Insertion of Acetylenes into Carbon–Titanium σ-Bonds

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Summary Photochemically induced reactions between $[(\eta^5\text{-}C_5H_5)_2TiMe_2]$ and either diphenylacetylene or bis(pentafluorophenyl)acetylene have been shown to produce σ-methylstilbenyltitanium derivatives resulting from insertions of these alkynes into the methyltitanium σ-bond.

IN recent years, there has been considerable interest in the so-called insertion reactions[1]† of unsaturated molecules into metal–carbon σ-bonds of the early transition metals, especially of the Group 4B metals Ti, Zr, and Hf.[2] Studies of this type may provide a better understanding of the mechanism of Ziegler-Natta catalysis, since this process presumably occurs *via* insertion of a π-co-ordinated olefin into a carbon–titanium σ-bond.[3] We now report the first definitive example of the insertion of unsaturated hydrocarbons of the type RC≡CR into carbon–titanium σ-bonds.

We have previously reported that photochemically induced reactions between $[(\eta^5\text{-}C_5H_5)_2MMe_2]$ (M = Ti, Zr, Hf) and diphenylacetylene in hydrocarbon solvents produce moderate yields of the corresponding metallocycles (Ia—c).[4] These products, whose structures have recently been conclusively established by *X*-ray crystallography,[5] are probably produced by a reaction mechanism involving the transient formation of titanocene, $[(\eta^5\text{-}C_5H_5)_2Ti]$, or at least some acetylene-co-ordinated analogue. We now find that such reactions involving $[(\eta^5\text{-}C_5H_5)_2TiMe_2]$ and diphenylacetylene can likewise produce a second type of organometallic product (IIa) derived from overall insertion of the acetylene into a carbon–titanium σ-bond of $[(\eta^5\text{-}C_5H_5)_2\text{-}TiMe_2]$.

Thus, photolysis of a dilute solution of $[(\eta^5\text{-}C_5H_5)_2TiMe_2]$ and diphenylacetylene (1:2 molar ratio) in hexane solution for 4 h, followed by chromatography on alumina under argon and elution with degassed hexane–benzene mixtures, produces a pale yellow band containing (IIa) followed immediately by a green band containing the titanacycle (Ia). Repeated and careful chromatography is necessary to

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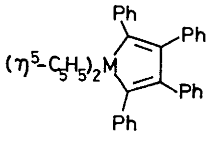
† These processes may also be classified as metal–complex 1:2 addition reactions (R. F. Heck, 'Organometallic Chemistry—A Mechanistic Approach,' Academic Press, New York, 1974, p. 32).

effect a complete separation of (IIa) (18%) and (Ia) (11%).

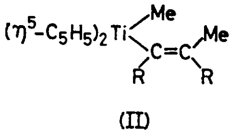
The golden-yellow insertion product (IIa) is an exceedingly thermally and oxidatively labile substance, whose structure is based primarily on n.m.r. and mass spectral data [$\tau(C_6D_6)$ 10·38 (3H, s, Ti–Me), 8·49 [3H, s, >C=C(Me)–], 4·06 (10H, s, η^5-C_5H_5), and 2·7—3·3 (10H, m, Ph); *m/e* 386 (M^+), 371 (M − Me)$^+$, 194 $\{(C_5H_5)_2TiHMe\}^+$ and/or $\{PhMeC{=}CHPh\}^+$], as well as on acid hydrolysis to give a mixture (3:1) of *cis*- and *trans*-1,2-diphenylpropene in addition to methane. Since the ^{1}H n.m.r. spectrum of (IIa) suggests that only a single isomeric organometallic compound is present, it seems likely that the mixture of 1,2-diphenylpropene isomers arises from isomerization of (IIa) during hydrolysis. This suggestion has previously been made for the hydrolysis reaction of the product derived from $[(Ph_3P)_3RhMe]$ and diphenylacetylene.[6] The stereochemical assignment of the insertion product as the *cis*-isomer (IIa) must be regarded as tentative at present, however.

An analogous photochemically induced reaction between $[(\eta^5\text{-}C_5H_5)_2TiMe_2]$ and bis(pentafluorophenyl)acetylene, $C_6F_5C{\equiv}CC_6F_5$, has produced a similar insertion product (IIb) [$\tau(CHCl_3)$ 10·23 (3H, s, Ti–Me), 8·53 [3H, s, >C=C(Me)–], and 3·64 (10H, s, η^5-C_5H_5); ν (KBr) 2950w (Me), 1525s and 925s (C_6F_5), and 1005s and 810s cm^{-1} (C_5H_5); *m/e* 566 (M^+), 551 (M − Me)$^+$, 374 $(C_6F_5CH{=}CMeC_6F_5)^+$, 193 $\{(C_5H_5)_2TiMe\}^+$, 178 $\{(C_5H_5)_2Ti\}^+$, and 113 $(C_5H_5Ti)^+$].‡ As might be anticipated,[7] the highly fluorinated product (IIb) exhibits appreciably enhanced stability relative to its hydrocarbon analogue (IIa). It is noteworthy that (IIb) is the sole organometallic product formed during the photolysis of $[(\eta^5\text{-}C_5H_5)_2TiMe_2]$ and bis(pentafluorophenyl)acetylene; a titanacycle analogous to (Ia) could not be detected.



(I)

a; M = Ti
b; M = Zr
c; M = Hf



(II)

a; R = Ph
b; R = C_6F_5

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‡ Satisfactory elemental analyses were obtained for this compound.

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