Synthesis and Catalytic Properties of Carbonyldiphenylacetylenebis-cyclopentadienyltitanium

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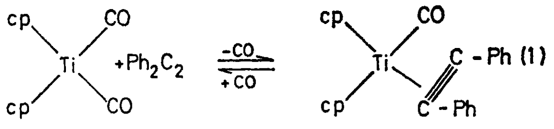
Summary Substitution of carbon monoxide by diphenylacetylene in dicarbonylbiscyclopentadienyltitanium(II) yields the title compound, which is an excellent catalyst for the hydrogenation of acetylenes dienes, and olefins.

One of the problems not yet fully understood in the chemistry of titanium is the existence of π-olefin or π-acetylene complexes, possible intermediates in the polymerisation of olefins.[1] A similar type of complex has also been invoked[2,3] in the hydrogenation of acetylenes catalysed by complex (I). To investigate these problems we studied the reaction between complex (I) and diphenylacetylene.

Complex (II) was obtained as yellow crystals (*ca.* 80%) from a solution in heptane of complex (I) and Ph_2C_2 at room temperature, the CO evolved being removed under reduced pressure. It is slightly soluble in heptane; it is rapidly converted into the starting dicarbonyl (I) in an atmosphere of CO.



(I) (II)

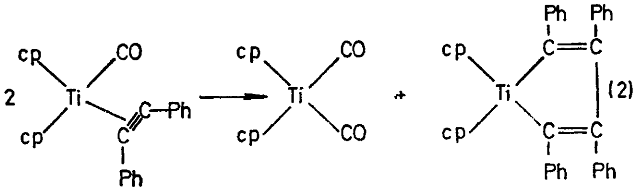
cp = π - C_5H_5

Oxidation of complex (II) with I_2 gave CO, Ph_2C_2, and $(cp)_2I_2Ti$ almost quantitatively. Complex (II) is formulated as a mononuclear complex on the basis of elemental analysis, quantitative determination of CO and Ph_2C_2 evolved upon decomposition, and i.r., n.m.r., and molecular weight measurements on freshly prepared (*vide infra*) solutions: ν_{CO} 1995 cm^{-1} (Nujol); ν_{CO} 1990 cm^{-1} (toluene); ν_{CC} 1780 cm^{-1} (Nujol); τ (C_6D_6) 2·9 (10H, m, Ph) and 5·0 (10H, s, cp); *M* (cryoscopy in benzene): found 356 (calc. 384). The i.r. data are in agreement with a mononuclear formulation for complex (II) since the observed CO[4] and CC[5] stretching vibrations are typical of terminal ligands.

Compound (II) is indefinitely stable in the solid state under nitrogen at *ca.* 0°, but is unstable in hydrocarbon solution. The i.r. and n.m.r. spectra in benzene under nitrogen change into those typical of (I) and (III)[2] as indicated in reaction (2). However, this conversion is slow and is complete only after a week at 30°. According to n.m.r. measurements freshly prepared solutions contain *ca.* 90% of (II). The molecular weight data cited above should therefore be regarded as meaningful within these limits of accuracy.

When reaction (1) was carried out in benzene at room temperature, complex (II) was formed transiently, and after a long reaction time complex (III) was obtained. A better route to complex (III) is therefore the reaction of (I) with Ph_2C_2 in refluxing pentane, from which the black-green titanium heterocycle was obtained almost quantitatively without any of the reported difficulties.[2]

The isolation of complex (II) seems relevant to catalytic hydrogenation. With a molar ratio of substrate (II) ranging from 15 to 50 we obtained complete hydrogenation [heptane; room temp.; $P(H_2)$ 1 atm.] within a few minutes of diphenylacetylene, styrene, *trans*-stilbene, oct-1-ene, and 1,4-diphenylbutadiene, to the corresponding saturated hydrocarbons. Under these mild conditions complex (I) showed no catalytic activity except towards Ph_2C_2, which was very slowly hydrogenated.



(II) (I) (III)

Olefins and butadiene do not react with complex (I).[2] This finding agrees with the unsuccessful hydrogenation of olefins and butadiene in the presence of (I). The catalytic properties of (II) in the same reactions can be explained in terms of possible π-olefin complex formation from (II) *via* hydrogenation of co-ordinated Ph_2C_2. The monocarbonyl (II) appears, from these results, to be not only the most plausible intermediate, but its solution in heptane the real catalyst in the hydrogenation of unsaturated substrates.

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