

(C₅Me₅)SiMe₃ as a mild and effective reagent for transfer of the C₅Me₅ ring: an improved route to monopentamethylcyclopentadienyl trihalides of the group 4 elements

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Abstract

The reaction between (C₅Me₅)SiMe₃ and group 4 element tetrahalides MX₄ (M = Ti, X = Cl, Br, I; M = Zr and Hf, X = Cl) gives the corresponding (η⁵-C₅Me₅)MX₃ derivatives in nearly quantitative yields in a one-step procedure without the need for further purification.

Introduction

The pentamethylcyclopentadienyl group (C₅Me₅, denoted by Cp^{*}) is of much importance in organometallic chemistry and has given rise to a rich chemistry that has no counterpart for the non-methylated C₅H₅ ring [1–5]. We have also demonstrated the utility of the Cp^{*} ligand in mono(pentamethylcyclopentadienyl)titanium chemistry [6]. Use of pentamethylcyclopentadienyl-transition metal complexes allows, for instance, the isolation of compounds with the oxidation state of the metal ranging from zero to seven [7].

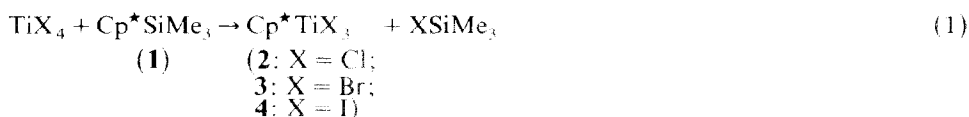
Both steric and electronic influences are usually invoked as the origin of these effects, and ESCA studies with Cp₂^{*}MX₂ (M = Ti, Zr and Hf; X = halogen) and decamethylferrocene and their cyclopentadienyl analogues reveal profound electronic differences between permethylated and unmethylated cyclopentadienyl compounds [8].

There are, however, few ways of introducing the Cp^{*} ring in a transition metal complex. We describe here the use of Cp^{*}SiMe₃ as a mild and effective reagent for the preparation of monopentamethylcyclopentadienyl trihalides of the group 4 elements in a simple and clean procedure giving practically quantitative yields.

Results and discussion

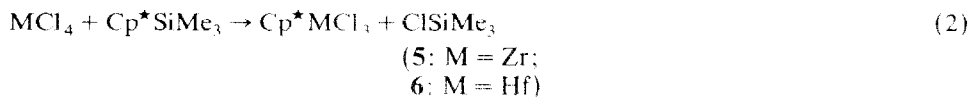
The routes to pentamethylcyclopentadienyl-transition metal complexes involve the use of C_5Me_5H when the metal is in a low oxidation state (metal carbonyls generally), and either $Cp^*Sn(n-Bu)_3$ or, more usually, Cp^*Li or Cp^*K when starting from a halide derivative. These organometallic reagents, however, have reducing properties which preclude their use with those complexes of some transition metals in high oxidation state that are prone to reduction, and in such cases indirect methods, with lower yields, have to be used [9]. Thus, the action of $Cp^*Sn(n-Bu)_3$ or Cp^*Li on $TiCl_4$ leads to extensive reduction and Cp^*TiCl_3 is isolated in 15% yield [10]; the best way of preparing the latter trichloride seems to be the oxidation of Cp^*TiCl_2 . THF with HCl [9b]. Cp^*TiBr_3 has been made from the reaction of $Cp^*Ti(OMe)_3$ with CH_3COBr [11], but no direct method was available up to now. Cp^*TiI_3 was previously unknown.

All these trihalides Cp^*TiX_3 ($X = Cl, Br, I$) can be directly and readily prepared by the action of Cp^*SiMe_3 on the corresponding titanium tetrahalide TiX_4 , according to eq. 1.



The slow addition of Cp^*SiMe_3 to a toluene solution of TiX_4 immediately causes the colour to change from red-orange to red ($X = Cl$) or to change the colour intensity from red to dark-red ($X = Br, I$). Subsequent evaporation of the solvent leads to crystallization of the Cp^*TiX_3 complexes **5**–**7** in nearly quantitative yield, the other, the volatile chlorotrimethylsilane, having been removed with the solvent. Such elimination of $ClSiMe_3$ has been observed before [12].

In the case of zirconium and hafnium the higher stability towards reduction of the oxidation state IV allows the preparation of the mono(pentamethylcyclopentadienyl) trichlorides by use of Cp^*Li ; the reaction has been carried out in several solvents [13] and in every case the separation of the formed $LiCl$ requires as we have ourselves found, a tedious sublimation step ($160^\circ C, 10^{-4}$ mmHg, 2 days). However, the use of Cp^*SiMe_3 enables the trihalides to be made in one step in quantitative yield, the chlorotrimethylsilane being pumped-off with the solvent (eq. 2).



The reaction can be carried out in several solvents such as chloroform or heptane, and the insoluble compounds **5** and **6** have only to be filtered off.

It will be seen that we have developed a simple method of preparing the three-legged piano stool complexes Cp^*MX_3 ($M = Ti, Zr$ and Hf ; $X = \text{halogen}$), and this opens up the study of their chemistry. The method might well be applicable to other halides or complex halides of transition elements, particularly those involving high oxidation state [14 *].

* A reference number with an asterisk indicates a note in the list of references.

Experimental

All manipulations were carried out under N_2 by Schlenk techniques. All the solvents were dried by standard methods and distilled. Me_3SiCl (Fluka) was degassed by pump-thaw cycles before use. $TiCl_4$ (Merck) was freshly distilled from Cu turnings, and the other metal tetrahalides ($TiBr_4$, TiI_4 , $ZrCl_4$ and $HfCl_4$; Fluka or Aldrich) were sublimed immediately before use. The compounds were characterized by analysis and by comparison of their 1H NMR spectra (Varian FT80A spectrometer) with those previously reported [10,13].

Pentamethylcyclopentadienyltrimethylsilane (1). This was prepared by a modification of the reported procedure [15]. Me_3SiCl (16 ml, 126 mmol) was added dropwise to a suspension of 21.9 g (126 mmol) of Cp^*K in 200 ml of THF at $0^\circ C$ and the resulting gelatinous mixture is stirred for 2 h, then filtered through Celite (sometimes twice) to give a completely clear slightly yellow solution. The THF is evaporated under moderate vacuum to leave 24.1 g of pure Cp^*SiMe_3 (92% yield). 1H NMR (CD_2Cl_2 , $35^\circ C$): δ (ppm) 1.76(s, 15H; C_5Me_5) and -0.14 (s, 9H; $SiMe_3$).

Pentamethylcyclopentadienyltitanium trichloride (2). A solution of Cp^*SiMe_3 (18.5 g, 88.9 mmol) in 50 ml of toluene was added dropwise to 16.86 g (88.9 mmols) of $TiCl_4$ in 200 ml of toluene. This red solution is stirred further for 2 h and the solvent then evaporated under vacuum to leave red crystals of the title compound. These are washed with pentane and vacuum-dried. Yield 25.5 g (99%). Found: C, 41.21; H, 5.42; calcd.: C, 41.49; H, 5.28%. 1H NMR ($CDCl_3$): δ (ppm) 2.3 (s); (C_6D_6): 1.93 (s).

Pentamethylcyclopentadienyltitanium tribromide (3). This is obtained by the method described above from 11.45 g (31 mmol) of $TiBr_4$ in 100 ml of toluene and 6.46 g (31 mmol) of Cp^*SiMe_3 in 20 ml of toluene. 12.60 g (96%) Cp^*TiBr_3 are typically obtained. Found: C, 28.61; H, 3.60 calcd.: C, 28.41; H, 3.58%. 1H NMR ($CDCl_3$): δ (ppm) 2.43 (s).

Pentamethylcyclopentadienyltitanium triiodide (4). This can be obtained from 6.73 g (12.1 mmol) of TiI_4 in 80 ml of toluene and 2.52 g (12.1 mmol) of Cp^*SiMe_3 in 10 ml of toluene by the same procedure except that after 2 h stirring the mixture is refluxed for 1 h. 6.50 g of fine deep red needles of Cp^*TiI_3 are obtained (95.2% yield). Found: C, 21.5; H, 2.66; calcd.: C, 21.30; H, 2.68%. 1H NMR ($CDCl_3$) δ (ppm) 2.55 (s).

Pentamethylcyclopentadienylzirconium trichloride (5). 6 g (25.7 mmol) of freshly sublimed $ZrCl_4$ are suspended in heptane and 5.89 g (28.3 mmol) of Cp^*SiMe_3 are added. The mixture is slowly warmed to $60^\circ C$ with stirring. After 4 h the yellowish suspension is cooled and filtered, and the solid washed with hexane and vacuum-dried. 8.40 g of light-yellow **5** are obtained (98% yield). Found: C, 36.53; H, 4.66; calcd.: C, 36.09; H, 4.54%. 1H NMR ($CDCl_3$): δ (ppm) 2.18 (s).

Pentamethylcyclopentadienylhafnium trichloride (6). This was obtained similarly from 6.50 g (20.3 mmol) of $HfCl_4$ and 4.65 g (22.3 mmol) of **1** to give 8.43 of **6** (99% yield). Found: C, 28.50; H, 3.58; calcd.: C, 28.59; H, 3.59%. 1H NMR ($CDCl_3$): δ (ppm) 2.28 (s).

Acknowledgements

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