested the reaction of (1-chlorodimethylsilyl)(3-trimethylsilyl) indene [7a] with TiCl_4 (Scheme 1). The trichloro complex was planned to react

[7b] with LiNHR to give the amido–indenyl complexes. At the moment, however, the reaction to form the trichloro complex $\text{Ti}(\eta^5\text{-C}_9\text{H}_6\text{SiMe}_2\text{Cl})\text{Cl}_3$ does not appear to proceed in the desired fashion in our hands.

Therefore, we turned to the more conventional method of assembling the ligand first. The addition of LiNHCM_3 to a cooled solution of $\text{C}_9\text{H}_7\text{SiMe}_2\text{Cl}$ [8] in hexane, at 0°C, gave $\text{C}_9\text{H}_7\text{SiMe}_2\text{NHCM}_3$ in 70% yield as a colorless oil (Scheme 2). The ^1H NMR spectrum of $\text{C}_9\text{H}_7\text{SiMe}_2\text{NHCM}_3$ shows multiplets for the protons of the six-membered ring, whereas the protons of the five-membered ring appear as three distinct signals. The *tert*-butyl group gives rise to a singlet in the expected region and the two diastereotopic methyl groups of the silicon bridge appear as two separate singlets.

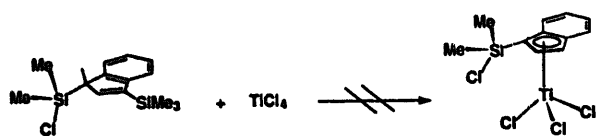
The ligand with an additional trimethylsilyl group in 3 position with respect to the lateral chain has also been synthesized in a similar way and made analogous complexes accessible.

The addition [2] of the dilithium salt $\text{Li}_2[\text{C}_9\text{H}_6\text{SiMe}_2\text{NCMe}_3]$ to a suspension of $\text{TiCl}_3(\text{THF})_3$ in THF, followed by oxidation using PbCl_2 [9] produced the amido–indenyl complex $\text{Ti}(\eta^5\text{-C}_9\text{H}_6\text{SiMe}_2\text{NCMe}_3)_2\text{Cl}_2$ (1a) (Scheme 2) as a dark red solid in over 90% yield.

The ^1H NMR spectrum of complex 1a shows multiplets in the aromatic region due to the protons of the six-membered ring and the proton in 3 position. The proton in 2 position appears as a doublet at 6.55 ppm.

* Corresponding author.

¹ Dedicated to the memory of Professor Hidemasa Takaya.



Scheme 1.

For the lateral chain a pattern similar to that found in the ^1H NMR of the ligand is observed. The solubility of the dichloro complex **1b** is significantly increased due to the additional SiMe_3 group in the amido-indenyl ligand.

The addition of methylmagnesium chloride or (trimethylsilyl)methylmagnesium chloride in the appropriate stoichiometric ratio to a solution of **1a** in hexane at -78°C produced $\text{Ti}(\eta^5\text{-}\eta^1\text{-C}_9\text{H}_6\text{SiMe}_2\text{NCMe}_3)\text{Me}_2$ (**2a**) and $\text{Ti}(\eta^5\text{-}\eta^1\text{-C}_9\text{H}_6\text{SiMe}_2\text{NCMe}_3)(\text{CH}_2\text{SiMe}_3)_2$ (**3a**) in 49% and 42% yields respectively (Scheme 2). The new complexes **2a** and **3a** were isolated as yellow oils which, so far, have resisted crystallization.

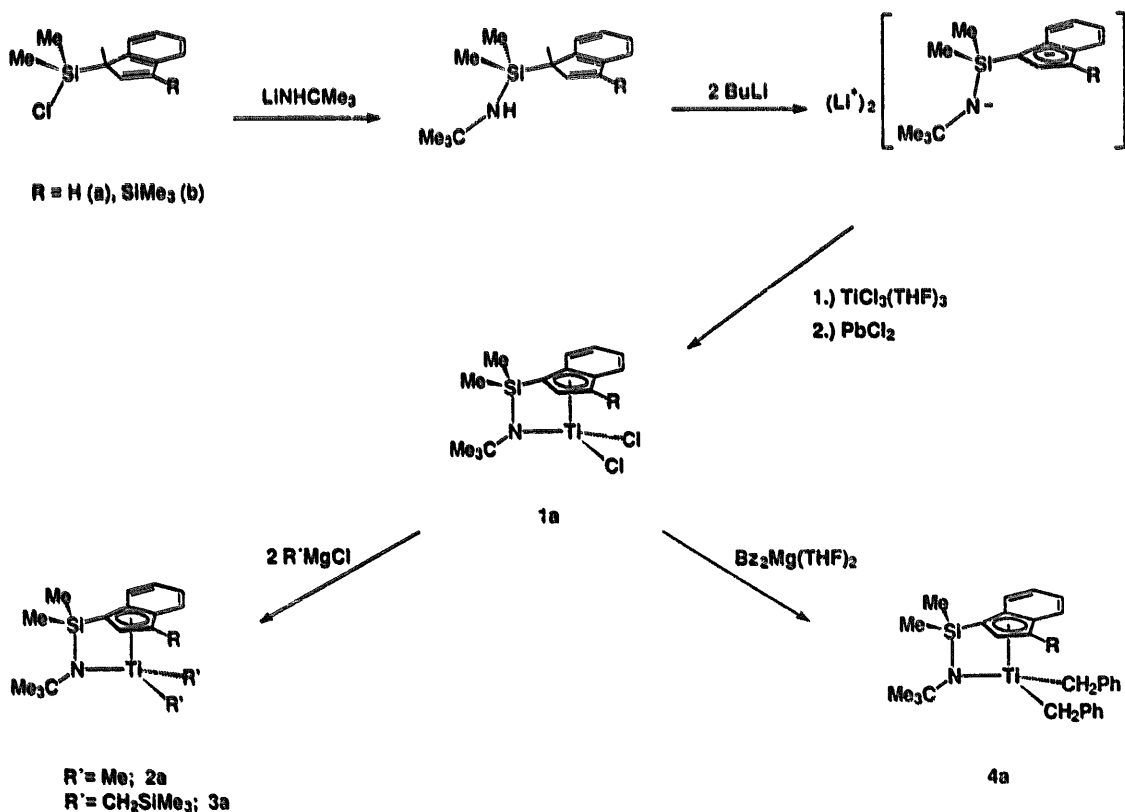
The reaction of **1a** with the THF adduct of dibenzylmagnesium in hexane gave $\text{Ti}(\eta^5\text{-}\eta^1\text{-C}_9\text{H}_6\text{SiMe}_2\text{NCMe}_3)(\text{CH}_2\text{Ph})_2$ (**4a**) in 53% yield as red crystals.

The ^1H NMR spectra of the alkyl complexes follow the same pattern as observed for the linked amido-indenyl ligand in **1a**. Owing to the ligand environment the two alkyl groups in each of the complexes are inequivalent. The ^1H NMR spectrum of the dimethyl complex

2a shows two singlets for the methyl groups at -0.60 and $+0.48$ ppm; the corresponding ^{13}C NMR signals are at 53.3 and 56.1 ppm. In the case of the bis(trimethylsilylmethyl) complex **3a**, each of the SiMe_3 groups in the alkyl ligands appears as a singlet at -0.21 and 0.00 ppm, while four AB-type doublets in the region from -1.69 to $+1.63$ ppm are assigned to the diastereotopic protons of CH_2 groups. For the dibenzyl complex **4a**, the ^1H NMR spectrum shows the signals of the phenyl groups as unresolved multiplets together with the indenyl ring protons. As in **3a**, the protons of the CH_2 groups give rise to four doublets in the region from -0.06 to $+2.97$ ppm. Clearly, the unusually strong high-field shift of one of the four CH_2 -signals in **3a** and **4a** is caused by the fairly rigid ligand structure, which forces the CH_2 -group into the anisotropy region of the indenyl ring. A comparable situation was observed for the fluorenyl complex $\text{Zr}(\eta^5\text{-}\eta^1\text{-C}_{13}\text{H}_8\text{SiMe}_2\text{NCMe}_3)(\text{CH}_2\text{SiMe}_3)_2$ [10]. Preliminary tests [11] of the described complexes **1–4** in the copolymerization of ethene with styrene gave, at acceptable activities, good rates of comonomer incorporation.

3. Experimental section

All experiments were performed under argon using standard Schlenk techniques. $\text{TiCl}_3(\text{THF})_3$ [12] and



Scheme 2.

(PhCH₂)₂Mg(THF)₂ [13] were synthesized according to published procedures. Indene (Merck) was distilled prior to use. Me₂SiCl₂ (Merck), NH₂CMe₃ (Aldrich), MeMgCl (Aldrich), Me₂SiCH₂MgCl (Aldrich) and BuLi (2.5 M solution in hexane, Aldrich) were used as-received. NMR spectra were recorded on a Bruker AC 300 spectrometer, and mass spectra were recorded on a Varian spectrometer CH 7.

3.1. C₉H₇SiMe₂NHCMe₃

LiNHCMe₃ (2.52 g, 31.88 mmol) was dissolved in hexane (30 ml) and added to a solution of C₉H₇SiMe₂Cl (6.6 g, 31.88 mmol) in hexane (50 ml) at 0°C. The solution was filtered and the solvent was removed to give C₉H₇SiMe₂NHCMe₃ (5.44 g, 70%) as a colorless oil, distillable at 66°C at 10⁻² mm Hg. ¹H NMR (CDCl₃): -0.05, 0.00 (s, 3 H, Si(CH₃)₂); 1.26 (s, 9 H, C(CH₃)₃); 3.65 (t, 1 H, H-1); 6.73 (dd, 1 H, H-2, ³J_{HH} = 5 Hz, ⁴J_{HH} = 2 Hz); 6.95 (ddd, 1 H, H-3, ³J_{HH} = 5 Hz, ⁴J_{HH} = 2 Hz, ⁵J_{HH} = 1 Hz); 7.6–7.19 (m, 4 H, H-5-8). ¹³C{¹H} NMR (CDCl₃): -1.1, -0.3 (Si(CH₃)₂); 33.6 (C(CH₃)₃); 48.8 (C-1); 49.6 (C(CH₃)₃); 121.2, 123.2, 123.8 (C-5-8); 124.8 (C-3); 128.9 (C-5-8); 136.7 (C-2); 144.6, 145.5 (C-4,9). EI-MS: *m/z* (%) 245 (1) [M⁺].

3.2. Ti(η⁵: η¹-C₉H₆SiMe₂NCMe₃)Cl₂ (1a)

To a cooled at 0°C solution of C₉H₇SiMe₂NHCMe₃ (3.23 g, 13.17 mmol) in hexane (40 ml) was added BuLi (10.54 ml of a 2.5 M solution in hexane) via syringe to obtain 3.04 g (90%) of Li₂[C₉H₆SiMe₂NCMe₃]. A solution of the dilithium salt (1.91 g, 7.42 mmol) in THF (40 ml) was added to a suspension of TiCl₄(THF)₄ (2.74 g, 7.42 mmol) in THF (20 ml) at -78°C. After warming to room temperature, solid PbCl₂ (2.06 g, 7.42 mmol) was added and the mixture was stirred (1/2 h). The solvent was removed completely and a red toluene solution was obtained (3 × 15 ml) from which a dark red solid (2.51 g, 94%) precipitated. ¹H NMR (CDCl₃): 0.53, 0.79 (s, 3 H, Si(CH₃)₂); 1.23 (s, 9 H, C(CH₃)₃); 6.55 (d, 1 H, H-2, ³J_{HH} = 3 Hz); 7.76–7.28 (m, 5 H, H-3,5-8). ¹³C{¹H} NMR (CDCl₃): 0.9, 3.4 (Si(CH₃)₂); 32.2 (C(CH₃)₃); 63.3 (C(CH₃)₃); 98.3 (C-1); 119.8 (C-3); 126.2, 127.3, 128.2 (C-5-8); 128.3 (C-2); 129.0 (C-5-8); 134.6, 135.8 (C-4,9). EI-MS: *m/z* (%) 361 (3) [M⁺]; 346 (100) [M⁺ - Me]; 290 (36) [M⁺ - NCMe₃]. Anal. Found: C, 47.92; H, 5.88; N, 3.66. C₁₅H₂₁Cl₂NSiTi. Calc.: C, 49.71; H, 5.80; N, 3.86%.

3.3. Ti(η⁵: η¹-C₉H₆SiMe₂NCMe₃)Me₂ (2a)

A suspension of 1a (1.06 g, 3 mmol) in hexane (40 ml) was cooled at -78°C and then methylmagnesium

chloride (2.05 ml of a 3 M solution in THF) was added via syringe. The mixture was stirred and warmed to room temperature. Solvents were removed and hexane added to give a yellow solution (3 × 15 ml) which was filtered and evaporated to give 2a (0.47 g, 49%) as a yellow oil that solidifies to a glassy solid. ¹H NMR (CDCl₃): -0.60 (s, 3 H, TiCH₃); 0.42 (s, 3 H, Si(CH₃)₂); 0.48 (s, 3 H, TiCH₃); 0.65 (s, 3 H, Si(CH₃)₂); 1.45 (s, 9 H, C(CH₃)₃); 6.16 (d, 1 H, H-2, ³J_{HH} = 3 Hz); 7.72–7.06 (m, 5 H, H-3,5-8). ¹³C{¹H} NMR (CDCl₃): 1.8, 3.9 (Si(CH₃)₂); 33.8 (C(CH₃)₃); 53.3, 56.1 (Ti-CH₃); 58.6 (C(CH₃)₃); 91.3 (C-1); 113.7 (C-3); 125.1, 125.6, 125.8 (C-5-8); 126.4 (C-2); 127.3 (C-5-8); 132.6, 132.9 (C-4,9). EI-MS: *m/z* (%) 306 (8) [M⁺ - Me]; 291 (9) [M⁺ - 2Me]; 276 (10) [M⁺ - 3Me]; 234 (100) [M⁺ - 2Me - NCMe₃]. Anal. Found: C, 59.94; H, 8.37; N, 3.98. C₁₇H₂₇NSiTi. Calc.: C, 63.50; H, 8.41; N, 4.36%.

3.4. Ti(η⁵: η¹-C₉H₆SiMe₂NCMe₃)(CH₂SiMe₃)₂ (3a)

Following a similar procedure described for the preparation of 2a, 1a (1.8 g, 2.9 mmol) was reacted with trimethylsilylmethylmagnesium chloride (7.45 ml of a 1 M solution in Et₂O) to give 3a as yellow oil (0.5 g, 42%). ¹H NMR (CDCl₃): -1.69 (d, 1 H, TiCH₂Si(CH₃)₃, ³J_{HH} = 10 Hz); -0.21, 0.00 (s, 9 H, TiCH₂Si(CH₃)₃); 0.48 (s, 3 H, Si(CH₃)₂); 0.6 (d, 1 H, TiCH₂Si(CH₃)₃, ³J_{HH} = 10 Hz); 0.71 (s, 3 H, Si(CH₃)₂); 1.23 (d, 1 H, Ti-CH₂-Si(CH₃)₃, ³J_{HH} = 10 Hz); 1.46 (s, 9 H, C(CH₃)₃); 1.63 (d, 1 H, TiCH₂Si(CH₃)₃, ³J_{HH} = 10 Hz); 6.19 (d, 1 H, H-2, ³J_{HH} = 3 Hz); 7.81–7.08 (m, 5 H, H-3,5-8). ¹³C{¹H} NMR (CDCl₃): 1.0 (Si(CH₃)₂); 1.9, 2.6 (TiCH₂Si(CH₃)₃); 4.3 (Si(CH₃)₂); 33.7 (C(CH₃)₃); 58.6 (C(CH₃)₃); 72.2 (TiCH₂Si(CH₃)₃); 86.7 (C-1); 88.2 (TiCH₂Si(CH₃)₃); 111.6 (C-3); 125.2 (C-2); 125.3, 125.4, 125.9, 127.0 (C-5-8); 132.3, 134.1 (C-4,9). EI-MS: *m/z* (%) 465 (2) [M⁺]. Anal. Found: C, 52.19; H, 6.29; N, 2.73. C₂₃H₄₃NSi₃Ti. Calc.: C, 59.35; H, 9.24; N, 3.01%.

3.5. Ti(η⁵: η¹-C₉H₆SiMe₂NCMe₃)(CH₂Ph)₂ (4a)

Hexane (50 ml) was added at -78°C to a mixture of 1a (0.96 g, 2.65 mmol) and the THF adduct of dibenzylmagnesium (0.93 g, 2.65 mmol). The mixture was stirred at room temperature and all volatiles were removed in vacuo. The residue was extracted with hexane (3 × 15 ml), filtered and the red solution was concentrated and cooled overnight to -30 °C to give 4a as red microcrystals (0.66 g, 53%). ¹H NMR (CDCl₃): -0.06 (d, 1 H, TiCH₂Ph, ³J_{HH} = 9 Hz); 0.29, 0.77 (s, 3 H, Si(CH₃)₂); 1.63 (s, 9 H, C(CH₃)₃); 1.68, 1.9, 2.97 (d, 1 H, TiCH₂Ph, ³J_{HH} = 9 Hz); 5.43 ppm (d, 1 H, H-2, ³J_{HH} = 3 Hz); 7.9–6.6 (m, 15 H, H-3,5-8 and phenyl)

protons). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 1.3, 3.9 ($\text{Si}(\text{CH}_3)_2$); 34.2 ($\text{C}(\text{CH}_3)_3$); 60.5 ($\text{C}(\text{CH}_3)_3$); 80.2, 86.1 (TiCH_2Ph); 94.4 (C-1); 116.0, 121.2 (C-para Ph); 122.3 (C-meta Ph); 125.2 (C-5-8); 125.6 (C-meta Ph); 125.7 (C-ortho Ph); 126.5 (C-3); 127.4 (C-ortho Ph); 127.7, 127.9, 128.4 (C-5-8); 129.6 (C-2); 133.2, 134.1 (C-4,9); 146.8, 150.5 (C-ipso Ph). EI-MS: m/z (%) 382 (20) $[\text{M}^+ - (\text{CH}_2\text{Ph})]$; 275 (32) $[\text{M}^+ - 2(\text{CH}_2\text{Ph}) - \text{Me}]$; 234 (40) $[\text{M}^+ - 2(\text{CH}_2\text{Ph}) - \text{SiMe}_3]$. Anal. Found: C, 73.11; H, 7.59; N, 3.05. $\text{C}_{29}\text{H}_{35}\text{NSiTi}$. Calc.: C, 73.50; H, 7.39; N, 2.95%.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie and the Volkswagen-Foundation. F.A. is indebted to the European Community for a Training and Mobility of Researchers Programme postdoctoral fellowship (30 category).

References and note

- [1] (a) P.J. Shapiro, E. Bunel, W.P. Shaefer and J.E. Bercaw, *Organometallics*, **9** (1990) 867; (b) P.J. Shapiro, W.A. Cotter, W.P. Shaefer, J.A. Labinger and J.E. Bercaw, *J. Am. Chem. Soc.*, **116** (1994) 4632.
- [2] (a) J. Okuda, *Chem. Ber.*, **123** (1990) 1649; (b) K.E. du Plooy, U. Moll, S. Wocadlo, W. Massa and J. Okuda, *Organometallics*, **14** (1995) 3129; (c) A.K. Hughes, A. Meetsma and J.H. Teuben, *Organometallics*, **12** (1993) 1936; (d) W.A. Herrmann, M.J.A. Morawietz and T. Priemeier, *Angew. Chem.*, **106** (1994) 2025; (e) W.A. Herrmann and M.J.A. Morawietz, *J. Organomet. Chem.*, **482** (1994) 169.
- [3] J. Okuda, *Comments Inorg. Chem.*, **16** (1994) 185.
- [4] (a) J.A. Canich, (Exxon Chemical Co.), US Patent 5 026 789, 1991; (b) J.C. Stevens, F.J. Timmers, G.W. Rosen, G.W. Knight and S.Y. Lai (Dow Chemical Co.), European Patent Application, EP 0 416 815 A2, 1991.
- [5] J.C. Stevens, *Metcon 93*, Houston, May 26–28, 1993 p. 157.
- [6] (a) J. Okuda, P. König, I.L. Rushkin, H.-C. Kang and W. Massa, *J. Organomet. Chem.*, **501** (1995) 37; (b) S.L. Shaw, R.J. Morris and J.C. Huffman, *J. Organomet. Chem.*, **489** (1995) C4; (c) S.E. Ready, R.O. Day, J.C. Chien and M.D. Rausch, *Macromolecules*, **26** (1993) 5822.
- [7] (a) G. Hidalgo, M. Mena, F. Palacios, P. Royo and R. Serrano, *J. Organomet. Chem.*, **340** (1988) 37; (b) S. Ciruelos, T. Cuenca, P. Gómez-Sal, A. Manzanedo and P. Royo, *Organometallics*, **14** (1995) 177.
- [8] $\text{C}_9\text{H}_7\text{SiMe}_2\text{Cl}$ was prepared by reacting (indenyl)lithium in hexane with Me_2SiCl_2 (50 ml, 40 mmol) at 0 °C to give a colorless oil in 70% yield, slightly contaminated with $(\text{C}_9\text{H}_7)_2\text{SiMe}_2$. ^1H NMR (CDCl_3): 0.17, 0.23 (s, 3 H, $\text{Si}(\text{CH}_3)_2$); 3.73 (t, 1 H, H-1); 6.64 (dd, 1 H, H-2, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 2$ Hz); 6.99 (ddd, 1 H, H-3, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 2$ Hz, $^5J_{\text{HH}} = 1$ Hz); 7.58–7.17 (m, 4 H, H-5-8). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): -0.3, -0.2 ($\text{Si}(\text{CH}_3)_2$); 47.3 (C-1); 121.3, 123.2, 124.3 (C-5-8); 125.7 (C-3); 131.2 (C-5-8); 133.5 (C-2); 142.7, 144.3 (C-4,9). EI-MS: m/z (%) 208 (13) $[\text{M}^+]$.
- [9] G.A. Luinstra, J.H. Teuben, *J. Chem. Soc. Chem. Commun.*, (1990) 1470.
- [10] J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, *Organometallics*, **14** (1995) 789.
- [11] F. Semetz, R. Mülhaupt, F. Amor and J. Okuda, unpublished results.
- [12] E. Manzer, *Inorg. Synth.*, **21** (1982) 135.
- [13] R.R. Schrock, *J. Organomet. Chem.*, **122** (1976) 209.