

## Synthesis and Insertion Reactions of Cationic Alkylbis(cyclopentadienyl)titanium Complexes

Manfred Bochmann\* and Ladislav M. Wilson

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

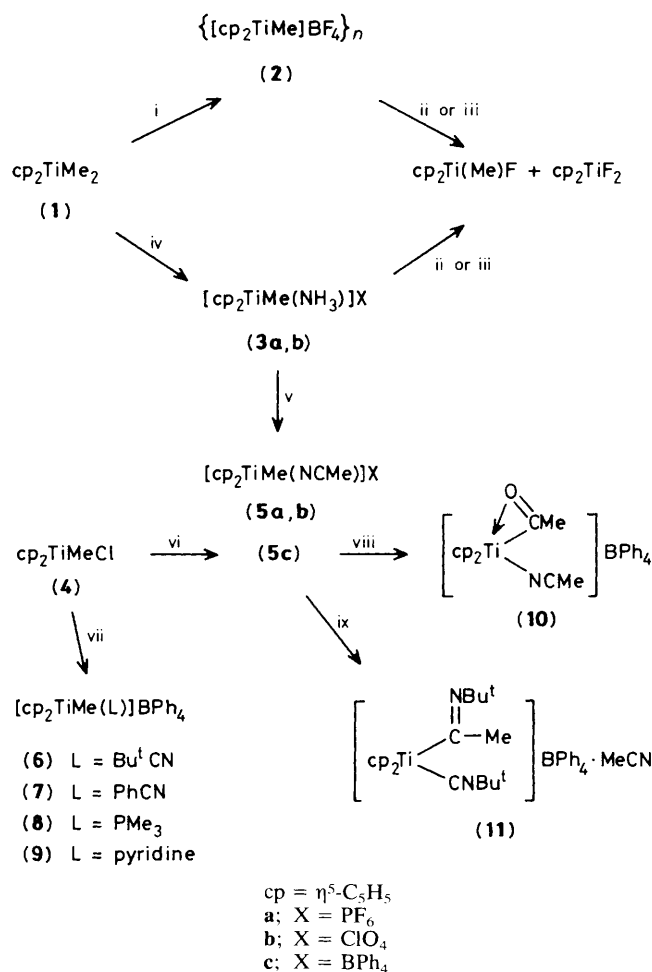
The electrophilic 14-electron alkyltitanium cations  $[\text{cp}_2\text{TiMe}]^+$  ( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ) and  $[\text{ind}_2\text{TiMe}]^+$  ( $\text{ind} = \eta^5\text{-indenyl}$ ), accessible *via* several routes, form stable complexes  $[\text{cp}_2\text{TiMe}(\text{L})]^+$  and  $[\text{ind}_2\text{TiMe}(\text{L})]^+$ ,  $\text{L} = \text{NH}_3$ ,  $\text{PMe}_3$ , pyridine,  $\text{MeCN}$ ,  $\text{Bu}^t\text{CN}$  and react readily with  $\text{CO}$  and  $\text{Bu}^t\text{NC}$ ; the insertion of nitriles into titanium-carbon bonds is described.

Although homogeneous catalysts for Ziegler-Natta polymerisations based on  $\text{cp}_2\text{TiCl}_2\text{-AlR}_n\text{Cl}_{3-n}$  ( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ) systems are well-known,<sup>1</sup> the mechanistic details of this reaction are still under discussion.<sup>2</sup> In earlier work the participation of cationic alkyl complexes  $[\text{cp}_2\text{TiR}]^+$  in polar solvents has been suggested,<sup>3</sup> though no such compound was isolated until the recently reported preparation of a cationic vinyltitanium complex<sup>4</sup> derived from alkyne insertion into a  $[\text{cp}_2\text{TiMe}]^+$  intermediate. Here we report the synthesis of the first cationic alkylbis(cyclopentadienyl)- and alkylbis(in-

denyl)-titanium complexes and their reactions with carbon monoxide, *t*-butyl isocyanide, and alkyl and aryl cyanides.

Treatment of  $\text{cp}_2\text{TiMe}_2$  (**1**), with hydrofluoroboric acid-diethyl ether in diethyl ether (Scheme 1) gives quantitatively methane and an orange, insoluble complex (**2**)<sup>†</sup> which analyses for  $\{[\text{cp}_2\text{TiMe}]\text{BF}_4\}_n$  and liberates a second equivalent of methane on addition of further  $\text{HBF}_4\cdot\text{OEt}_2$ . The solid state <sup>13</sup>C magic angle spinning (m.a.s.) n.m.r. spectrum of (**2**) shows two signals at  $\delta$  121.5 ( $\text{C}_5\text{H}_5$ ) and 38.1 (Me). In spite of the expected highly electrophilic character of the  $[\text{cp}_2\text{TiMe}]^+$  ion, there is no i.r. evidence for co-ordination of  $\text{BF}_4^-$  in the solid state,<sup>5</sup> though in refluxing tetrahydrofuran (THF) or on addition of N-bases (pyridine, aniline, or acetonitrile) electrophilic attack on the anion leads to the formation of  $\text{cp}_2\text{Ti}(\text{Me})\text{F}$  and  $\text{cp}_2\text{TiF}_2$ ; the latter is isolated as bright-yellow needles in 60% yield. Surprisingly and contrary to the behaviour of related  $\text{Zr}^{\ddagger}$  and  $\text{Sc}^6$  compounds, formation of a THF complex  $[\text{cp}_2\text{Ti}(\text{Me})(\text{THF})]^+$  is not observed.<sup>§</sup>

Treatment of (**1**) with  $\text{NH}_4\text{X}$  ( $\text{X} = \text{PF}_6, \text{ClO}_4$ ) in THF affords the ammine complexes  $[\text{cp}_2\text{TiMe}(\text{NH}_3)]\text{X}$  (**3a,b**). Attempted ligand exchange with pyridine or aniline leads to the isolation of  $\text{cp}_2\text{TiF}_2$  and is only successful with acetonitrile to give  $[\text{cp}_2\text{TiMe}(\text{NCMe})]\text{X}$ , (**5a,b**). The facile  $\text{F}^-$  abstraction from  $\text{BF}_4^-$  and  $\text{PF}_6^-$  anions in the presence of base necessitated the synthesis of the  $\text{BPh}_4^-$  salt (**5c**) which is accessible in

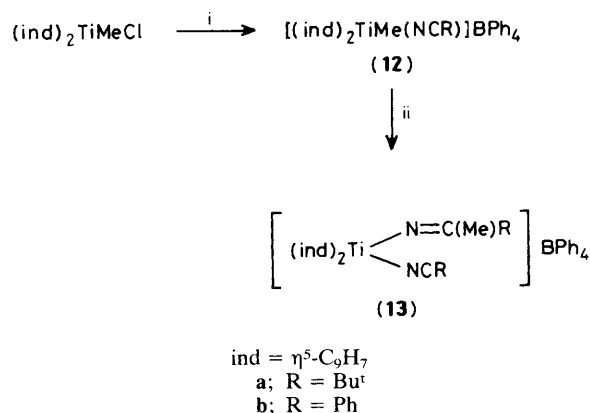


**Scheme 1.** Reagents and conditions: i,  $\text{HBF}_4\cdot\text{OEt}_2$  (1 equiv.),  $-\text{CH}_4$ , room temp.; ii, pyridine or aniline; iii, THF, reflux; iv,  $\text{NH}_4\text{X}$ , THF, room temp.,  $-\text{CH}_4$ ; v,  $\text{MeCN}$ ; vi,  $\text{NaBPh}_4$  in  $\text{MeCN}$ , room temp.; vii,  $\text{NaBPh}_4$  and  $\text{L}$  in THF; viii, (**5c**) in  $\text{MeCN}$ , 1 bar  $\text{CO}$ , room temp.; ix, (**5c**) in  $\text{MeCN}$ ,  $\text{Bu}^t\text{NC}$  (2 equiv.).

<sup>†</sup> Satisfactory elemental analyses were obtained for all new compounds. Selected spectroscopic data are: Compound (**2**): i.r. ( $\text{cm}^{-1}$ ) ( $\text{CCl}_4$  mull): 3120 (cp), 2980, 2940 sh, 2900, 2870 (Me); (Nujol mull): 500 m, br (Ti-C). (**3a**): i.r. (Nujol): 3370, 3300 m, 3210 w, 1625 s ( $\text{NH}_3$ ), 3120 (cp), 840 vs, 560 s ( $\text{PF}_6$ ); ( $\text{CCl}_4$  mull): 2970, 2895 (Me). (**3b**): i.r. (Nujol): 3340, 3275, 3190 ( $\text{NH}_3$ ), 3110 (cp), 1090, 642 ( $\text{ClO}_4$ ). (**5c**): i.r. (Nujol): 3110 (cp), 2310 w, 2282 m ( $\text{C}\equiv\text{N}$ ); <sup>1</sup>H n.m.r. (in  $\text{CD}_3\text{CN}$ , rel.  $\text{SiMe}_4$ ):  $\delta$  6.3 (10H, cp), 1.95 (3H, MeCN), 0.69 (3H, Me); <sup>13</sup>C:  $\delta$  49.0 (Ti-Me). (**6**): i.r. (Nujol): 3110 (cp), 2262 (CN); <sup>1</sup>H n.m.r. (in  $\text{CD}_3\text{CN}$ ):  $\delta$  6.30 (10H, cp), 1.36 (9H,  $\text{Bu}^t$ ), 0.74 (3H, Me). (**7**): i.r. (Nujol): 2260 (CN); <sup>1</sup>H n.m.r.:  $\delta$  7.15–7.61 (m,  $\text{PhCN}$ ,  $\text{BPh}_4$ ), 6.30 (10H, cp), 0.72 (3H, Me). (**8**): <sup>1</sup>H n.m.r.:  $\delta$  7.15 (m, 20H,  $\text{BPh}_4$ ), 6.30 (10H, cp), 1.10 br (s, 9H,  $\text{PMe}_3$ ), 0.7 (s, 3H, Me). (**9**): <sup>1</sup>H n.m.r. (in  $\text{CD}_3\text{CN}$ ):  $\delta$  8.35–7.75 (m, py), 7.15 (m,  $\text{BPh}_4$ ), 6.28 (10H, cp), 0.73 (3H, Me). (**10**): i.r. (Nujol): 2315 w, 2290 m (MeCN), 1630 ( $\text{C}=\text{O}$ ); <sup>1</sup>H n.m.r. (in  $\text{CD}_3\text{CN}$ ): 5.81 (10H, cp), 3.08 (s, 3H, MeCO), 1.95 (s, 3H, MeCN). (**11**): i.r. (Nujol): 2290 w, 2245 m (MeCN), 2190 s ( $\text{Bu}^t\text{NC}$ ), 1740 ( $\text{C}=\text{N}$ ); <sup>1</sup>H n.m.r.: 5.53 (10H, cp), 2.86 (3H, Me-C=), 1.95 (3H, MeCN), 1.66 br (9H,  $\text{Bu}^t\text{NC}$ ), 1.33 (9H,  $\text{Bu}^t$ ). (**12a**): i.r. (Nujol): 3100 w (ind), 3050 s ( $\text{BPh}_4$ ), 2262 ( $\text{C}\equiv\text{N}$ ); <sup>1</sup>H n.m.r.: 7.2–6.1 (m, ind,  $\text{BPh}_4$ ), 1.33 (9H,  $\text{Bu}^t$ ), -0.29 (3H, Me). (**13a**): i.r. (Nujol): 2262 ( $\text{C}\equiv\text{N}$ ), 1662 ( $\text{C}=\text{N}$ ); <sup>1</sup>H n.m.r.: 1.83 (3H, Me), 1.40 (9H,  $\text{Bu}^t\text{C}\equiv\text{N}$ ), 0.9 (9H,  $\text{Bu}^t\text{-C}\equiv\text{N}$ ). (**13b**): i.r. (Nujol): 2265 ( $\text{C}\equiv\text{N}$ ), 1642 ( $\text{C}=\text{N}$ ); <sup>1</sup>H n.m.r.:  $\delta$  2.20 (1.8H), 1.81 (1.2H) (Me, two isomers).

<sup>‡</sup> While this work was in progress, an independent preliminary note on related zirconium chemistry has appeared: R. F. Jordan, W. E. Dasher, and S. F. Echols, *J. Am. Chem. Soc.*, 1986, **106**, 1718.

<sup>§</sup> There is evidence for the formation of the acetonitrile complex  $[\text{cp}_2\text{TiMe}(\text{NMeCN})]\text{BF}_4$ , though it was not isolated in pure form.



**Scheme 2.** Reagents and conditions: i, NaBPh<sub>4</sub> and RCN in THF, room temp., 2 h; ii, RCN in THF, room temp., 48 h.

high yield *via* the reaction of cp<sub>2</sub>Ti(Me)Cl (**4**) with NaBPh<sub>4</sub> in acetonitrile; (**5c**) is isolated as brown, rhombic crystals. No reaction takes place in THF alone, though the addition of pivalonitrile, benzonitrile, trimethylphosphine, or pyridine generates (**6**), (**7**), (**8**), and (**9**), respectively, as light orange to brown crystalline solids.

Complex (**5c**) readily inserts CO to give [cp<sub>2</sub>Ti(COME)(NCMe)]BPh<sub>4</sub> (**10**). The acyl group gives rise to an i.r. band at 1630 cm<sup>-1</sup>, suggesting η<sup>2</sup>-co-ordination as in cp<sub>2</sub>Ti(COME)Cl (ν<sub>CO</sub> 1620 cm<sup>-1</sup>).<sup>7</sup> By contrast, reaction of (**5c**) with the sterically demanding Bu<sup>t</sup>NC gives the η<sup>1</sup>-iminoacyl compound (**11**) (ν<sub>C=N</sub> 1740 cm<sup>-1</sup>) as pale-yellow air-stable prisms. The complex contains co-ordinated isocyanide (ν<sub>C≡N</sub> 2190 cm<sup>-1</sup>) and unco-ordinated acetonitrile of crystallisation [ν<sub>C≡N</sub> 2290, 2245 cm<sup>-1</sup>; *cf.* ν<sub>C≡N</sub> in (**5c**): 2310, 2282 cm<sup>-1</sup>].<sup>¶</sup>

Replacing cyclopentadienyl ligands by indenyl groups results in an enhanced reactivity towards the insertion of nitriles into titanium-carbon bonds (Scheme 2). Thus the nitrile adducts [(ind)<sub>2</sub>TiMe(NCR)]BPh<sub>4</sub> (**12a,b**) react with an excess of pivalonitrile or benzonitrile to give the ketimido complexes (**13a**) (R = Bu<sup>t</sup>; ν<sub>C=N</sub> 1662, ν<sub>C≡N</sub> 2262 cm<sup>-1</sup>) and (**13b**) (a 3:2 mixture of stereoisomers, R = Ph, ν<sub>C=N</sub> 1642,

ν<sub>C≡N</sub> 2262 cm<sup>-1</sup>). These cationic titanium complexes resemble in this respect structurally related scandium compounds; for example, the insertion of nitriles into the scandium-methyl bond of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ScMe is a facile process,<sup>8</sup> but has, to our knowledge, not been reported for titanium. ||

None of the complexes described reacts with ethylene, butadiene, or acetylenes (including PhC≡CSiMe<sub>3</sub>, *cf.* ref. 4) under the mild conditions employed in the presence or absence of Lewis acids.

We are grateful to the S.E.R.C. for a postdoctoral fellowship (to L. M. W.) and to David J. Williamson for solid state <sup>13</sup>C measurements.

Received, 7th July 1986; Com. 926

## References

- H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, 1980, **18**, 99; P. D. Gavens, M. Bottrill, J. W. Kelland, and J. McMeeking in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, vol. 3, ch. 22.5, Pergamon Press, 1982.
- L. Clawson, J. Soto, S. L. Buchwald, M. L. Steigerwald, and R. H. Grubbs, *J. Am. Chem. Soc.*, 1985, **107**, 3377; G. Fink, W. Fenzl, and R. Mynott, *Z. Naturforsch.*, 1985, **40B**, 158; and cited references.
- O. N. Babkina, E. A. Grigoryan, F. S. Dyachkovskii, A. E. Shilov, and N. I. Shuvalova, *Zh. Fiz. Khim.*, 1969, **43**, 1759 (*Chem. Abstr.*, **71**, 123380x); E. A. Grigoryan, F. S. Dyachkovskii, N. M. Semenova, and A. E. Shilov, *Kinet. Mech. Polyreactions, Int. Symp. Macromol. Chem. Prepr.*, 1969, **2**, 267 (*Chem. Abstr.*, **75**, 64406t).
- J. J. Eisch, A. M. Piotrowski, S. K. Brownstein, E. J. Gabe, and F. L. Lee, *J. Am. Chem. Soc.*, 1985, **107**, 7219.
- W. Beck and K. Schlöter, *Z. Naturforsch.*, 1978, **33B**, 1214.
- J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1979, 54.
- G. Fachinetti and C. Floriani, *J. Organomet. Chem.*, 1974, **71**, C5.
- J. E. Bercaw, D. L. Davies, and P. T. Wolczanski, *Organometallics*, 1986, **5**, 443.
- M. R. Collier, M. F. Lappert, and J. McMeeking, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 689.

<sup>¶</sup> Added in proof. The X-ray structure of (**11**) shows the iminoacyl ligand to be η<sup>2</sup>-co-ordinated, irrespective of the high i.r. C=N frequency: M. B. Hursthouse and R. L. Short, to be published.

|| Neither cp<sub>2</sub>TiMeCl (ref. 9) nor (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>MMe<sub>2</sub> (M = Zr, Hf) (ref. 8) insert nitriles.