2,4,6-Trimethylpyridine–bishydrofluoride: a novel fluorinating reagent for organo transition-metal alkyls

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Complexes $[M(\eta^5\text{-}C_5Me_5)F_3]$ (M = Zr 2, Hf 5), $[Zr(\eta^5\text{-}C_5H_5)F_2]$ 7 and $[Hf(\eta^5\text{-}C_5Me_5)_2F_2]$ 8 are obtained by treating the corresponding metal alkyls with $[tmpy\cdot(HF)_2]$ (tmpy = 2,4,6-trimethylpyridine); using an excess of $[tmpy\cdot(HF)_2]$ in the preparation of 2 and 5 leads to the complexes $[Htmpy][\{M(\eta^5\text{-}C_5Me_5)F_2\}(\mu\text{-}F)_3]$ (M = Zr 3, Hf 6), respectively and a crystal structure determination of 3 confirms its ionic nature; $[Ti(\eta^5\text{-}C_5Me_5)Cl_2F]$ 10 and 2 were synthesised also from their corresponding alkyls by alkyl–fluorine exchange using Me_3SnF.

Versatile fluorinating reagents for the syntheses of organometallic fluorides are limited.[1] However, recently we found that Me_3SnF or $Bu^n{}_3SnF$ are suitable fluorinating reagents for high yield preparations of cyclopentadienyl substituted fluorides of group 4 metals by chlorine–fluorine metathesis reactions.[2] In order to increase the synthetic methods for preparing organo metal fluorides we were interested to study whether it is possible to introduce fluorine into a metal centre by the reaction of organo metal alkyls using HF with elimination of the corresponding hydrocarbons.

Due to the hydrolytic sensitivity of organometallic alkyls of the early transition metals, adducts of Lewis acids should be used preferentially instead of anhydrous HF. The reaction of $HF\cdot BF_3$ has been studied for synthesising $[Zr(\eta^5\text{-}C_5H_5)_2F_2]$[3] and $[Ta(CH_2Bu^t{}_3)F_2]$[4] using $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ and $[Ta(=CH\text{-}Bu^t)(CH_2Bu^t{}_3]$, respectively.

To the best of our knowledge no HF adducts of tertiary amines, $[R_3N\cdot(HF)_x]$,[5] have been used as fluorinating reagents for the preparation of organometallic fluorides. Herein, we report on the results of our investigations studying the reactions of organo transition metal alkyls with $[R_3N\cdot(HF)_x]$.

Compounds $[R_3N\cdot(HF)_x]$ are mild HF transfer reagents which do not corrode glassware surfaces. Anhydrous systems are obtained by distillation or sublimation of the adducts. 2,4,6-Trimethylpyridine (tmpy) and HF form a solid adduct of composition $[tmpy\cdot(HF)_2]$ after sublimation [50 °C (1 Pa)].† The reaction of $[Zr(CH_2Ph)_3(\eta^5\text{-}C_5Me_5)]$ **1**[6] with an equimolar amount of $[tmpy\cdot(HF)_2]$ at room temp. resulted in the formation of the zirconium complex $[Zr(\eta^5\text{-}C_5Me_5)F_3]$[2] **2** and unreacted starting material instead of the mixed complex $[Zr(CH_2Ph)(\eta^5\text{-}C_5Me_5)F_2]$ [Scheme 1(*a*)]. ^1H and ^{19}F NMR spectra showed that the compounds **1** and **2** are present in a molar ratio of 1 : 2 indicating that both HF molecules of $[tmpy\cdot(HF)_2]$ are active in the metathesis reaction. Hence, as expected, treatment of **1** with 1.5 equiv. of $[tmpy\cdot(HF)_2]$ affords **2** in a quantitative yield [Scheme 1(*b*)].

(*a*) 3 $[MR_3(\eta^5\text{-}C_5Me_5)]$ + 3 $[tmpy\cdot(HF)_2]$ → (i) $[MR_3(\eta^5\text{-}C_5Me_5)]$ + 2 $[M(\eta^5\text{-}C_5Me_5)F_3]$
1(4) **2(5)**

(*b*) 2 $[MR_3(\eta^5\text{-}C_5Me_5)]$ + 3 $[tmpy\cdot(HF)_2]$ → (i) 2 $[M(\eta^5\text{-}C_5Me_5)F_3]$

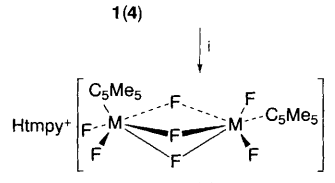
M = Zr(Hf); R = CH_2Ph **1** or Me **4**

Scheme 1 *Reagents and conditions*: i, toluene, room temp., 1 h, −3 tmpy, −6 RH

However, for the preparation of **2** in accordance to Scheme 1(*b*) an excess of $[tmpy\cdot(HF)_2]$ has to be avoided. Reaction of **1** with 3 equiv. of $[tmpy\cdot(HF)_2]$ leads to the complex $[Htmpy][\{Zr(\eta^5\text{-}C_5Me_5)F_2\}_2(\mu\text{-}F)_3]$ **3** in high yield (Scheme 2).

Single crystals of **3** suitable for X-ray analysis could be obtained from diffusion of diethyl ether into a solution of **3** in CH_2Cl_2. The crystals contain CH_2Cl_2 molecules as non-coordinating solvent. The structure of **3** reveals its ionic nature (Fig. 1).‡ Two Zr atoms are bridged by three F atoms. The distorted octahedral coordination of each of the Zr atoms is completed by two terminally bonded F atoms and the $\eta^5\text{-}C_5Me_5$ group. In the solid state the 2,4,6-trimethylpyridinium molecule forms a hydrogen bridge to one of the terminal F atoms [F(2)] and inclines towards the second Zr centre [Zr(2)]. The Zr(1)–

2 $[MR_3(\eta^5\text{-}C_5Me_5)]$ + 6 $[tmpy\cdot(HF)_2]$
1(4)



3(6)

M = Zr(Hf); R = CH_2Ph **1** or Me **4**

Scheme 2 *Reagents and conditions*: i, toluene, room temp., 1 h, −3 tmpy, −6 RH, −2 $[tmpy\cdot(HF)_2]$

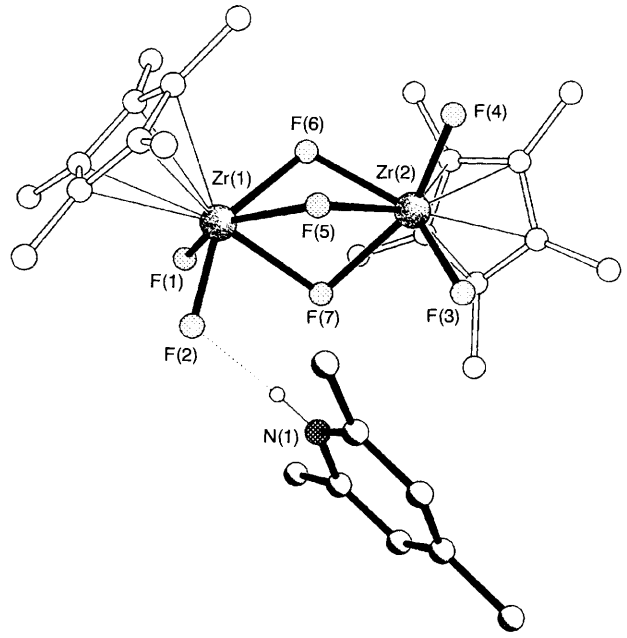
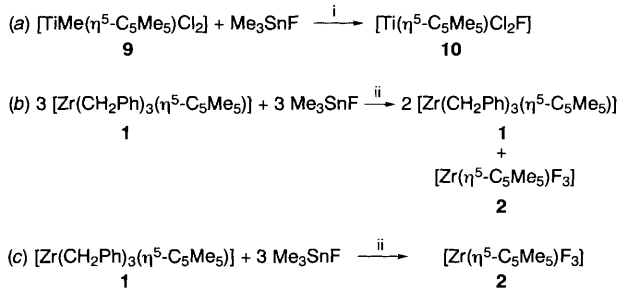


Fig. 1 Crystal structure of **3**. Selected bond distances (pm) and angles (°): Zr(1)–F(1) 194.3(3), Zr(1)–F(2) 199.0(3), Zr(1)–F(5) 212.1(2), Zr(1)–F(7) 218.2(2), F(1)–Zr(1)–F(2) 95.70(14), Zr(1)–F(7)–Zr(2) 97.70(09), F(2)···N(1) 269.3(3).



Scheme 3 *Reagents and conditions*: i, toluene, room temp., 8 h, $-SnMe_4$; ii, toluene, room temp., 3 h, $-3\ Me_3SnCH_2Ph$

F(2) bond length is on average 4 pm longer than the three remaining Zr–F(terminal) bonds (mean 195 pm). The bond lengths of the latter correlate with those in $[\{Zr(\eta^5\text{-}C_5Me_5)F_3\}_4]$ **2** (mean 195.5 pm) whereas the Zr–(μ-F) bond distances in **3** (mean 215.7 pm) are slightly longer than the average Zr–(μ-F) bond distances in **2** (mean 213.6 pm)[2] due to higher electronic density at the metal centres.

The ^{19}F NMR spectrum of the vacuum-dried crystals of **3** (C_6D_6) exhibits two singlets of equal intensity for the terminal F atoms (μ 59.6, 20.4). In solution therefore, the Htmpy cation does not form a separate hydrogen bridge exclusively to one of the terminal F atoms. The F atoms connecting the Zr atoms are also found to be chemically non equivalent. They resonate as two singlets (δ −58.8, −66.5) with a relative integral ratio of 2 : 1. The proton of the hydrogen bridge of **3** can be detected in its ^1H NMR spectrum, measured in $CDCl_3$, as a broad signal in the 'off-set' region at low field (δ 14.0).

The described reactions of **1** using $[tmpy\cdot(HF)_2]$ have been studied analogously with $[HfMe_3(\eta^5\text{-}C_5Me_5)]$ **4**[7] as the precursor complex (Schemes 1 and 2). The homologous complexes of Hf compared to **2** and **3**, $[Hf(\eta^5\text{-}C_5Me_5)F_3]$ **5**[2] and $[Htmpy][\{Hf(\eta^5\text{-}C_5Me_5)F_2\}_2(\mu\text{-}F)_3]$ **6**, respectively, have been obtained in quantitative yield.§

Furthermore, $[Zr(\eta^5\text{-}C_5H_5)_2F_2]$ **7**[8] and $[Hf(\eta^5\text{-}C_5Me_5)_2F_2]$[8] **8**[2] are synthesised in high yields from the reactions of the corresponding methyl derivatives[7] using $[tmpy\cdot(HF)_2]$ in equimolar ratios.

Additionally, it is shown for the first time, that Me_3SnF is a useful fluorinating reagent in reactions using organo transition metal alkyls. Comparable reactions are reported for the syntheses of Me_2GaF[9] and Bu^nMgF.[10]

The reaction of $[TiMe(\eta^5\text{-}C_5Me_5)Cl_2]$ **9**[11] and Me_3SnF yielded exclusively $[Ti(\eta^5\text{-}C_5Me_5)Cl_2F]$ **10**. This demonstrates that Me–F exchange rather than halogen metathesis at the metal centres is the preferred pathway [Scheme 3(*a*)]. The reactions of **1** using different stoichiometric amounts of Me_3SnF always resulted in the formation of $[Zr(\eta^5\text{-}C_5Me_5)F_3]$ **2** [Scheme 3(*b*)]. However, no reaction of $[Zr(CH_2SiMe_3)_3(\eta^5\text{-}C_5Me_5)]$ and Me_3SnF is observed, even using boiling toluene. Obviously, the ability of transition-metal alkyls to undergo an alkyl–fluorine exchange depends highly on the electronic nature of the alkyl substituents.

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Footnotes

† The composition of $[tmpy\cdot(HF)_x]$ varies (x = 1.5–2).

‡ *Crystal data* for **3** (−85 °C): $C_{28}H_{42}F_7Zr_2\cdot1.5CH_2Cl_2$, M = 835.46, monoclinic, space group $P2_1/c$, a = 1556.2(2), b = 1594.3(2), c = 1531.4(2) pm, β = 106.131(13)°, U = 3.6499(8) nm^3, Z = 4, D_c = 1.520 Mg m^{-3}, μ = 0.846 mm^{-1}, 8982 measured reflections, 6472 independent, 6468 employed in the refinement, $2\theta_{max}$ = 50°, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.064$ [$F > 4\sigma(F)$]; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]^{1/2} = 0.1513$ (all data) with $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = [F_o^2 + 2F_c^2]/3$ and $g_1 = 0.0765$ and $g_2 = 7.6337$, max. residual density: 1.8×10^2 e nm^{-3}. Data for structure **3** were collected on a Stoe–Siemens AED diffractometer using graphite-monochromated Mo-Kα radiation (λ = 71.073 pm). Absorption correction was made semi-empirically with 255 ψ-scans (transmission max./min.: 0.860/0.788). The structure was solved by direct methods[12] and refined on (F^2) using full-matrix least squares.[13] There are $1.5CH_2Cl_2$ molecules as non-coordinated lattice solvent per asymmetric unit. All non-hydrogen atoms were refined with anisotropical displacement parameters. Hydrogen atoms were set geometrically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Syntheses*: **2** route (*a*); 0.98 g (6 mmol) $[tmpy\cdot(HF)_2]$ and 2.0 g (4 mmol) $[Zr(CH_2Ph)_3(\eta^5\text{-}C_5Me_5)]$ were stirred in toluene (40 ml) for 1 h at room temp. The solvent was evaporated *in vacuo* and the residue was washed with cold *n*-hexane. Yield 1.0 g (90%) as a colourless solid.

Route (*b*); A mixture of 2.0 g (4 mmol) $[Zr(CH_2Ph)_3(\eta^5\text{-}C_5Me_5)]$ and 2.2 g (12 mmol) Me_3SnF was stirred in toluene (40 ml) for 3 h at 60 °C. After evaporation of the solvent *in vacuo* the remaining residue was washed twice with cold *n*-hexane. Yield 0.9 g (79%) as a colourless solid.

3: A mixture of 1.0 g (6.2 mmol) $[tmpy\cdot(HF)_2]$ and 1.0 g (2 mmol) $[Zr(CH_2Ph)_3(\eta^5\text{-}C_5Me_5)]$ was stirred in toluene (60 ml) at room temp. for 3 h. Filtration and evaporation of the solvent from the filtrate *in vacuo* afforded analytical pure product. Yield 0.67 g (95%) as a colourless solid. mp 212 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 14.00 (br s, 1 H, NH), 7.16 (s, 2 H, Ar H), 2.70 (s, 6 H, *o*-CH_3), 2.50 (s, 3 H, *p*-CH_3), 1.87 (s, 30 H, C_5Me_5). ^{19}F NMR (235 MHz, C_6D_6) δ 59.6 (s, 2 F, F_t), 20.4 (s, 2 F), −58.8 (s, 2 F), −66.5 (s, 1 F). IR (CsI) ν/cm^{-1} 3300 (NH), 3189, 3127, 3053, 3033, 1640, 1263, 1091, 1042, 868, 804, 744, 558, 537, 484, 437, 372. MS (EI): *m/z* 999 {$[Zr(\eta^5\text{-}C_5Me_5)F_3]_4^+ - C_5Me_5$; 10}, 831 {$[Zr(\eta^5\text{-}C_5Me_5)F_3]_3 - F$; 100%}.

5: According to the preparation of **2** [route (*a*)], 1.0 g (6.2 mmol) $[tmpy\cdot(HF)_2]$ and 1.43 g (4 mmol) $[HfMe_3(\eta^5\text{-}C_5Me_5)]$ were reacted in toluene (40 ml). Yield 1.3 g (88%) as a colourless solid.

6: According to the preparation of **3**, 0.98 g (6 mmol) $[tmpy\cdot(HF)_2]$ and 0.72 g (2 mmol) $[HfMe_3(\eta^5\text{-}C_5Me_5)]$ were reacted in toluene (40 ml). Yield 1.0 g (91%) as a colourless solid. mp 215 °C. ^1H NMR (200 MHz, C_6D_6) δ 12.00 (br s, 1 H, NH), 5.89 (s, 2 H, Ar H), 2.35 (s, 6 H, *o*-CH_3), 2.17 (s, 30 H, C_5Me_5), 1.49 (s, 3 H, *p*-CH_3). ^{19}F NMR (188 MHz, C_6D_6) δ 10.8 (s, 2 F, F_t), −17.9 (s, 2 F), −81.1 (s, 2 F), −91.6 (s, 1 F). MS (EI): *m/z* 1092 {$[Hf(\eta^5\text{-}C_5Me_5)F_3]_3 - F$; 40}, 121 (Htmpy; 100%).

7: 1.0 g (6.2 mmol) $[tmpy\cdot(HF)_2]$ and 0.78 g (3.1 mmol) $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ were stirred in CH_2Cl_2 (30 ml) at room temp. for 1 h. The solvent was evaporated *in vacuo* and the residue was washed with *n*-hexane. Yield 0.74 g (92%).

8: A mixture of 1.0 g (6.2 mmol) $[tmpy\cdot(HF)_2]$ and 1.48 g (3.1 mmol) of $[HfMe_2(\eta^5\text{-}C_5Me_5)_2]$ was stirred in toluene (30 ml) at room temp. for 1 h. The solvent was evaporated *in vacuo* and the residue was washed with cold *n*-hexane. Yield 1.2 g (82%) as a colourless solid.

10: To 1.56 g (5.8 mmol) of $[TiMe(\eta^5\text{-}C_5Me_5)Cl_2]$ dissolved in toluene (30 ml) was added 1.06 g (5.8 mmol) of Me_3SnF. The mixture was stirred at room temp. for 8 h. All volatiles were evaporated *in vacuo*. The red residue was crystallised from *n*-hexane at −30 °C. Yield 1.05 g (68%) as red microcrystalline solid, mp 128 °C. ^1H NMR (250 MHz, C_6D_6) δ 1.87 (s, C_5Me_5). ^{13}C NMR (63 MHz, C_6D_6) δ 134.0 (s, C_5Me_5), 14.3 (s, C_5Me_5). ^{19}F NMR (235 MHz, C_6D_6) δ 167.4 (br s) MS (EI): *m/z* 253 {$[Ti(\eta^5\text{-}C_5Me_5)Cl_2]$; 100}, 237 {$[Ti(\eta^5\text{-}C_5Me_5)ClF]$; 84}, 202 {$[Ti(\eta^5\text{-}C_5Me_5)F]$; 18%}.

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