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Published in:
Journal of the Chemical Society%2C Chemical Communications

DOI:
[10.1039/c39900001470](https://doi.org/10.1039/c39900001470)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1990

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Luinstra, G. A., & Teuben, J. H. (1990). Lead Dichloride: a Mild Reagent for the Oxidation of Tervalent Titanium Compounds ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{TiR}$ to Monochloride derivatives ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{TiR}(\text{Cl})$. *Journal of the Chemical Society%2C Chemical Communications*, 29(21). <https://doi.org/10.1039/c39900001470>

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Lead Dichloride: a Mild Reagent for the Oxidation of Tervalent Titanium Compounds ($\eta^5\text{-C}_5\text{Me}_5$)₂TiR to Monochloride derivatives ($\eta^5\text{-C}_5\text{Me}_5$)₂TiR(Cl)

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Lead dichloride reacts smoothly and stoichiometrically with ($\eta^5\text{-C}_5\text{Me}_5$)₂TiR (R = Cl, alkoxide, alkyl, hydride, *etc.*) complexes to form diamagnetic ($\eta^5\text{-C}_5\text{Me}_5$)₂TiR(Cl) derivatives and elemental lead.

In comparison to their group III congeners the biscyclopentadienyl complexes of titanium(III), ($\eta^5\text{-C}_5\text{Me}_5$)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 determinations⁴). 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, AgBPh₄ and Cp₂FeBPh₄^{2b,5} (Cp = $\eta^5\text{-C}_5\text{H}_5$). However, none of these is generally applicable and often side reactions or consecutive reactions take place.[†]

[†] For example, when ($\eta^5\text{-C}_5\text{Me}_5$)₂TiMe is treated with AgCl, ($\eta^5\text{-C}_5\text{Me}_5$)₂TiCl₂ is formed, while oxidation of ($\eta^5\text{-C}_5\text{Me}_5$)₂TiMe with bromine yields a mixture of ($\eta^5\text{-C}_5\text{Me}_5$)₂TiMeBr, ($\eta^5\text{-C}_5\text{Me}_5$)₂TiMe₂ and ($\eta^5\text{-C}_5\text{Me}_5$)₂TiBr₂. Oxidation of ($\eta^5\text{-C}_5\text{Me}_5$)₂TiR with PhSSPh gives a mixture of oily products.

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 PbBr₂.

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 ($\eta^5\text{-C}_5\text{Me}_5$)₂TiR intermediates, *e.g.* the oxidation of the thermally very unstable propyl compound ($\eta^5\text{-C}_5\text{Me}_5$)₂-TiPrⁿ to ($\eta^5\text{-C}_5\text{Me}_5$)₂TiPrⁿ(Cl). Oxidation occurred in both polar and non-polar solvents, even in pentane. The best

[‡] All compounds were characterized by elemental analysis, IR, ¹H NMR and ¹³C NMR spectroscopy.

results were obtained in diethyl ether or tetrahydrofuran, where the solubility of the product $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}(\text{Cl})$ prevented precipitation on PbCl_2 . After filtration, the $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}(\text{Cl})$ compounds were crystallized at low temperature and then isolated. The diamagnetic $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}(\text{Cl})$ 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 $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}$, e.g. halides, alkoxides ($\text{R} = \text{OEt}$, OPr^n),⁴ (imino)acyls or azomethine [$\text{R} = \text{NC}(\text{H})\text{Bu}^1$], are also readily converted into their monochloride derivatives. Also, alkyl ($\text{R} = \text{Me}$, Et , Pr , $\text{CH}=\text{CH}_2$) and aryl ($\text{R} = \text{Ph}$) complexes⁶ yield stable $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}(\text{Cl})$ products.⁶ Oxidation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiH}(\text{Cl})$, a titanium analogue of the hydrozirconation complex $\text{Cp}_2\text{ZrH}(\text{Cl})$,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 $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}$ complexes which are difficult to characterise without complicated NMR spectroscopic analysis. The interest in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}(\text{Cl})$ complexes is not just limited to a convenient way of characterising the parent $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}$ compounds. They also form excellent starting materials for the synthesis of mixed alkyl complexes $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}^1\text{R}^2$ ($\text{R}^1, \text{R}^2 = \text{alkyl, aryl}$). 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. $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2$ are also cleanly converted into $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3$ using PbCl_2 .⁹ Also, Cp_2V and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{V}$ are monochlorinated to Cp_2VCl and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{VCl}$, 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

Received, 11th July 1990; Com. 0/03128C

References

- For leading references see: M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 203; B. J. Burger, M. E. Thompson, W. D. Cotter and J. E. Bercaw, *J. Am. Chem. Soc.*, 1990, **112**, 1566; K. H. den Haan, Y. Wielstra and J. H. Teuben, *Organometallics*, 1987, **6**, 2053; W. J. Evans, *Adv. Organomet. Chem.*, 1985, **24**, 131.
- (a) J. W. Pattiasina, F. van Bolhuis, A. Meetsma and J. H. Teuben, *J. Am. Chem. Soc.*, 1985, **107**, 7758; (b) E. Klei and J. H. Teuben, *J. Organomet. Chem.*, 1980, **188**, 97; (c) D. G. Sekutowski and G. D. Stucky, *J. Am. Chem. Soc.*, 1976, **98**, 1376.
- K. G. Orrell, *Ann. Rep. N.M.R. Spectrosc.*, 1979, **9**, 1.
- J. W. Pattiasina, H. J. Heeres, F. van Bolhuis, A. Meetsma and J. H. Teuben, *Organometallics*, 1987, **6**, 1004.
- J. W. Pattiasina, Thesis, Groningen University, 1988; M. P. Castellani, S. J. Geib, A. L. Rheingold and W. C. Troglor, *Organometallics*, 1987, **6**, 2524; H. Bochmann, A. J. Jagger, L. M. Wilson, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1989, **8**, 1838.
- L. C. ten Cate, F. T. Agricola, H. J. Heeres, H. Jansen, G. A. Luinstra, J. W. Pattiasina, J. L. de Boer, A. Meetsma, J. H. Teuben and A. L. Spek, to be published.
- P. C. Wailes, H. Weigold and A. P. Bell, *J. Organomet. Chem.*, 1972, **43**, C72.
- ' $\text{Cp}_2\text{TiH}(\text{Cl})$ ' has been claimed, see: K. Narasaka, N. Iwasawa, M. Inoue, T. Yamada, M. Nakashima and J. Sugimori, *J. Am. Chem. Soc.*, 1989, **111**, 5340.
- For an alternative work-up, see: J. E. Bercaw, R. H. Marvich, L. G. Bell and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1989, **94**, 1219.
- S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1984, **23**, 1739.
- G. A. Razuvaev, P. Ya. Bayuskin, V. K. Cherkasov, E. N. Gladyshev and A. P. Phokeev, *Inorg. Chim. Acta*, 1980, **44**, L103.