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Preliminary communication

OXIDATIVE-ADDITION REACTIONS OF MONOCYCLOPENTADIENYLTITANIUM(III) DIHALIDES

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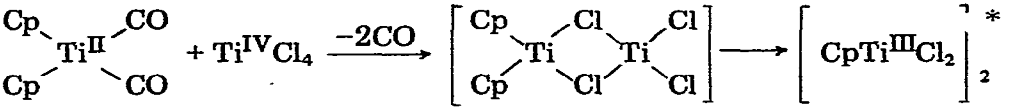
Summary

Oxidative-addition reactions of $CpTi^{III}Cl_2$ are described, and, in particular, the reactions with compounds containing disulphide linkages.

Oxidative-addition reactions of organotitanium(II) derivatives have received attention in recent years [1]. The usual starting material for such reactions is "titanocene" (the nature of which varies with the method of preparation), although dicarbonyldicyclopentadienyltitanium(II) is more satisfactory because it maintains the di-π-cyclopentadienyltitanium moiety throughout the reactions [2-4]; e.g. eqn. 1. We now wish to report that $CpTi^{III}Cl_2$ itself undergoes oxidative-addition reactions. In particular we describe its oxidation by compounds containing disulphide linkages.



(1)

A blue-green solution of $CpTi^{III}Cl_2$ in tetrahydrofuran (THF) slowly turns orange brown over several hours at room temperature upon addition of dialkyl (or diaryl) disulphides (eqn. 2). The reaction does not proceed in benzene as solvent, although $Cp_2Ti^{III}Cl$ under the same reaction conditions gave rapid reaction and high yields of the monothiolato derivatives $Cp_2Ti^{IV}(SR)Cl$ [5]. The products from reaction (2) (see Table 1) are malodorous, soluble, orange solids, very sensitive to hydrolysis. The derivative $R = C_2H_5$ was not obtained analytically pure.

This cleavage of the disulphide linkage prompted examination of the

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*NQR measurements made by Dr. D.E. Scaife, CSIRO Division of Mineral Chemistry, support a previous proposal by one of us [7] that $CpTiCl_2$ is oligomeric not dimeric.

$$2CpTi^{III}Cl_2 + RS{-}SR \xrightarrow[R.T.]{THF} 2CpTi^{IV}(SR)Cl_2 \qquad (2)$$

$$(R = CH_3,\ C_2H_5 \text{ and } C_6H_5)$$

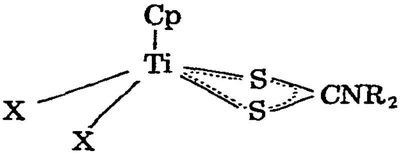
TABLE 1

PHYSICAL DATA

Compound[a]	Colour	M.p. (°C)	PMR[b]: δ (in $CDCl_3$)
$CpTiCl_2(SCH_3)$	Orange	143-146	6.85s(Cp); 3.71s(CH_3)
$CpTiCl_2(SC_6H_5)$[c]	Orange	120-125	6.80s(Cp); 7.4m(C_6H_5)
$CpTiCl_2[S_2CN(CH_3)_2]$	Orange-red	252-256	6.84s(Cp); 3.40s(CH_3)
$CpTiBr_2[S_2CN(CH_3)_2]$	Orange	244-247	6.94s(Cp); 3.39s(CH_3)
$CpTiCl_2[S_2CN(C_2H_5)_2]$	Red	181-184	6.85s(Cp); 3.83q(CH_2); 1.31t(CH_3)
$CpTiBr_2[S_2CN(C_2H_5)_2]$	Red-brown	189-190	6.92s(Cp); 3.81q(CH_2); 1.31t(CH_3)

[a] All compounds are analytically pure. [b] s = singlet, t = triplet, q = quartet, m = centre of multiplet.
[c] This compound has been previously reported; ref. 6.

analogous reaction of thiuram disulphides $[R_2NC(S)S{-}SC(S)NR_2]$. Unlike the dialkyl and diaryl disulphides these compounds react spontaneously in THF at room temperature, with precipitation of orange-red crystalline products $CpTi^{IV}(S_2CNR_2)X_2$ (I; see Table 1). Unlike most monocyclopentadienyltitanium(IV) dihalide derivatives, the products show considerable hydrolytic stability and can be left for some hours in air without evident hydrolysis. Another unexpected property of these derivatives was their lack of disagreeable odour.



(I)

Molecular weights of I in chloroform ($R = CH_3$, X = Cl or Br) and benzene ($R = C_2H_5$, X = Cl or Br) coupled with infrared data, indicate monomeric structures with bidentate dithiocarbamato ligands. They are thus rare examples of five-coordinate organotitanium(IV) derivatives.

Preliminary studies of the analogous reactions of peroxides (ROOR, R = t-butyl, cumyl and benzoyl) indicated similar cleavage reactions with the formation of the corresponding alkoxides or carboxylates.

References

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