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Preliminary communication

INSERTION OF CARBON MONOXIDE INTO TITANIUM—CARBON BONDS

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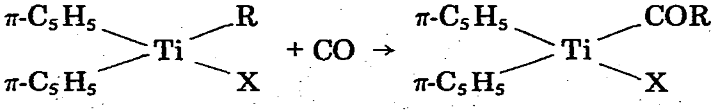
Summary

The reaction of CO with dicyclopentadienylhaloalkyltitanium(IV) derivatives, $(\pi\text{-}C_5H_5)_2Ti(X)R$, gives the acyl derivatives, $(\pi\text{-}C_5H_5)_2Ti(X)(COR)$; with the corresponding benzyl compound the carbonylation is reversible.

Many reactions of importance in organometallic chemistry or homogeneous catalysis, fall into the category of insertions [1]. In spite of considerable progress in this field, especially in insertions into metal—alkyl bonds, only recently has an example of insertion into a titanium—carbon bond been reported, that of SO_2 [2]. Considerable interest centers around the insertions into titanium—carbon σ-bonds because of their relevance to polymerisation systems [3].

We report [4] here the carbonylation of dicyclopentadienylhaloalkyltitanium(IV), $(\pi\text{-}C_5H_5)_2Ti(X)R$ (I), ($R = CH_3$, $CH_2C_6H_5$, $X = Cl$; $R = C_2H_5$, $X = Cl, I$) to give the corresponding dicyclopentadienylhaloacyltitanium(IV), $(\pi\text{-}C_5H_5)_2$-$Ti(X)(COR)$ (II), as represented in eqn. 1. This reaction offers a synthetic route


(1)

(I) (II)

to acyl derivatives (II) in addition to those involving the oxidative additions of acyl halides and alkyl iodides to $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ [5].

The reactions of type (1) were carried out during two days in heptane or toluene solutions under CO at room temperature. The acyl derivatives (II) were obtained (yields > 50%) as microcrystalline yellow or yellow-orange solids, insoluble in hydrocarbons but soluble in $CHCl_3$ or other polar solvents, such as tetrahydrofuran. Satisfactory elemental analyses were found in all cases. The compounds constitute a new class of organometallic derivatives of titanium(IV)

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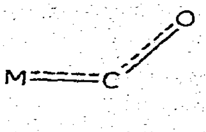
TABLE 1

IR AND ^{1}H NMR DATA FOR ACYL DERIVATIVES OF TITANIUM(IV) OF FORMULA $(\pi\text{-}C_5H_5)_2Ti(X)(COR)$

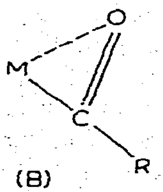
R	X	IR spectrum (cm^{-1})	^{1}H NMR spectrum ^{c}		
		acyl CO stretch	Chem. shift (ppm) ^{d}	Rel. int.	Assignment
CH_3	Cl	1620 ^{a}	4.2 s	10	C_5H_5
		1620 ^{b}	7.0 s	3	CH_3
C_2H_5	I	1605 ^{a}	4.2 s	10	C_5H_5
		1615 ^{b}	6.7 q	2	CH_2
			8.6 t	3	CH_3
C_2H_5	Cl	1603 ^{a}	4.2 s	10	C_5H_5
		1615 ^{b}	6.7 q	2	CH_2
			8.6 t	3	CH_3
$CH_2C_6H_5$	Cl	1625 ^{a}	2.7 s	5	C_6H_5
			4.3 s	10	C_5H_5
			5.5 s	2	CH_2

^{a} Nujol mull. ^{b} $CHCl_3$ solution. ^{c} $CDCl_3$ solution. ^{d} s, singlet; t, triplet; q, quartet.

with some unusual properties, such as high thermal and oxidative stability. The CO stretching values (Table 1) are rather lower than those usually found for acyl-metal complexes of transition metals. Molecular weight determinations in $CHCl_3$ (found 228, calcd. 256.5 for R = CH_3, X = Cl; found 271, calcd. 270.5 for R = C_2H_5, X = Cl) exclude a dimeric formula, and the low ν(CO) frequencies may arise from intramolecular interaction between the metal and the acyl group, as in (A) or (B).

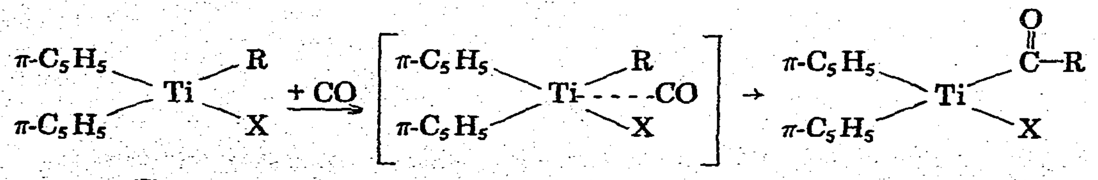


(A)



(B)

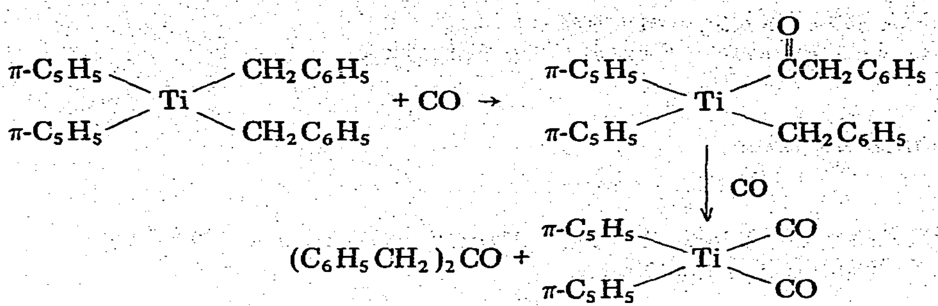
Reaction 1 probably involves an intermediate (C), analogous to $[(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_3]^-$ [6] (eqn. 2).



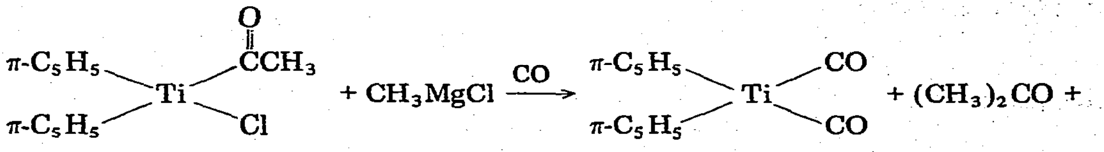
(2)

(I) (C) (II)

The result of carbonylation of the dicyclopentadienyldibenzyltitanium, $(\pi\text{-}C_5H_5)_2Ti(CH_2C_6H_5)_2$, which gives $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ and $(C_6H_5CH_2)_2CO$, was previously attributed to the instability of a complex in which an acyl and an alkyl group are bound to the same metal atom [7]:



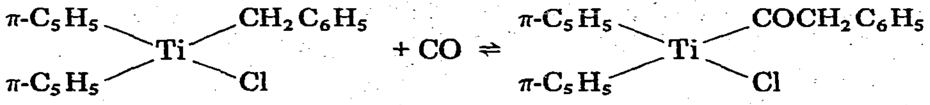
Support for this interpretation comes from formation of the acyl complexes (II) in reaction 1 and from the observation that complex III reacts with CH_3MgCl under an atmosphere of CO (see eqn. 3) to give good yields of $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ and $(CH_3)_2CO$.



(III)

MgCl$_2$ (3)

It is noteworthy that for R = $CH_2C_6H_5$ (IV), reaction 1 offers the only available route to $(\pi\text{-}C_5H_5)_2Ti(COCH_2C_6H_5)Cl$ (V), since oxidative addition of $C_6H_5CH_2Cl$ or $C_6H_5CH_2COCl$ to $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ gives $(\pi\text{-}C_5H_5)_2TiCl_2$ as the main product. The benzyl derivative is the only alkyl—titanium compound which is carbonylated reversibly. (V) can be obtained quantitatively at 20°C in heptane, in which it is only slightly soluble, and can be reconverted almost completely to the starting benzyl compound by heating the heptane suspension at 40°C for 30 minutes. The interconversion (IV) $\rightleftharpoons$ (V) can be observed by NMR spectral ($CDCl_3$) or CO-absorption measurements.



(IV) (V)

Acknowledgment

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