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$(C_5Me_5)SiMe_3$ as a mild and effective reagent for transfer of the C_5Me_5 ring: an improved route to monopentamethylcyclopentadienyl trihalides of the group 4 elements

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Abstract

The reaction between $(C_5Me_5)SiMe_3$ and group 4 element tetrahalides MX_4 ($M = Ti$, $X = Cl$, Br, I; $M = Zr$ and Hf, $X = Cl$) gives the corresponding $(\eta^5\text{-}C_5Me_5)MX_3$ derivatives in nearly quantitative yields in a one-step procedure without the need for further purification.

Introduction

The pentamethylcyclopentadienyl group (C_5Me_5, denoted by $Cp^\star$) is of much importance in organometallic chemistry and has given rise to a rich chemistry that has no counterpart for the non-methylated C_5H_5 ring [1–5]. We have also demonstrated the utility of the $Cp^\star$ 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 $Cp^\star_2MX_2$ ($M = Ti$, 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 $Cp^\star$ ring in a transition metal complex. We describe here the use of $Cp^\star SiMe_3$ 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.

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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 $Cp^\star Sn(n\text{-}Bu)_3$ or, more usually, $Cp^\star Li$ or $Cp^\star K$ 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 $Cp^\star Sn(n\text{-}Bu)_3$ or $Cp^\star Li$ on $TiCl_4$ leads to extensive reduction and $Cp^\star TiCl_3$ is isolated in 15% yield [10]; the best way of preparing the latter trichloride seems to be the oxidation of $Cp^\star TiCl_2$. THF with HCl [9b]. $Cp^\star TiBr_3$ has been made from the reaction of $Cp^\star Ti(OMe)_3$ with CH_3COBr [11], but no direct method was available up to now. $Cp^\star TiI_3$ was previously unknown.

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

$$TiX_4 + \underset{(\mathbf{1})}{Cp^\star SiMe_3} \rightarrow \underset{\substack{(\mathbf{2}:\ X = Cl;\\ \mathbf{3}:\ X = Br;\\ \mathbf{4}:\ X = I)}}{Cp^\star TiX_3} + XSiMe_3 \qquad (1)$$

The slow addition of $Cp^\star SiMe_3$ 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 $Cp^\star TiX_3$ 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 $Cp^\star Li$; 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 °C, 10^{-4} mmHg, 2 days). However, the use of $Cp^\star SiMe_3$ enables the trihalides to be made in one step in quantitative yield, the chlorotrimethylsilane being pumped-off with the solvent (eq. 2).

$$MCl_4 + Cp^\star SiMe_3 \rightarrow \underset{\substack{(\mathbf{5}:\ M = Zr;\\ \mathbf{6}:\ M = Hf)}}{Cp^\star MCl_3} + ClSiMe_3 \qquad (2)$$

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 $Cp^\star MX_3$ (M = Ti, Zr and Hf; X = 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 *].

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* 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 $Cp^{\star}K$ in 200 ml of THF at 0 °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 $Cp^{\star}SiMe_3$ (92% yield). ^1H NMR (CD_2Cl_2, 35 °C): δ(ppm) 1.76(s, 15H; C_5Me_5) and -0.14 (s, 9H; $SiMe_3$).

Pentamethylcyclopentadienyltitanium trichloride (2). A solution of $Cp^{\star}SiMe_3$ (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 $Cp^{\star}SiMe_3$ in 20 ml of toluene. 12.60 g (96%) $Cp^{\star}TiBr_3$ 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 $Cp^{\star}SiMe_3$ 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 $Cp^{\star}TiI_3$ 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 $Cp^{\star}SiMe_3$ are added. The mixture is slowly warmed to 60 °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).

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