Lead Dichloride: a Mild Reagent for the Oxidation of Tervalent Titanium Compounds $(\eta^5\text{-}C_5Me_5)_2TiR$ to Monochloride derivatives $(\eta^5\text{-}C_5Me_5)_2TiR(Cl)$

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Lead dichloride reacts smoothly and stoichiometrically with $(\eta^5\text{-}C_5Me_5)_2TiR$ (R = Cl, alkoxide, alkyl, hydride, *etc.*) complexes to form diamagnetic $(\eta^5\text{-}C_5Me_5)_2TiR(Cl)$ derivatives and elemental lead.

In comparison to their group III congeners the biscyclopentadienyl complexes of titanium(III), $(\eta^5\text{-}C_5Me_5)_2TiR$, have attracted little attention.[1] This is in part due to their instability (thermal decomposition, disproportionation,[2] *etc.*) but also to difficulties in characterisation (extensive paramagnetic line-broadening is observed in the NMR spectra,[3] and EPR spectra are often not helpful for structure determinations[4]). One way to solve these problems of characterisation is to convert the complexes to tetravalent analogues. To achieve this one-electron oxidation a number of reagents (non-Brønsted acids) have been tried, including dihalogens, PhSSPh, AgCl, $AgBPh_4$ and Cp_2FeBPh_4[2b,5] (Cp = $\eta^5\text{-}C_5H_5$). However, none of these is generally applicable and often side reactions or consecutive reactions take place.†

We report here lead dichloride as a convenient reagent to oxidize cleanly a wide variety of tervalent bispermethylcyclopentadienyltitanium complexes to their tetravalent monochloride analogues,‡ eqn. (1). Monobromide complexes can be obtained by the same procedure using $PbBr_2$.

$$(\eta^5\text{-}C_5Me_5)_2TiR + \tfrac{1}{2}\,PbCl_2 \rightarrow (\eta^5\text{-}C_5Me_5)_2TiR(Cl) + \tfrac{1}{2}\,Pb \quad (1)$$

The oxidation proceeded smoothly (with most substrates the reaction was complete within 15 min) at room temperature, but also took place at a reasonable rate at temperatures as low as −30 °C. This opens up the possibility of trapping reactive $(\eta^5\text{-}C_5Me_5)_2TiR$ intermediates, *e.g.* the oxidation of the thermally very unstable propyl compound $(\eta^5\text{-}C_5Me_5)_2TiPr^n$ to $(\eta^5\text{-}C_5Me_5)_2TiPr^n(Cl)$. Oxidation occurred in both polar and non-polar solvents, even in pentane. The best

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† For example, when $(\eta^5\text{-}C_5Me_5)_2TiMe$ is treated with AgCl, $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ is formed, while oxidation of $(\eta^5\text{-}C_5Me_5)_2TiMe$ with bromine yields a mixture of $(\eta^5\text{-}C_5Me_5)_2TiMeBr$, $(\eta^5\text{-}C_5Me_5)_2TiMe_2$ and $(\eta^5\text{-}C_5Me_5)_2TiBr_2$. Oxidation of $(\eta^5\text{-}C_5Me_5)_2TiR$ with PhSSPh gives a mixture of oily products.

‡ All compounds were characterized by elemental analysis, IR, ^1H NMR and ^{13}C NMR spectroscopy.

results were obtained in diethyl ether or tetrahydrofuran, where the solubility of the product $(\eta^5\text{-}C_5Me_5)_2TiR(Cl)$ prevented precipitation on $PbCl_2$. After filtration, the $(\eta^5\text{-}C_5Me_5)_2TiR(Cl)$ compounds were crystallized at low temperature and then isolated. The diamagnetic $(\eta^5\text{-}C_5Me_5)_2TiR(Cl)$ complexes were obtained in essentially quantitative yields, and were generally analytically pure. They show little tendency to decompose or to disproportionate at room temperature.

The scope of this oxidation is very broad, which makes this method of substantial practical importance. Anionic derivatives of $(\eta^5\text{-}C_5Me_5)_2TiR$, *e.g.* halides, alkoxides ($R = OEt$, $OPr^{n,i}$),[4] (imino)acyls or azomethine [$R = NC(H)Bu^t$], are also readily converted into their monochloride derivatives. Also, alkyl (R = Me, Et, Pr, $CH{=}CH_2$) and aryl (R = Ph) complexes[6] yield stable $(\eta^5\text{-}C_5Me_5)_2TiR(Cl)$ products.[6] Oxidation of $(\eta^5\text{-}C_5Me_5)_2TiH$ with lead dichloride yields $(\eta^5\text{-}C_5Me_5)_2TiH(Cl)$, a titanium analogue of the hydrozirconation complex $Cp_2ZrH(Cl)$.[7] So far, there have been no successful syntheses of this complex by other routes,[8] which shows the attractive synthetic potential of this reaction (*vide infra*).

In conclusion this route offers considerable potential for the preparation of diamagnetic derivatives of paramagnetic $(\eta^5\text{-}C_5Me_5)_2TiR$ complexes which are difficult to characterise without complicated NMR spectroscopic analysis. The interest in $(\eta^5\text{-}C_5Me_5)_2TiR(Cl)$ complexes is not just limited to a convenient way of characterising the parent $(\eta^5\text{-}C_5Me_5)_2TiR$ compounds. They also form excellent starting materials for the synthesis of mixed alkyl complexes $(\eta^5\text{-}C_5Me_5)_2TiR^1R^2$ (R^1, R^2 = alkyl, aryl). The latter compounds are expected to decompose by CH activation processes, and mechanistic studies of these processes are in progress.

The oxidation of tervalent titanium compounds with $PbCl_2$ is not limited to bent-sandwich complexes. Monocyclopentadienyl derivatives, *e.g.* $(\eta^5\text{-}C_5Me_5)TiCl_2$ are also cleanly converted into $(\eta^5\text{-}C_5Me_5)TiCl_3$ using $PbCl_2$.[9] Also, Cp_2V and $(\eta^5\text{-}C_5Me_5)_2V$ are monochlorinated to Cp_2VCl and $(\eta^5\text{-}C_5Me_5)_2VCl$, respectively. Although other routes for these complexes are known, this route is proposed as a convenient alternative.[10] Subsequent oxidation by excess of $PbCl_2$ to tetravalent vanadium complexes was not observed.[11]

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