

**Preliminary communication**

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**ORGANOTITANIUM CARBONYLS. REACTION OF TETRABENZYL-  
TITANIUM WITH CARBON MONOXIDE**

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**Summary**

Tetrabenzyltitanium and its dicyclohexylamine adduct react with carbon monoxide to form acylbenzyltitanium compounds, which have been characterized. The presence of  $(\text{PhCH}_2)_4\text{Ti}(\text{CO})_2$  and  $(\text{PhCH}_2)_4\text{Ti}(\text{CO})$  (amine) as intermediates was indicated by the IR spectra.

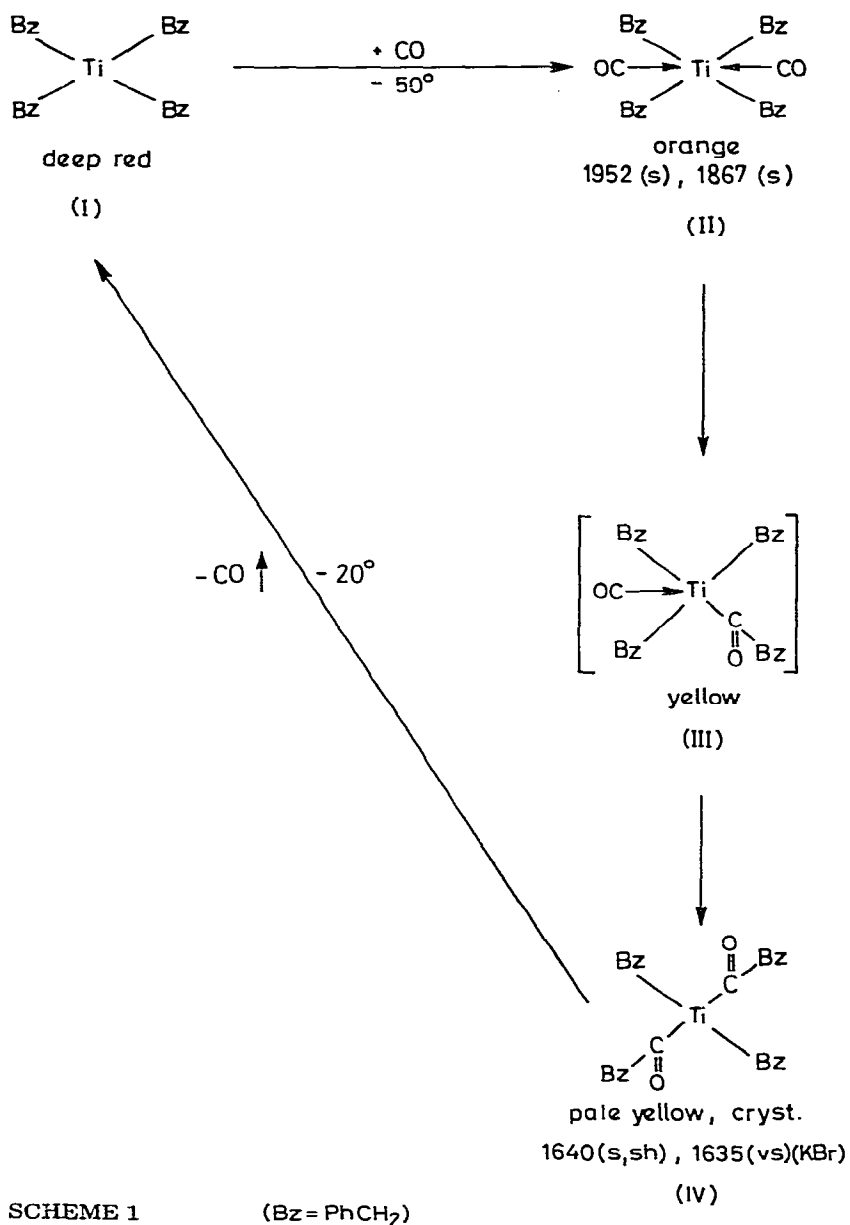
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Two interesting features of organotitanium chemistry have attracted our attention: (i) The few reported titanium carbonyls [1—4] all contain  $\eta^5$ -cyclopentadienyl ligands, and (ii) in spite of the higher stability of benzyl derivatives of metal carbonyls [5—11] the metal carbonyl species which must obviously be intermediates in the carbonylation of cyclopentadienyl benzyltitanium [12] (and also -zirconium [13, 14]) derivatives were not detected.

As a part of systematic studies on *per-σ*-organotitanium compounds we decided to investigate the interaction between benzyltitanium compounds and carbon monoxide. We choose tetrabenzyltitanium,  $(\text{PhCH}_2)_4\text{Ti}$  (I) [15] for the initial study, and we report our initial results below.

A solution of I in *n*-pentane changes in colour from deep-red to brick-red then to orange when a CO stream is led in at  $-50^\circ\text{C}$ . The observed reactions can be seen in Scheme 1. The assumed formation of II was proved by IR spectroscopy. When the orange colour starts to appear a pale-yellow substance begins to precipitate. This process is complete when the solution has absorbed nearly 2 mol CO per titanium atom (found by gas volumetry  $\text{CO}/\text{Ti} = 1.85$  and 2.10), which are inserted into the Ti—C bonds. The resulting acyl compound (IV) has been isolated. If the solution is allowed to warm to  $-20^\circ\text{C}$  evolution of CO is observed and the original red colour of the solution of I returns.

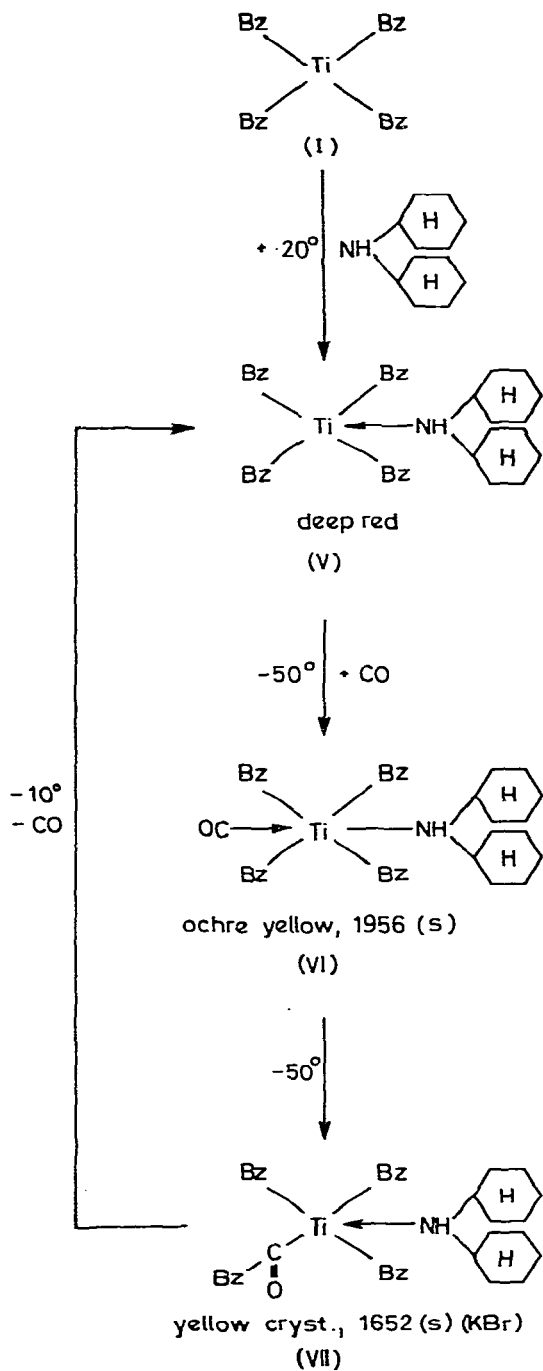
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In the course of the reactions samples were analyzed by IR spectroscopy. The red solution shows only one weak band at  $1938\text{ cm}^{-1}$  (which can be attributed to the presence of the  $\text{PhCH}_2\text{Ti}$  group [15] and remains virtually constant), the orange solution shows two bands in the  $\nu(\text{CO})$  range at  $1952\text{ s}$  and  $1867\text{ s}\text{ cm}^{-1}$ , the start of the precipitation is accompanied by a decrease and then the disappearance of these bands. A KBr pellet prepared at low temperature from the precipitate of IV shows  $\nu(\text{C}=\text{O})$  absorptions at  $1640\text{ s}$  (sh) and  $1635\text{ vs}$ . The isolated acyl compound was identified as dibenzylbis(phenylacetyl)titanium

(IV). The formulation is confirmed by elementary analysis, the IR spectrum and by hydrolysis, which gave toluene and phenylacetaldehyde (as shown by GC/MS).

I reacts with dicyclohexylamine (1.1 mol/Ti atom) in n-pentane. After



SCHEME 2

evaporation of the solvent a red crystalline substance is obtained, which analyses as  $(\text{PhCH}_2)_4\text{Ti}[\text{NH}(\text{C}_6\text{H}_{11})_2]$  (V) (Scheme 2). This adduct is stable at room temperature.

It was of interest to test the reactivity of this substance towards CO. Therefore the saturated n-pentane solution of V (containing some solid) was treated with CO (bubbled through) at  $-50^\circ\text{C}$ . The solution became ochre-yellow.

This solution was investigated by IR spectroscopy and a strong band observed at  $1956\text{ cm}^{-1}$ . We attributed this band to the (intermediate) formation of  $(\text{PhCH}_2)_4\text{Ti}(\text{CO})[\text{NH}(\text{C}_6\text{H}_{11})_2]$  (VI), although this could not be isolated in pure form.

After prolonged standing (6–10 h) a yellow crystalline precipitate is formed and the band at  $1956\text{ cm}^{-1}$  disappears as a new band at  $1652\text{ cm}^{-1}$  increases. The latter band is also observed in a n-pentane solution or a KBr pellet prepared from the yellow precipitate. On the basis of these observations and elementary analyses this yellow substance can be formulated as  $(\text{PhCH}_2)_3(\text{PhCH}_2\text{CO})\text{Ti}[\text{NH}(\text{C}_6\text{H}_{11})_2]$  (VII). The formulation of VII is supported by its hydrolysis products, namely toluene, phenylacetaldehyde and dicyclohexylamine (as shown by GC/MS).

When the solution of VII is left to warm to  $-10^\circ\text{C}$  CO is evolved and V is obtained.

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## References

- 1 J.G. Murray, *J. Amer. Chem. Soc.*, **83** (1961) 1287.
- 2 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, *J. Amer. Chem. Soc.*, **94** (1972) 1219.
- 3 H.G. Alt and M.D. Rausch, *Z. Naturforsch. B*, **30** (1975) 813; B. Demerseman, G. Bouquet and M. Bigorgne, *J. Organometal. Chem.*, **93** (1975) 199.
- 4 B. Demerseman, M. Pankowski, G. Bouquet and M. Bigorgne, *J. Organometal. Chem.*, **117** (1976) C10.
- 5 Z. Nagy-Magos, G. Bor and L. Markó, *J. Organometal. Chem.*, **14** (1968) 205.
- 6 P.J. Craig and M. Green, *J. Chem. Soc. A*, (1968) 1978; (1969) 157.
- 7 M. Kubota, D.M. Blake and S.A. Smith, *Inorg. Chem.*, **10** (1971) 1430.
- 8 M. Kubota and D.M. Blake, *J. Amer. Chem. Soc.*, **93** (1971) 1368.
- 9 F. Calderazzo, *Angew. Chem.*, **89** (1977) 305.
- 10 G. Pályi, *Transition Met. Chem.*, **2** (1977) 273.
- 11 J.N. Cawse, R.A. Fiato and P.L. Pruett, *J. Organometal. Chem.*, **172** (1979) 405.
- 12 G. Fachinetti and C. Floriani, *J. Organometal. Chem.*, **71** (1974) C5.
- 13 C.J. Attridge, B. Dobbs and S.J. Maddock, *J. Organometal. Chem.*, **57** (1973) C55.
- 14 G. Fachinetti, C. Floriani, F. Marchetti and S. Merlino, *Chem. Commun.*, (1976) 522.
- 15 W. Brüser, K.-H. Thiele, P. Zdunek and F. Brune, *J. Organometal. Chem.*, **32** (1971) 335.