Thermal Decomposition and Carbonylation of Bis(cyclopentadienyl)titanium(IV) and Bis(cyclopentadienyl)zirconium(IV) Derivatives

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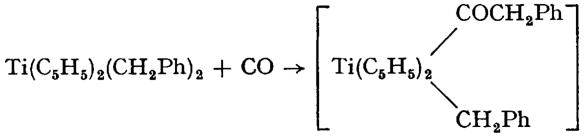
Summary The reactivity and thermal lability of bis(cyclopentadienyl)dibenzyl-titanium(IV) and -zirconium(IV) have been studied; the titanium(IV) compound undergoes reductive cleavage in the presence of carbon monoxide with formation of bis(cyclopentadienyl)dicarbonyltitanium(II).

As part of our study on the chemical reactivity of titanium– and zirconium–carbon σ-bonds, we have investigated the thermal decomposition and the carbonylation of $Ti(C_5H_5)_2(CH_2Ph)_2$, (I) and $Zr(C_5H_5)_2(CH_2Ph)_2$, (II).

(I) has been already reported,[1] whereas (II) is novel, despite recent reports of other bis(cyclopentadienyl)dialkylzirconium(IV) derivatives.[2] (II) was prepared (*ca.* 60%) by reaction of $Zr(C_5H_5)_2Cl_2$ with benzyl Grignard reagent (2 mol. equiv.) in Et_2O; it is soluble in toluene from which it can be recrystallised as yellow needles.† The i.r. spectrum of (II) is similar to that of (I); its n.m.r. spectrum (room temp.; values for the titanium complex in parentheses) shows: τ 4·54 (4·40) (s), 8·16 (8·10) (s) and 3·33—2·65 (3·3—2·6) (m) with the expected intensities for the formulation given with σ-bonded benzyl groups. (II) can be recrystallised from boiling heptane, thus showing an unexpected[3] thermal stability, but (I) decomposes in benzene solution even at 30° according to the stoicheiometry in reaction (1). Compound (III) is a black solid, sparingly soluble in benzene, extremely sensitive to oxygen.† The presence of C_5H_4 units was established as follows: (I) was heated for 3 days at 30° in C_6D_6 solution and the intensity of the peak of the methyl protons in the n.m.r. spectrum was 1·5 times that of CH_2-protons in the starting $Ti(C_5H_5)_2(CH_2Ph)_2$, thus showing that the hydrogen of the methyl group originated from the cyclopentadienyl rings (*cf.* recent reports on hydrogen migration from titanium-bonded C_5H_5 groups[4–6]). We are presently investigating compound (III), whose molecular weight is still unknown.

$$\underset{\text{(I)}}{Ti(C_5H_5)_2(CH_2Ph)_2} \rightarrow \tfrac{1}{n}\,\underset{\text{(III)}}{[Ti(C_5H_4)_2]_n} + 2PhMe \qquad (1)$$

Compounds (I) and (II) also show different reactivity towards carbon monoxide. (II) does not react even under rather drastic conditions (40 atm; 100°), the titanium analogue was carbonylated at 25—30° at atmospheric pressure [reactions (2)].



$$Ti(C_5H_5)_2(CH_2Ph)_2 + CO \rightarrow \left[Ti(C_5H_5)_2 \begin{matrix} \diagup COCH_2Ph \\ \diagdown CH_2Ph \end{matrix} \right]$$

(IV)

$$\text{(IV)} + 2CO \rightarrow \underset{\text{(V)}}{Ti(C_5H_5)_2(CO)_2} + (PhCH_2)_2CO \qquad (2)$$

The choice of the solvent is critical. Whereas in benzene both thermal decomposition (1) and carbonylation (2) take place, in heptane reaction (2) predominates. The stoicheiometry of reaction (2) was established by direct measurements of the volume of CO absorbed (2·6 mol per Ti; 3 days at 25°) and by measurement of the CO evolved by decomposition of the carbonyltitanium (V) formed with iodine in pyridine (1·7 mol). Dibenzyl ketone was quantitatively determined by g.l.c. and (V) was identified by its i.r. spectrum in the CO stretching region (bands at 1882 and 1965 cm^{-1}; *cf.* ref. 7).

Reaction (2) provides a simpler synthesis of $Ti(C_5H_5)_2(CO)_2$ than that in the literature,[7] which requires the use of high pressure and temperature. The yield of recrystallised $Ti(C_5H_5)_2(CO)_2$ is *ca.* 80% based on (I).

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† Satisfactory analytical data were obtained.

Our results are to be compared with those recently reported[8] for the carbonylation of the phenyl derivative, $Ti(C_5H_5)_2Ph_2$: good yields of benzophenone were reported, but no carbonyltitanium was obtained.

In heptane reaction (2) may occur *via* preco-ordination of CO to titanium, followed by benzyl migration to give the acyl intermediate (IV).

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