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

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Reaction of titanium(III) alkyls, (η^5-C₅Me₅)₂TiR (R = Et or Pr⁵), in toluene solution with CO₂ proceeds at room temperature with formation of the titanium formate (η^5-C₅Me₅)₂TiO₂CH, and the corresponding alkene (ethene or propene).

Paramagnetic titanium(III) hydrocarbysls of the type (η^5-C₅H₅)₂TiR or (η^5-C₅Me₅)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 Ti²⁺ and Ti⁴⁺ 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.

For (η^5-C₅Me₅)₂TiR compounds where the alkyl group R bears β-hydrogen we observed an interesting reaction with carbon dioxide. Insertion of CO₂ into the Ti-C bond was expected but when solutions of (η^5-C₅Me₅)₂TiR (R = Et or Pr⁵) in toluene were exposed to CO₂ (1 atm, 20 °C) quantitative formation of the titanium formate (η^5-C₅Me₅)₂TiO₂CH^− and the corresponding alkene was observed [reaction (1)].†

Extrusion of an alkene from a transition metal alkyl, induced by CO₂, is unprecedented and illustrates the unique, extraordinarily interesting reactivity of the Ti-C bond in paramag-

\[
(\eta^5-C₅Me₅)₂TiCH₂CH₂R + CO₂ \rightarrow (\eta^5-C₅Me₅)₂TiO₂CH + R(-H) \quad (1)
\]

\[
(\eta^5-C₅Me₅)₂TiCH₂CH₂R \rightarrow (\eta^5-C₅Me₅)₂TiO₂CH + \text{R} \quad (2)
\]

† CO₂ (0.26 mmol) was admitted to a solution of (η^5-C₅Me₅)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. C₆H₆ (0.24 mmol, 96% yield) was obtained. The blue product was identified (i.r., n.m.r.) as (η^5-C₅Me₅)₂TiO₂CH by comparison with an authentic sample of the formate. A similar reaction with (η^5-C₅Me₅)₂TiPr (0.081 mmol) and CO₂ (0.081 mmol) gave (η^5-C₅Me₅)₂TiO₂CH (i.r., n.m.r.) and MeCH=CH₂ (0.084 mmol). Traces of ethane (or propane) were found, probably arising from thermal decomposition of the original alkyls.
netic Ti\textsuperscript{III} derivatives. The presence of β-hydrogen in the alkyl ligand seems to be essential since compounds (η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}TiR with R = alkyl lacking β-hydrogen (e.g. R = Me, CH\textsubscript{2}Bu\textsubscript{t} or Ph) cleanly give the corresponding carboxylates, (η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}TiO\textsubscript{2}CR.\textsuperscript{5} 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.

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\textsubscript{2} substitution of the alkene followed by insertion into the Ti-H bond could lead to the observed products. However, the available theoretical\textsuperscript{5} and experimental\textsuperscript{6} evidence gives little support for β-hydrogen shift in these d\textsuperscript{3} bent metallocene derivatives. Moreover, co-ordination of available ligands, e.g. CO\textsubscript{2}, will fix the complex in an alkyl-substrate configuration as has been observed for d\textsuperscript{5} systems (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}MR (M = Nb or Ta)\textsuperscript{7} and (η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}NbR.\textsuperscript{8} Another possibility, i.e. decomposition of an intermediate carboxylate, can be ruled out, since (η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}TiO\textsubscript{2}CR (R = Et or Pr\textsuperscript{5}) prepared independently\textsuperscript{9} proved to be stable under the experimental conditions employed. It seems more likely that in the observed reaction

\[ \text{(A)} \]

a; R = Et
b; R = Pr

(1) direct β-hydrogen transfer between the alkyl group and co-ordinated CO\textsubscript{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\textsubscript{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\textsubscript{2}. The same goes for substrates like but-2-yne; hydrogen transfer from the alkyl to the acetylene, and formation of a titanium vinyl, (η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}TiCMe\textsubscript{2}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.

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