Some Reactions of Di-π-cyclopentadienyldiphenyltitanium

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(Received September 7, 1967)

In the course of our study of the isomerization of olefin catalyzed by $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ and related complexes,*1 it was found that the isomerization was inhibited by diphenylacetylene and carbon monoxide (CO). These phenomena were studied in some detail in relation to the investigation of the mechanism of the isomerization, and the following results were obtained.

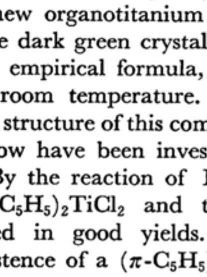
When $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ was refluxed in benzene with diphenylacetylene under nitrogen, a new organotitanium complex (I) was obtained. The dark green crystals of the complex (I), having the empirical formula, $C_{30}H_{24}Ti$, are stable in air at room temperature. For the determination of the structure of this complex, the reactions described below have been investigated.

By the reaction of I with aq. HCl in $CHCl_3$, $(\pi\text{-}C_5H_5)_2TiCl_2$ and triphenylethylene were isolated in good yields. This result suggests the existence of a $(\pi\text{-}C_5H_5)_2Ti$ fragment in I.

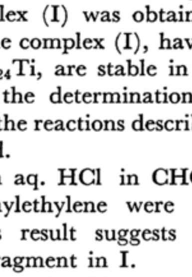
The complex (I) easily reacted with pressured CO at room temperature to afford 2, 3-diphenylindone in good yields. An attempt to isolate the organotitanium fragment was, in this case, unsuccessful.

The decomposition of the complex (I) by iodine in benzene gave *cis*-1-iodo-1, 2-diphenyl-2-(*o*-iodophenyl)-ethylene in good yields.

These facts lead us to the structure (A), namely, *Ti*-di-π-cyclopentadienyl-2, 3-diphenylbenztitanacyclopentadiene.



(A) (R=C_6H_5)



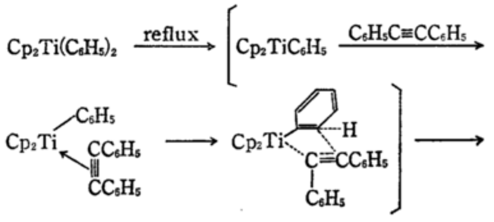
(B) (R=C_6H_5)

An analogous complex (B) has been prepared by us[1] and by Vol'pin *et al.*[2] independently. We obtained the complex (B) from the reaction of $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ with diphenylacetylene.

The structure of the complex (I) is also supported by the NMR spectrum, which shows a sharp singlet at τ 3.9 and a multiplet centered at τ 3.4. The former is assignable to the cyclopentadienyl protons, and the later to the aromatic protons. The relative intensities observed are 10 and 13.5 (calcd for the structure (A): 10 and 14) respectively.

The infrared spectrum of I shows no bands due to Ti–H and coordinated C≡C stretching absorptions.

An attempt to prepare the analogous complex from the reaction of $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ with diphenylacetylene by the similar procedure was unsuccessful.[3] Therefore, it is not likely that the complex (I) is formed through the insertion of acetylene in the Ti-alkyl bond. It seems more reasonable to describe the route of the formation of the complex (I) as follows:



(Cp=π-C_5H_5)

The complex (I) was not attacked by atmospheric hydrogen at the reflux temperature in benzene, while diphenyl and dimethyl derivatives easily reacted under the same conditions.[4] This might be due to the stability of the titanacyclopentadiene ring caused by the partial double-bond character of the Ti–C σ-bond.

When $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ was reacted with pressured CO at room temperature, benzophenone was isolated in good yields. It is considered that CO should initially coordinate to the vacant orbital of Ti. The insertion of CO in the Ti-phenyl bond will occur in the next step, and finally another phenyl group will migrate to the acyl group, producing benzophenone.

Experimental

$(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ was prepared by the method reported by Summers *et al.*[5]

Synthesis of I. A solution of 0.5 g of $(\pi\text{-}C_5H_5)_2$-$Ti(C_6H_5)_2$ and 0.28 g of diphenylacetylene in 10 m*l*

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*1 H. Masai, K. Sonogashira and N. Hagihara, *Mem. Inst. Sci. and Ind. Res., Osaka Univ.*, **25**, (1968), in press.

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2) M. E. Vol'pin, V. A. Dubovitskii and O. V. Nogina, *Dokl. Akad. Nauk S. S. S. R.*, **151**, 1100 (1963).

3) H. Masai, K. Sonogashira and N. Hagihara, unpublished results.

4) K. Clauss and H. Bestian, *Ann.*, **654**, 8 (1962).

5) L. Summers, R. H. Uloth and A. Holms, *J. Am. Chem. Soc.*, **77**, 3604 (1954).

of benzene was refluxed under nitrogen for 1 hr. The orangecolored solution turned dark green. The solution was then purified by column chromatography, using alumina under nitrogen. A dark green band eluted by benzene was collected. After the removal of the benzene, 0.18 g of crude, dark green crystals were obtained (46%). An analytical sample was obtained by recrystallization from CH_2Cl_2 - petroleum ether, mp 227—228°C.

Found: C, 83.64; H, 5.58%; mol wt (cryoscopic method in benzene using a Dampfdruckosmometer des Dr-Ing Herbert Knauer), 435. Calcd for $C_{30}H_{24}Ti$: C, 83.33; H, 5.59%; mol wt, 432.

The NMR spectrum of I in CCl_4 was recorded by a Varian A-60 spectrometer, using TMS as the internal standard.

The infrared spectrum was taken with a KBr tablet.

This complex was hydrogenated in Hershberg's apparatus in benzene at a reflux temperature. No hydrogen was absorbed.

Reaction of I with Aq. HCl. To a solution of 0.4 g of I in 15 m*l* of $CHCl_3$, an excess of aq. HCl was added. The color of the $CHCl_3$ layer immediately changed to red. The organic layer was then separated, and the aqueous layer was extracted by $CHCl_3$. After the removal of the $CHCl_3$, the residual mass was extracted by petroleum ether. Fine red crystals remained in the flask. The infrared spectrum of these crystals, obtained by the KBr method, was thoroughly coincident with that of authentic $(\pi\text{-}C_5H_5)_2TiCl_2$6) (0.199 g, 70%).

The extract was purified by chromatography over alumina. After the evaporation of the solvent, white crystals were obtained, and the crystals were recrystalized from petroleum ether. The melting point and the infrared absorption spectrum of these crystals were identical with those of authentic triphenylethylene7) (0.166 g, 70%), mp 72.5—73.5°C. Found: C, 93.63; H, 6.51%; mol wt (by vapor pressure osmometer, Dampfdruckosmometer des Dr-Ing Herbert Knauer), 256.8. Calcd for $C_{20}H_{16}$: C, 93.61; H, 6.29%; mol wt, 256.3.

Carbonylation of I. A solution of 0.068 g of I in 10 m*l* of benzene was reacted with CO under 200 atm at room temperature for 7 hr. An orange-yellow solution containing a yellow precipitate was thus obtained. This reaction mixture was chromatographed over alumina and eluted with benzene. After the removal of the benzene, 0.03 g of ruby-red crystals was obtained and recrystallized from benzene-petroleum ether. The melting point and the infrared spectrum of these crystals were identical with those of authentic 2, 3-diphenylindone8) (70%), mp 156.5—157.5°C.

Found: C, 89.28; H, 5.07%. Calcd for $C_{21}H_{14}O$: C, 89.33; 5.00%.

Decomposition of I by Iodine. To a solution of 0.2 g of I in 10 m*l* of benzene, an excess of an iodine solution in benzene was gradually added at room temperature. After the addition, the mixture was left for 1 hr. After the removal of the solvent, the residue was extracted by petroleum ether, and the extract was chromatographed. A slightly-colored solution eluted by petroleum ether was thus obtained. After the removal of the solvent, 0.15 g of yellowish crystals recrystalized from benzene-petroleum ether were obtained. The melting point of these crystals was identical with that of *cis*-1-iodo-1, 2-diphenyl-2-(*o*-iodophenyl)-ethylene found in the literature9) (64%), mp 172—173°C. Found: C, 47.33; H, 2.70%. Calcd for $C_{20}H_{14}I_2$: C, 47.27; H, 2.78%.

Carbonylation of $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$. A solution of 3.2 g of this complex in 20 m*l* of benzene was reacted with CO by a procedure similar to that used in the case of I. After the removal of the solvent, the residue was extracted by petroleum ether. The extract was concentrated in a vacuum, and then the residual liquid was distilled. A colorless liquid of benzophenone was thus obtained (bp 118°C/3 mmHg). The infrared spectrum in CCl_4 was coincident with that of authentic benzophenone (1.5 g, 83%).

Found: C, 85.00; H, 5.64%. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53%.

2, 4-Dinitrophenylhydrazone of this sample showed the same melting point as that of authentic benzophenone 2, 4-dinitrophenylhydrazone, mp 247—248°C.

Found: C, 62.94; H, 3.66; N, 15.45%. Calcd for $C_{19}H_{14}N_4O_4$: C, 62.98; H, 3.39; N, 15.45%.

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