

Preliminary communication

Lewis base functionalised cyclopentadienyl complexes of titanium¹

Andrew K. Hughes*, Sarah M.B. Marsh, Judith A.K. Howard, Peter S. Ford

Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, UK

Received 4 April 1996; revised 17 May 1996

Abstract

The reaction of $\text{Ti}(\text{NMe}_2)_4$ with the amine functionalised cyclopentadiene $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CMe}_3$ gives the titanium cyclopentadienyl–amide complex $[\text{Ti}(\eta^5\text{-}\sigma^1\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CMe}_3))(\text{NMe}_2)_2]$ which reacts with aniline to generate the phenylimido bridged dimer $[\{\text{Ti}(\eta^5\text{-}\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CMe}_3)(\text{NHPH})\}_2(\mu\text{-NPh})_2]$ whose molecular structure has been determined by X-ray diffraction, revealing a slightly asymmetric $\text{Ti}(\mu\text{-NPh})_2\text{Ti}$ core.

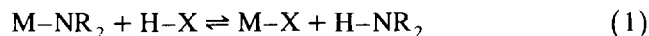
Keywords: Titanium; Cyclopentadienyl; Imide; Amide; Crystal structure

1. Introduction

In recent years, we and other workers have applied early transition metal homoleptic dialkyl amide $[\text{M}(\text{NR}_2)_n]$ complexes (for a review of early work see Ref. [1]), especially those of Group 4 metals, to the synthesis of substituted cyclopentadienyl complexes through the reaction of $\text{M}(\text{NR}_2)_n$ with cyclopentadienes, bis-cyclopentadienes, or Lewis base functionalised cyclopentadienes, displacing one or more equivalents of HNR_2 [2,3]. These syntheses of cyclopentadienyl complexes yield complexes which still retain dialkyl amide ligands, and are thus potentially less useful as starting materials for subsequent reactions than equivalent complexes containing halide ligands, given the greater familiarity of halide complexes. Dialkyl ammonium hydrohalides $[\text{NR}_2\text{H}_2\text{X}; \text{X} = \text{Cl}, \text{I}]$ have been used to convert M-NR_2 into M-X [2,4], and this protocol appears to have a wide application for the preparation of metal halide complexes.

As an alternative to the conversion of M-NR_2 into M-Cl , dialkyl amide complexes themselves are potential starting materials for a range of complexes, by reaction with selected acids. Given that the $\text{p}K_a$ of HNR_2 is typically around 40, there is a wide range of weak acids, HX , which will react with a transition metal amide M-NR_2 . Such a reaction presupposes that the hydroamination reaction (Eq. (1)) is simply an acid–base

reaction, and that the position of the equilibrium depends only on the acidity of the species involved.



Other workers have demonstrated that this reaction is sensitive to steric effects in H-X [5], and we have begun an investigation to determine which weak acids (H-X , being alcohols, thiols, diketones, amines) are applicable to reactions with a linked cyclopentadienyl–amide complex of titanium bearing dimethylamide ligands. In this report we describe preliminary results of the reaction with aniline.

2. Results and discussion

The *t*-butyl amine substituted cyclopentadienyl ligand $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CMe}_3$ (HCpN^{H} , **2**) can be synthesised using a method slightly modified from the published synthesis of the N-CH_3 substituted ligand [2]. As shown in Scheme 1, reaction of the chloride salt $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CMe}_3 \cdot \text{HCl}$ (**1**) with an excess of two equivalents of NaC_5H_5 in THF gives good yields of **2** as a brown oil. This oil can be freed of C_5H_6 by distillation, or by extraction into dilute aqueous HCl followed rapidly by addition of base.

Although we have found that it is possible to react **2** with one or two equivalents of BuLi to give mono- and dilithiated species [6], we have found these species to be not very successful in the preparation of titanium complexes. In contrast, the reaction of one equivalent of **2** with $\text{Ti}(\text{NMe}_2)_4$ in toluene proceeds cleanly to give

* Corresponding author.

¹ Dedicated to Malcolm L.H. Green on the occasion of his 60th birthday.

good yields of the titanium complex $[\text{Ti}\{\eta^5\text{-}\sigma^1\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_3)\}(\text{NMe}_2)_2]$ (**3**) as a deep yellow oil, which has been characterised by ^1H and ^{13}C NMR and EI mass spectroscopy. Attempts to vacuum distil this oil were not successful, and resulted in extensive decomposition and the isolation of two volatile fractions, one of which was identified as $\text{Ti}(\text{NMe}_2)_4$ and the other as titanium complex **4**, tentatively characterised as $[\text{Ti}\{\eta^5\text{-}\sigma^1\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_3)\}_2]$. This lack of thermal stability under reduced pressure of **3** contrasts with the behaviour of the zirconium and hafnium species $[\text{M}\{\eta^5\text{-}\sigma^1\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe})\}(\text{NMe}_2)_2]$, which distil cleanly in high yield [2].

A standardised toluene solution of compound **3** reacts with an excess of aniline (PhNH_2) at room temperature to give a dark red coloured solution which gives a solid material when the solvent is removed. Recrystallisation from CH_2Cl_2 /light petroleum mixtures yields dark red block-shaped crystals of $[\{\text{Ti}(\eta^5\text{-}\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CMe}_3)(\text{NHPh})\}_2(\mu\text{-NPh})_2]$ (**5**) suitable for X-ray diffraction. The asymmetric unit of **5** contains two independent half molecules (described as molecules A and B) located near to crystallographic inversion centres which generate the other half of each dimer. Fig. 1 shows the structure of one dimer (molecule A) together with the adopted numbering scheme. The two independent dimers appear to be geometrically very similar, with no significant differences in distances or angles. Compound **5** is identified as the product of the loss from **3** of both Ti-NMe_2 ligands as HNMe_2 together with cleavage of the Ti-N bond of the CpN' ligand. Compound **5** thus contains a phenylimido ligand (PhN), a phenylamido ligand (PhNH), as well as a free amine.

The central core of the structure of **5** contains the $\text{Ti}(\mu\text{-NR})_2\text{Ti}$ unit, with two phenylimido ligands bridging two titanium atoms. The Ti-NPh distances within the Ti_2N_2 core of molecule A are 1.902(2) Å and

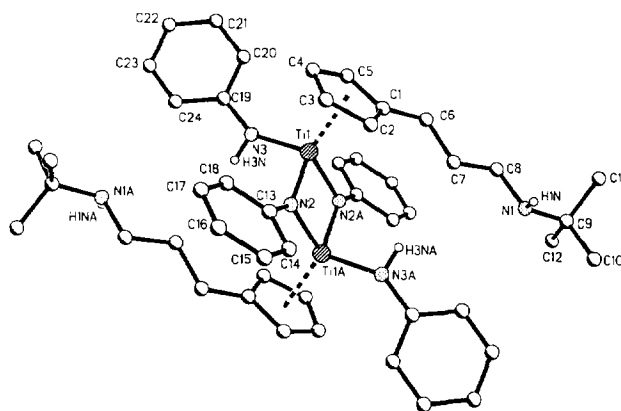


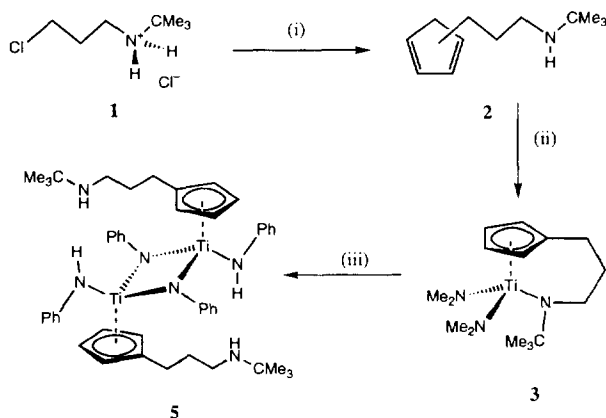
Fig. 1. View of the molecular structure of molecule A of $[\{\text{Ti}(\eta^5\text{-}\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CMe}_3)(\text{NHPh})\}_2(\mu\text{-NPh})_2]$ showing the adopted numbering scheme. Carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) for molecule A: $\text{Ti}(1)\text{-N}(2)$ 1.902(2), $\text{Ti}(1)\text{-N}(3)$ 1.969(2), $\text{Ti}(1)\text{-N}(2a)$ 1.991(2), $\text{Ti}(1)\text{-Ti}(1a)$ 2.8688(9), $\text{N}(3)\text{-C}(19)$ 1.397(3), $\text{N}(2)\text{-C}(13)$ 1.402(4), $\text{N}(2)\text{-Ti}(1)\text{-N}(3)$ 103.89(10), $\text{N}(2)\text{-Ti}(1)\text{-N}(2a)$ 85.08(10), $\text{N}(3)\text{-Ti}(1)\text{-N}(2a)$ 106.06(10), $\text{C}(19)\text{-N}(3)\text{-Ti}(1)$ 145.2(2), $\text{C}(13)\text{-N}(2)\text{-Ti}(1)$ 136.9(2), $\text{C}(13)\text{-N}(2)\text{-Ti}(1a)$ 127.3(2), $\text{Ti}(1)\text{-N}(2)\text{-Ti}(1a)$ 94.92(10).

1.991(2) Å [1.891(2) Å and 2.008(2) Å in molecule B], whilst the terminal $\text{Ti-NH}(\text{Ph})$ distances are 1.969(2) Å [1.967(2) Å]. The Ti_2N_2 core thus suffers a marked distortion with one Ti-N distance longer than the other, the differences ($\Delta\text{M-N}$) being 0.089 Å [0.117 Å]. Examination of the metal–nitrogen distances in other structures containing the $\text{M}(\mu\text{-NR})_2\text{M}$ core shows that $\text{M}(\mu\text{-NR})_2\text{M}$ fragments fall into two classes: relatively undistorted structures with $\Delta\text{M-N}$ values from 0.0 to 0.15 Å; and highly distorted structures with $\Delta\text{M-N}$ from 0.36 to 0.516 Å, where the distortion is believed to be due to a second-order Jahn–Teller effect [7], although alternative explanations have been proposed [8,9]. Compound **5** is an example of a relatively undistorted structure, and is not expected to undergo a Jahn–Teller distortion; the origin of the small distortion in the $\text{Ti}(\mu\text{-NR})_2\text{Ti}$ core of **5** and compounds related to it appears to be more subtle.

The dimeric structure of **5** is retained in solution, although ^1H and ^{13}C NMR spectra in both benzene- d_6 and CDCl_3 indicate the formation in solution of a second species. Studies to more completely characterise this second species, including variable-concentration cryoscopy [10], are underway.

3. Experimental

Air sensitive compounds were manipulated under a nitrogen atmosphere using standard Schlenk and glovebox techniques. NMR spectra were run on Varian VXR-200 (^1H) or Bruker AC-250 (^1H and ^{13}C) spectrometers. Infrared spectra were run as liquid films or KBr



Scheme 1. Reaction conditions: (i) excess NaC_5H_5 , THF, 69%; (ii) $\text{Ti}(\text{NMe}_2)_4$, toluene, 60°C, 74%; (iii) PhNH_2 , toluene, 40%.

discs on a Perkin–Elmer 1615 FTIR spectrometer. Solvents were pre-dried and distilled from appropriate drying agents. $\text{Me}_3\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \cdot \text{HCl}$ was prepared from $\text{Me}_3\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ [11] by reaction with SOCl_2 [12], and $\text{Ti}(\text{NMe}_2)_4$ [13] was prepared by a literature procedure.

3.1. Preparation of $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCMe}_3$ 2

Under nitrogen, a rapidly stirred solution of $\text{Me}_3\text{NH}(\text{CH}_2)_3\text{Cl} \cdot \text{HCl}$ (1) (30 g, 0.16 mol) in tetrahydrofuran (THF, 500 ml) was cooled to 0°C and treated with a THF solution of freshly prepared NaC_5H_5 (0.35 mol). The solution turned pink in colour and a fine white precipitate appeared. The solution was refluxed for 4 h. Water (100 ml) was added, giving a pale brown aqueous layer and a dark organic layer. The organic layer was decanted and the aqueous layer extracted with ether (2×100 ml) and light petroleum (100 ml). The combined organic extracts were dried (MgSO_4) and the solvent removed to give a brown, free-flowing oil shown by ^1H and ^{13}C NMR and GC-MS to be a mixture of three isomers. This product was used without further purification, although it can be purified by distillation (b.p. 180°C at 0.05 Torr) or protonation and extraction into water followed by deprotonation. Yield 20 g, 69%.

Characterising data. ^1H NMR: δ (ppm, CDCl_3) 6.5, 6.3, 6.2, 6.0, 5.5 (m, $\text{CH}=\text{CH}$ of all three isomers); 3.0 (d, 2H $J = 1.4$ Hz, 2H, ring CH_2 of A or B); 2.9 (d, 2H, $J = 1.3$ Hz, ring CH_2 of A or B); 2.6 (td, 6H, $^1J_{\text{H-H}} = 7.2$ Hz, $^2J_{\text{H-H}} = 1.5$ Hz, $\text{CH}_2\text{NHCMe}_3$ of all three isomers); 2.4 (m, 6H, $\text{C}_5\text{H}_4\text{CH}_2$ of all three isomers); 1.8 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$ of all three isomers); 1.13 (s, 27H, CMe_3 of all three isomers). $^{13}\text{C}\{^1\text{H}\}$ NMR: 149, 147 (*ipso*); 135, 134, 132, 126, 125 (ring CH); 50 (ring CH_2); 43 (CMe_3); 42 ($\text{CMe}_3\text{NHCH}_2$); 41 ($\text{C}_5\text{H}_5\text{CH}_2$); 29 (CMe_3); 27 ($\text{CH}_2\text{CH}_2\text{CH}_2$). IR: $\nu(\text{cm}^{-1})$ 3059 (N–H); 1098, 1024, 806 (C–H bends). Anal. Found: C, 80.4; H, 11.6; N, 7.6. $\text{C}_{12}\text{H}_{21}\text{N}$ Calc.: C, 80.4; H, 11.8; N, 7.8%.

3.2. Preparation of $[\text{Ti}(\eta^5\text{-}\sigma^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{-NHCMe}_3)_2(\text{NMe}_2)_2]$ 3

A solution of $\text{Ti}(\text{NMe}_2)_4$ (15.27 g, 0.068 mol) in toluene (50 ml) in a Young's ampoule was treated dropwise with **2** (12.21 g, 0.068 mol). The ampoule was evacuated and sealed and the solution was heated at 60°C (2 h), after which the solvent was removed under reduced pressure to give **3** as a yellow–brown oil. Yield 15.7 g, 74%. Attempted distillation at 0.01 Torr caused decomposition of the product before distillation temperature was reached. The product was dissolved in toluene to give a 0.73 M solution.

Characterising data. ^1H NMR: δ (ppm, C_6D_6) 5.90 (t, 2H, $J = 2.5$ Hz, C_5H_4); 5.85 (t, 2H, $J = 2.5$ Hz,

C_5H_4); 3.12 (s, 12H, NMe_2); 2.57 (m, 4H, $\text{C}_5\text{H}_4\text{CH}_2$ and $\text{CH}_2\text{NHCMe}_3$ superimposed); 1.71 (quin, 2H, $J = 7$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$); 1.02 (s, 9H, CMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ (ppm, C_6D_6 , *ipso* missing) 110, 109 (C_5H_4); 49 (NMe_2); 42.5 (CMe_3); 42 ($\text{CH}_2\text{NHCMe}_3$); 39 ($\text{C}_5\text{H}_4\text{CH}_2$); 29 ($\text{CH}_2\text{CH}_2\text{CH}_2$). MS (CI): m/z (%) 358 (33) [$\text{M}^+ + \text{HNMe}_2$], 313 (100) [M^+], 269 (40) [$\text{M}^+ - \text{NMe}_2$]. Anal. Found: C, 61.2; H, 10.5; N, 13.8. $\text{C}_{16}\text{H}_{31}\text{N}_3\text{Ti}_1$ Calc.: C, 61.3; H, 10.0; N, 13.4%.

3.3. Preparation of $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{-N(H)CMe}_3)(\text{NPh})\}_2(\mu\text{-NPh})_2]$ 5

Aniline (0.68 g, 7.3 mmol) was added dropwise to a stirred toluene solution of **3** (5 ml of 0.73 M solution, 3.65 mmol) at room temperature, giving an immediate colour change from dark yellow to dark red. After stirring overnight the solvent was removed under reduced pressure and the solid residue recrystallised from a 1:1 mixture of CH_2Cl_2 and petroleum ether (b.p. $40\text{--}60^\circ\text{C}$) at -30°C .

Characterising data. ^1H NMR: δ (ppm, CDCl_3) 7.40 (t, 2H, *para* CH); 7.21 (overlapping m, 8H, *meta* CH), 6.94 (m, 2H, *para* CH); 6.65 (d, 4H, *ortho* CH); 6.19 (t, 4H, C_5H_4); 6.12 (t, 4H, C_5H_4); 3.75 (br. s, 2H, PhNH); 2.37 (dt, 4H, $\text{CH}_2\text{NHCMe}_3$); 2.21 (dd, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 1.40 (quin, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 1.09 (s, 18H, NHCMe_3); 0.46 (t, 2H, NHCMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ (ppm, CDCl_3) 128.9, 128.5, 122.5, 120.7, 119.0, 117.6 (aromatic CH's); 114.0 (C_5H_4); 113.6 (C_5H_4); 41.9 ($\text{CH}_2\text{NHCMe}_3$); 31.7 ($\text{CH}_2\text{CH}_2\text{CH}_2$); 29.0 (CMe_3); 26.9 ($\text{C}_5\text{H}_4\text{CH}_2$). Anal. Found: C, 70.3; H, 7.2; N, 10.9. $\text{C}_{48}\text{H}_{62}\text{N}_6\text{Ti}_2$ Calc.: C, 70.4; H, 7.6; N, 10.3%.

3.4. Crystal structure determination of 5

A dark red crystal ($0.2 \times 0.1 \times 0.1 \text{ mm}^3$) of **5** ($\text{C}_{48}\text{H}_{62}\text{N}_6\text{Ti}_2$) was selected in a perfluorinated oil and mounted at 150 K on a glass filament on a Siemens SMART diffractometer equipped with a dry N_2 stream low temperature device. Lattice parameters were obtained by least squares refinement of 25 high angle reflections. Graphite monochromator, $\lambda = 0.71073 \text{ \AA}$, $\text{Mo K}\alpha$. Triclinic system, space group $P\bar{1}$, $a = 11.57050(10)$, $b = 12.0315(2)$, $c = 17.2718(3) \text{ \AA}$, $\alpha = 78.3580(10)^\circ$, $\beta = 83.0390(10)^\circ$, $\gamma = 67.9640(10)^\circ$, $V = 2180.16(6) \text{ \AA}^3$, $\delta_{\text{calc}} = 1.247 \text{ Mg m}^{-3}$, $Z = 2$, $\mu = 0.406 \text{ mm}^{-1}$, $F(000) = 872$. Data were collected at room temperature, using omega scans. All computations used SHELXTL [14], data reduction and corrections were by XPREP. 16296 reflections were collected, with 11067 reflections independent [$R(\int) = 0.0877$], 10912 reflections with $I > 2\sigma(I)$ were used for refinement. The structure was solved by direct methods using XS, refined by Fourier and least squares using XL. Fourier

difference maps indicated which Ti-bound nitrogen atoms bore hydrogens, but these were placed geometrically along with other hydrogens and all were refined isotropically. 575 parameters were refined, mean shift/error 0.067 and maximum shift/error 1.738 for $U(\text{H32B})$ in the last cycle of refinement, residual electron density $+0.677$ and $-0.929 \text{ e } \text{\AA}^{-3}$, GooF on F^2 1.116, $R = 0.0647$, $R_w = 0.1615$. Tables of atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank the Department of Chemistry, University of Durham for a studentship (to S.M.B.M.) and The Royal Society for a Small Equipment Grant (to A.K.H.). E.P.S.R.C. and Oxford Materials Ltd. are thanked for a CASE award (to P.S.F.).

References

- [1] M.F. Lappert, P.P. Power, A.R. Sanger and R.C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, New York, 1980; M.H. Chisholm and I.P. Rothwell, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon Press, Oxford, 1987, Chap. 13.4.
- [2] A.K. Hughes, A. Meetsma and J.H. Teuben, *Organometallics*, **12** (1993) 1936.
- [3] W.A. Herrmann, M.J.A. Morawietz and T. Priermeier, *Angew. Chem., Int. Ed. Engl.*, **33** (1994) 1946; Y. Mu, W.E. Piers, L.R. MacGillivray and M.J. Zaworotko, *Polyhedron*, **14** (1995) 1; W.A. Herrmann, W. Baratta and M.J.A. Morawietz, *J. Organomet. Chem.*, **497** (1995) C4; W.A. Herrmann and W. Baratta, *J. Organomet. Chem.*, **506** (1996) 357; Y. Mu, W.E. Piers, M.A. MacDonald and M.J. Zaworotko, *Can. J. Chem.*, **73** (1996) 2233; W.A. Herrmann, M.J. Morawietz, H.-F. Herrmann and F. Küber, *J. Organomet. Chem.*, **509** (1996) 115; P. Jutzi and J. Kleimeier, *J. Organomet. Chem.*, **486** (1995) 287.
- [4] G.M. Diamond, S. Rodewald and R.F. Jordan, *Organometallics*, **14** (1995) 5.
- [5] W.A. Herrmann, M.J. Morawietz and T. Priermeier, *J. Organomet. Chem.*, **506** (1996) 351.
- [6] A.K. Hughes and S.M.B. Marsh, in preparation.
- [7] D.L. Thorn, W.A. Nugent and R.L. Harlow, *J. Am. Chem. Soc.*, **103** (1981) 357.
- [8] M.H. Chisholm, K. Folting, J.C. Huffman and A.L. Ratermann, *Inorg. Chem.*, **21** (1982) 978.
- [9] B.R. Ashcroft, A.J. Nielson, D.C. Bradley, R.J. Errington, M.B. Hursthouse and R.L. Short, *J. Chem. Soc., Dalton Trans.*, (1987) 2059.
- [10] M.G. Davidson, R. Snaith, D. Stalke and D.S. Wright, *J. Org. Chem.*, **58** (1993) 2810.
- [11] R.A.Y. Jones, A.R. Katritzky and D.L. Trepanier, *J. Chem. Soc. (B)*, (1971) 1300.
- [12] L.A.R. Hall, V.C. Stephens and J.H. Burkhalter, *Org. Synth. Collect.*, **4** (1963) 333.
- [13] D.C. Bradley and I.M. Thomas, *J. Chem. Soc.*, (1960) 3857.
- [14] SHELXTL, Version 5.03, Siemens Analytical Instruments.