Hydrogenation of Alkynes with Water and a Titanium(II) Complex

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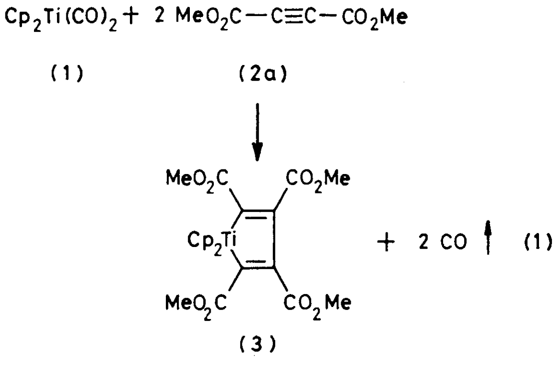
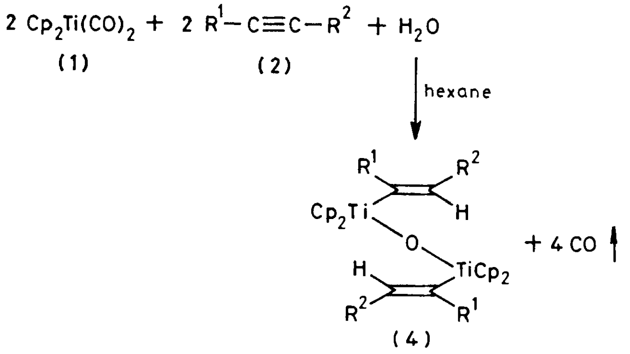
Summary μ-Oxobis(dicyclopentadienyl)(alkenyl)titanium(IV) complexes were prepared from $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(CO)}_2$ and alkyne in the presence of water and gave the corresponding *cis*-olefins.

Titanium(II) complexes have been shown recently to actively promote the stoicheiometric reductions of dinitrogen[1] or carbon dioxide[2] and $\text{Cp}_2\text{Ti(CO)}_2$ (**1**) (Cp = $\eta^5\text{-C}_5\text{H}_5$) has been used as a catalyst for the hydrogenation of alkynes[3] in which the active species was $\text{Cp}_2\text{Ti(CO)}$ (η^2-alkyne).[4] We now report a novel hydrogenation reaction of alkynes involving the complex (**1**) and water as a source of hydrogen.

When the derivative (**1**) and freshly distilled dimethyl acetylenedicarboxylate (**2a**) (2 equiv.) were stirred at room temperature in dry hexane, the red metallocene (**3**)† [ν (Nujol) 1730 and 1685 cm^{-1} (CO_2Me); ^{1}H n.m.r. (CDCl_3) δ 6·59 (s, Cp), 3·68 (s, CO_2Me), and 3·63 (s, CO_2Me)] precipitated quantitatively [equation (1)]. However, when wet hexane was used, a mixture of compound (**3**) and a yellow product was obtained. The same reaction, but performed with an excess of water (2 equiv.) led to, after 24 h, the evolution of 1·9 mol of CO per Ti atom and to the formation of the yellow precipitate only, which was identified as the μ-oxo-complex (**4a**)† (see the Scheme) [95%; ν (Nujol) 690 cm^{-1} vs, br (Ti–O–Ti); ^{1}H n.m.r. (CDCl_3) δ 6·15 (s, Cp), 6·00 (s, HC=), and 3·75 and 3·65 (CO_2Me)]. When the reaction was carried out with compounds (**1**), (**2a**) (1 equiv.), dry hexane, and D_2O, the ^{1}H n.m.r. spectrum of the isolated derivative $[\text{Cp}_2(\text{MeO}_2\text{C})\text{CD}{=}\text{C}(\text{CO}_2\text{Me})\text{Ti}]_2\text{O}$ was identical with that of (**4a**) except for the absence of the resonance at δ 6·00, which confirmed that the vinylic hydrogen originated from water.





a; R^1 = R^2 = CO_2Me
b; R^1 = R^2 = CO_2Et
c; R^1 = R^2 = Ph
d; R^1 = Ph, R^2 = H

Scheme

Similarly, we were able to obtain the derivatives (**4b**) (95%) and (**4c**)† [orange crystals, 80%; *M* (cryoscopy in benzene), 730. Calc. *M*, 731; ν (Nujol) 675 vs cm^{-1} (Ti–O–Ti); ^{1}H n.m.r. (CDCl_3) δ 7·05 (m, HC=, Ph) and 6·12 (s, Cp)]. Phenylacetylene gave (**4d**)† [orange crystals, 77%; ^{1}H n.m.r. (CDCl_3) δ 7·30 (s, Ph), 6·07 (s, Cp), and 5·65 and 5·25 (dd,

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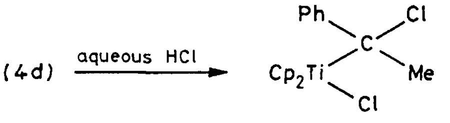
† Elemental analyses were satisfactory; recrystallisation from CH_2Cl_2–hexane (or toluene–hexane).

$=CH_2$, $^2J_{HH}$ 3·1 Hz)] which indicates the regioselectivity of the insertion of the alkyne.

Treatment of the derivatives (**4**) in dichloromethane with an excess of aqueous HCl led, after 15 min, to the formation of the *cis*-olefins: (**4b**) afforded $Cp_2Ti(Cl)C(CO_2Et){=}CH(CO_2Et)$ (**5**)[†] [red-orange crystals, 35%; ^1H n.m.r. ($CDCl_3$) δ 6·47 (s, Cp) and 5·67 (s, HC=)] and diethyl maleate (20%) was isolated as the sole organic product. In contrast, similar treatment of (**4c**) led to the isolation of Cp_2TiCl_2 (50%) and *cis*-stilbene (60%). Therefore, the acidic cleavage of the Ti–C (vinyl) bond seems stereospecific and confirms the configuration indicated (see the Scheme) for the vinyl group in compounds (**4a**), (**4b**), and (**4c**). The behaviour of compounds (**4**) is versatile, for (**4d**) gave, with HCl, a product (**6**)[†] [red crystals, 35%; ^1H n.m.r. ($CDCl_3$) δ 7·30 (s, Ph), 6·52 and 6·50 (s, Cp), and 1·46 and 1·32 (s, Me)] which resulted from the formal addition of HCl to the corresponding chloro-derivative [equation (2)].

$$Cp_2Ti(Cl)C(CO_2Et){=}CH(CO_2Et)$$

(**5**)



(2)

(6)

To understand the formation of the μ-oxo-complexes (**4**), it has to be pointed out that (i) deoxygenated water does not react with $Cp_2Ti(CO)_2$ (**1**) in hexane, (ii) H_2O prevents the formation of a metallocene of type (**3**) from (**1**) and an excess of alkyne, and (iii) in the absence of water, a compound $Cp_2Ti(CO)(\eta^2\text{-}C_2Ph_2)$ (**7**) has been obtained from (**1**) and diphenylacetylene.[4] The formation of the oxo-titanium derivatives (**4**) may result from the reaction of an intermediate of type (**7**) by initial displacement of the carbon monoxide group by water. We were able to show (i) that the addition of the basic phosphine PMe_3 to a mixture of (**1**) and diphenylacetylene (2 equiv.) also prevented formation of the metallocene of type (**3**), even in hexane at reflux [under these conditions (**7**) disproportionates into (**1**) and (**3**)], and afforded a compound analogous to (**7**), namely $Cp_2Ti(PMe_3)(\eta^2\text{-}C_2Ph_2)$ (**8**)[†] [yellow-orange crystals, 88%; ν (Nujol) 1740 cm^{-1} (C=C); ^1H n.m.r. (C_6D_6) δ 7·20 (Ph), 5·16 (s, Cp), and 0·79 (d, PMe_3, $^2J_{P-H}$ 3·0 Hz)] and (ii) that (**8**) was converted in wet solvents into the μ-oxo-derivative (**4c**) (88%).

$$Cp_2Ti(CO)(\eta^2\text{-}C_2Ph_2)$$

(**7**)

$$Cp_2Ti(PMe_3)(\eta^2\text{-}C_2Ph_2)$$

(**8**)

The derivative $[Cp_2\{CF_3CH{=}(CF_3)C\}Ti]_2O$ has been isolated from the reaction of (**1**) with hexafluorobutyne.[5] Our results indicate that water is only responsible for the formation of this μ-oxo-titanium(IV) complex.

The yields of the transformation of alkynes into *cis*-olefins have not been optimized. However, it should be noted that the overall reaction starting from the commonly and readily available $Cp_2Ti(CO)_2$[6] and water, proceeded *via* oxidative addition of water to (**7**) and does not require the isolation of a hydride complex, as in hydro-zirconation.[7]

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[1] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1972, **94**, 1219.
[2] G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1979, **101**, 1767.
[3] K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1178.
[4] G. Fachinetti, C. Floriani, F. Marchetti, and M. Mellini, *J. Chem. Soc., Dalton Trans.*, 1978, 1799.
[5] M. D. Rausch, D. J. Sikora, D. C. Hrncir, W. E. Hunter, and J. L. Atwood, *Inorg. Chem.*, 1980, **19**, 3817.
[6] B. Demerseman, G. Bouquet, and M. Bigorgne, *J. Organomet. Chem.*, 1975, **101**, C24.
[7] J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 333.