Carbon Dioxide Induced Alkene Extrusion from Bis(pentamethylcyclopentadienyl)titanium(III) Alkyls

Gerrit A. Luinstra and Jan H. Teuben*

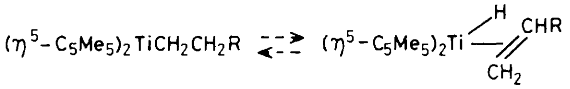
Department of Chemistry, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Reaction of titanium(III) alkyls, $(\eta^5\text{-}C_5Me_5)_2TiR$ (R = Et or Pr^n), in toluene solution with CO_2 proceeds at room temperature with formation of the titanium formate $(\eta^5\text{-}C_5Me_5)_2TiO_2CH$, and the corresponding alkene (ethene or propene).

Paramagnetic titanium(III) hydrocarbyls of the type $(\eta^5\text{-}C_5H_5)_2TiR$ or $(\eta^5\text{-}C_5Me_5)_2TiR$ where R = aryl or alkyl without β-hydrogen have been studied in some detail with respect to insertion into the Ti–C bond. Apart from a certain tendency towards disproportionation to give Ti^{II} and Ti^{IV} compounds the results are as expected for a polarized Ti–C bond with negative charge on the hydrocarbyl fragment. The presence of an unpaired electron in the complexes is chemically expressed in reductive coupling reactions when ketones or nitriles are used as substrates.[1]

For $(\eta^5\text{-}C_5Me_5)_2TiR$ compounds where the alkyl group R bears β-hydrogen we observed an interesting reaction with carbon dioxide. Insertion of CO_2 into the Ti–C bond was expected but when solutions of $(\eta^5\text{-}C_5Me_5)_2TiR$ (R = Et or Pr^n) in toluene were exposed to CO_2 (1 atm, 20 °C) quantitative formation of the titanium formate $(\eta^5\text{-}C_5Me_5)_2TiO_2CH$[2] and the corresponding alkene was observed [reaction (1)].† Extrusion of an alkene from a transition metal alkyl, induced by CO_2, is unprecedented and illustrates the unique, extraordinarily interesting reactivity of the Ti–C bond in paramag-

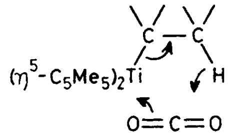
$$\underset{(1)}{(\eta^5\text{-}C_5Me_5)_2TiR} + CO_2 \longrightarrow \underset{(2)}{(\eta^5\text{-}C_5Me_5)_2TiO_2CH} + R(-H) \quad (1)$$



$$(\eta^5\text{-}C_5Me_5)_2TiCH_2CH_2R \rightleftharpoons (\eta^5\text{-}C_5Me_5)_2Ti(H)(CH_2{=}CHR) \quad (2)$$

---

† CO_2 (0.26 mmol) was admitted to a solution of $(\eta^5\text{-}C_5Me_5)_2TiEt$ (0.26 mmol) in 2 ml of toluene at −80 °C. The mixture was warmed to room temperature and stirred for 12 h. The colour changed from brown to blue. The gaseous products were analysed by Töpler pump and gas chromatographic–mass spectral techniques. C_2H_4 (0.24 mmol, 96% yield) was obtained. The blue product was identified (i.r., n.m.r.) as $(\eta^5\text{-}C_5Me_5)_2TiO_2CH$ by comparison with an authentic sample[2] of the formate. A similar reaction with $(\eta^5\text{-}C_5Me_5)_2TiPr^n$ (0.081 mmol) and CO_2 (0.081 mmol) gave $(\eta^5\text{-}C_5Me_5)_2TiO_2CH$ (i.r., n.m.r.) and $MeCH{=}CH_2$ (0.084 mmol). Traces of ethane (or propane) were found, probably arising from thermal decomposition of the original alkyls.[1,6]



(A)

a; R = Et
b; R = Pr^n

netic Ti^{III} derivatives. The presence of β-hydrogen in the alkyl ligand seems to be essential since compounds $(\eta^5\text{-}C_5Me_5)_2TiR$ with R = alkyl lacking β-hydrogen (*e.g.* R = Me, CH_2Bu^t, or Ph) cleanly give the corresponding carboxylates, $(\eta^5\text{-}C_5Me_5)_2TiO_2CR$.[3] This also seems to be the normal reaction of the M–C bond for a variety of metals ranging from transition metals, f elements, to main group metals.[4]

A plausible explanation of the observed alkene extrusion might be an alkyl hydride–alkene equilibrium (2). Even with the equilibrium lying far to the left, CO_2 substitution of the alkene followed by insertion into the Ti–H bond could lead to the observed products. However, the available theoretical[5] and experimental[6] evidence gives little support for β-hydrogen shift in these d^1 bent metallocene derivatives. Moreover, co-ordination of available ligands, *e.g.* CO_2, will fix the complex in an alkyl–substrate configuration as has been observed for d^2 systems $(C_5H_5)_2MR$ (M = Nb or Ta)[7] and $(\eta^5\text{-}C_5Me_5)_2NbR$.[8] Another possibility, *i.e.* decomposition of an intermediately formed carboxylate, can be ruled out, since $(\eta^5\text{-}C_5Me_5)_2TiO_2CR$ (R = Et or Pr^n) prepared independently‡ proved to be stable under the experimental conditions employed. It seems more likely that in the observed reaction (1) direct β-hydrogen transfer between the alkyl group and co-ordinated CO_2 takes place [structure (A)].

This transfer of β-hydrogen from a titanium alkyl to a substrate molecule with formation of an alkene and a new organotitanium compound is not limited to CO_2. Methyl chloride and iodide give an analogous reaction with formation, among other products, of methane, alkene, and Ti–X species, but the reaction is considerably more complicated than with CO_2. The same goes for substrates like but-2-yne; hydrogen transfer from the alkyl to the acetylene, and formation of a titanium vinyl, $(\eta^5\text{-}C_5Me_5)_2TiCMe{=}CHMe$, and alkene was observed. It seems that β-hydrogen transfer is more general with respect to both metal and substrate and the scope of this reaction is currently under investigation.

Received, 12th February 1987; Com. 191

References

1 J. H. Teuben, in 'Fundamental and Technological Aspects of Organo-f-element Chemistry,' eds. T. J. Marks and I. L. Fragala, Reidel, Dordrecht, 1985, p. 195, and references therein.

2 J. W. Pattiasina, H. J. Heeres, and J. H. Teuben, *Organometallics*, accepted for publication.

3 G. A. Luinstra, J. W. Pattiasina, H. J. Heeres, and J. H. Teuben, manuscript in preparation.

4 I. S. Kolomnikov and M. Kh. Grigoryan, *Russ. Chem. Rev.*, 1978, **47**, 334; R. P. A. Sneeden in 'Comprehensive Organometallic Chemistry,' vol. 8, ed. G. Wilkinson, Pergamon, Oxford, 1982, p. 225; D. A. Palmer and R. van Eldik, *Chem. Rev.*, 1983, **83**, 651; K. G. Moloy and T. J. Marks, *Inorg. Chim. Acta*, 1985, **110**, 127.

5 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **98**, 1726.

6 Thermal decomposition of $(\eta^5\text{-}C_5Me_5)_2TiR$ gives exclusively RH; no traces of alkene R(−H) or H_2 are found: J. W. Pattiasina, C. E. Hissink, J. L. de Boer, A. Meetsma, J. H. Teuben, and A. L. Spek, *J. Am. Chem. Soc.*, 1985, **107**, 7758.

7 F. van Bolhuis, A. H. Klazinga, and J. H. Teuben, *J. Organomet. Chem.*, 1981, **206**, 185; L. J. Guggenberger, P. Meakin, and F. N. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 5420; J. A. Labinger and J. Schwartz, *ibid.*, 1975, **97**, 1596.

8 N. M. Doherthy and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107**, 2670.

---

‡ Carboxylates $(\eta^5\text{-}C_5Me_5)_2TiO_2CR$ (R = Et or Pr^n) were made by reaction of (**1a**) with the acids RCO_2H. The blue compounds were crystallized from pentane and characterized spectroscopically (n.m.r., i.r.).