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Cyclopentadienyl metal teflate ($OTeF_5$) complexes

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The $[M(cp)_2(OTeF_5)_2]$ (M = Ti, Zr, Hf, Mo or W; cp = η^5-C_5H_5) complexes have been readily prepared in halide–teflate metathesis reactions of $[M(cp)_2Cl_2]$ with $TeF_5(OH)$. They extend the fluoride–teflate analogy to a new class of high-oxidation-state transition-metal complex. The compounds, which have been characterised by a combination of IR, mass spectrometry and multinuclear NMR spectroscopy, are shown to have polar metal–teflate interactions.

The pentafluorooxotellurate(VI) ('teflate' $OTeF_5^-$) group, as a highly electronegative bulky fluoride analogue, is well established as a ligand for high-oxidation-state transition-metal and main group element complexes.[1] As part of our investigations on low-valent metal fluoride complexes[2] we have investigated whether the fluoride–teflate analogy is applicable in these systems.[3,4] In particular, this research has established the compatibility of teflate and carbonyl, alkyl and phosphine ligands bound to low-valent metal centres. There is, however, only one previous report of a cyclopentadienylmetal teflate derivative, $[Fe(cp)(CO)_2(OTeF_5)]$,[5] and, in view of the extensive chemistry of higher-oxidation-state early transition-metal cyclopentadienyl halide complexes, we have investigated the syntheses of the related Group 4 and 6 metal teflate complexes. Previous work on teflate complexes of these metals has been limited to the neutral $[TiCl_{4-x}(OTeF_5)_x]$ (x = 1–4),[6,7] $[WF_{6-x}(OTeF_5)_x]$ (x = 1–6),[8,9] $[WCl(OTeF_5)_5]$,[6] $[Mo(OTeF_5)_6]$[9] and $[MO(OTeF_5)_4]$ (M = Mo or W)[8,9] and the anionic $[M(OTeF_5)_6]^{2-}$ (M = Ti, Zr or Hf).[7,10,11]

Experimental

Proton, ^{19}F and ^{125}Te NMR spectroscopic studies were carried out on a Bruker AM300 spectrometer at 300.13, 282.41 and 94.69 MHz, respectively. Spectra were recorded on samples in 4 mm outside diameter FEP (perfluoroethylene–propylene copolymer) NMR tubes held coaxially in 5 or 10 mm precision-glass NMR tubes containing a small quantity of $(CD_3)_2CO$ as lock substance. Proton NMR spectra were referenced to external $SiMe_4$, ^{19}F spectra to external $CFCl_3$ and ^{125}Te spectra to external neat $TeMe_2$ using the high-frequency-positive convention. Initial ^{19}F NMR spectra were recorded for *ca.* 400 scans between δ +200 and −600 using 125 000 Hz windows (*ca.* 7 Hz per point), acquisition times of 0.5 s without relaxation delays and pulse widths of 3 μs (28°). Higher-resolution spectra were recorded for narrower spectral widths dependent upon the experiment; typical data-point resolutions for 4000 scan acquisitions were *ca.* 1 Hz. Fourier transforms were carried out without exponential smoothing. The ^{125}Te NMR spectra were recorded for *ca.* 12 000 scans using a 30 000 Hz window (*ca.* 2 Hz per point), acquisition times of 0.4 s with relaxation delays of 1 s and pulse widths of 21 μs (45°). Fourier transforms were carried out with Lorenztian line broadening of 1 Hz. The IR spectra were recorded using a Digilab FTS40 instrument at 4 cm^{-1} resolution on solid samples as Nujol mulls between KBr discs, and, for gaseous samples, in a copper gas-cell (pathlength 10 cm) fitted with AgCl windows. Data are expressed as the wavenumber (cm^{-1}) and relative intensity (s = strong, m = medium, sh = shoulder, w = weak). Elemental analyses were performed by Butterworth Laboratories Ltd. and electron impact (EI) and FAB mass spectra were recorded on a Kratos Concept 1H instrument.

All preparative manipulations were carried out on a metal vacuum line with facilities to connect Teflon and FEP reaction vessels. Bis(cyclopentadienyl)-titanium, -zirconium, -hafnium and -molybdenum dichlorides (Aldrich) were used as supplied. The compounds $TeF_5(OH)$,[12] $[W(cp)_2Cl_2]$,[13] $[Ti(cp)_2F_2]$,[14] $[Ti(cp)_2Me_2]$,[15] $[Mo(cp)(CO)_3Me]$[16] and $[W(cp)(CO)_3Me]$[16] were prepared by the literature routes.

In a typical reaction, the metal complex (*ca.* 0.07 mmol) was loaded, in a dry-box, into a pre-passivated FEP tube (4 or 6 mm outside diameter) fitted with a poly(tetrafluoroethylene) valve. After evacuation on the vacuum line, an excess of $TeF_5(OH)$ (*ca.* 1 mmol) and dry dichloromethane (1 cm^3) were transferred to the metal complex. The valve was closed and the reaction vessel allowed to warm slowly to room temperature, when the reaction commenced with the production of a gas. The reactions typically lasted for between 1 and 30 min (as judged by ^1H NMR spectroscopy, see below) with periodic cooling to −78 °C to remove all the volatiles produced. For the reactions involving methyl metal complexes, these volatiles were transferred to a gas-cell for IR characterisation. After the reaction had been judged to have finished, the excess of $TeF_5(OH)$ and the solvent were removed *in vacuo*, and the product pumped to dryness overnight. The products were then either redissolved in dry CD_2Cl_2 and the reaction tube sealed as described previously[17] for multinuclear NMR investigation, or transferred to the dry-box and stored in a closed FEP tube for further characterisation.

$[Ti(\eta^5\text{-}C_5H_5)_2(OTeF_5)_2]$: red solid (Found: C, 18.4; H, 1.5; F, 30.2. $C_{10}H_{10}F_{10}O_2Te_2Ti$ requires C, 18.3; H, 1.5; F, 29.0%). EI mass spectrum: m/z 656 (M^+), 636 ($[M - HF]^+$), 438 ($[M - OTeF_4]^+$) and 216 $[(cp)_2TiF_2]$. IR: 3132m, 1302w, 1131w, 1077w, 1031 (sh), 1020s, 893vs, 864vs, 835vs, 688vs, 623w and 593w cm^{-1}. NMR: ^1H, δ 6.69 (s, cp); ^{19}F, AB_4 spectrum, δ −32.8 (1 F, m, F_{ax}) and −45.3 (4 F, m, F_{eq}), $^2J_{FF}$ 187; ^{125}Te, δ 581 [d of qnt, $^1J(TeF_{ax})$ 3237, $^1J(TeF_{eq})$ 3492 Hz].

$[Zr(\eta^5\text{-}C_5H_5)_2(OTeF_5)_2]$: dusky yellow solid (Found: C, 17.6; H, 1.4; F, 26.9. $C_{10}H_{10}F_{10}O_2Te_2Zr$ requires C, 17.2; H, 1.4; F, 27.2%). IR: 3123s, 1314w, 1170w, 1154w, 1126w, 1074w, 1023s, 1019 (sh), 888vs, 860vs, 830vs, 694vs, 686 (sh), 630w and 606w cm^{-1}. NMR: ^1H, δ 6.59 (s, cp); ^{19}F, AB_4 spectrum, δ −35.6 (1 F, m, F_{ax}) and −47.0 (4 F, m, F_{eq}), $^2J_{FF}$ 188; ^{125}Te, δ 573 [d of qnt, $^1J(TeF_{ax})$ 3300, $^1J(TeF_{eq})$ 3488 Hz].

$[Hf(\eta^5\text{-}C_5H_5)_2(OTeF_5)_2]$: cream solid. EI mass spectrum: m/z 788 (M^+), 723 ($[M - cp]^+$), 568 ($[M - OTeF_4]^+$) and 348 $\{[(cp)_2HfF_2]^+\}$. IR: 3123m, 1305w, 1170w, 1150w, 1126w, 1074w, 1023 (sh), 1019s, 900vs, 870vs, 831vs, 697vs, 686 (sh), 632w and 611w cm^{-1}. NMR: ^1H, δ 6.50 (s, cp); ^{19}F, AB_4 spectrum, δ −35.9 (1 F, m, F_{ax}) and −46.8 (4 F, m, F_{eq}), $^2J_{FF}$ 188; ^{125}Te, δ 571 [d of qnt, $^1J(TeF_{ax})$ 3372, $^1J(TeF_{eq})$ 3488 Hz].

$[Mo(\eta^5\text{-}C_5H_5)_2(OTeF_5)_2]$: red powder. EI mass spectrum: m/z 639 ($[M - cp]^+$). IR: 3121m, 1169w, 1126m, 1083w, 1030w, 921w, 864vs, 836w, 762s, 684vs, 657 (sh), 629 (sh) and 573w cm^{-1}. NMR: ^1H, δ 7.88 (s, cp); ^{19}F, AB_4 spectrum, δ −37.8 (1 F, m, F_{ax}) and −44.6 (4 F, m, F_{eq}), $^2J_{FF}$ 180; ^{125}Te, δ 607 [d of qnt, $^1J(TeF_{ax})$ 3342, $^1J(TeF_{eq})$ 3582 Hz].

$[W(\eta^5\text{-}C_5H_5)_2(OTeF_5)_2]$: red powder. FAB mass spectrum: m/z 772 ($[M - HF]^+$). IR: 3116m, 1303w, 1159w, 1007w, 960w, 866vs, 833s, 773s, 669m, 625w, 567m and 493m cm^{-1}. NMR: ^1H, δ 6.99 (s, cp); ^{19}F, AB_4 spectrum, δ −38.0 (1 F, m, F_{ax}) and −45.5 (4 F, m, F_{eq}), $^2J_{FF}$ 179; ^{125}Te, δ 605 [d of qnt, $^1J(TeF_{ax})$ 3320, $^1J(TeF_{eq})$ 3576 Hz].

Results and Discussion

Halide–teflate metathesis, in the reactions of $[M(cp)_2X_2]$ (M = Ti, Zr, Hf, Mo or W, X = Cl; M = Ti, X = F) with an excess of $TeF_5(OH)$ occurs readily at room temperature in dichloromethane yielding $[M(cp)_2(OTeF_5)_2]$ in all cases. For the Group 4 metals, these derivatives are direct analogues of the bis(cyclopentadienyl)metal difluorides, which give further support for the fluoride–teflate analogy in high-oxidation-state metal complexes. However, the molybdenum(IV) and tungsten(IV) fluoride complexes, $[M(cp)_2F_2]$, have not yet been reported; *i.e.* $[Mo(cp)_2(OTeF_5)_2]$ and $[W(cp)_2(OTeF_5)_2]$ are two further examples of metal teflate complexes without metal fluoride counterparts, *cf.* $[Mn(CO)_5(OTeF_5)]$,[5] $[Pt(PEt_3)_2(OTeF_5)_2]$[3] and $[Os(CO)_4Me(OTeF_5)]$.[4] For M = Ti, Mo or W these reactions are relatively slow, typically taking 10–30 min to reach completion. However, for M = Zr or Hf they are very quick (typically a few seconds at room temperature) and it is essential that any excess of $TeF_5(OH)$ is removed rapidly *in vacuo* to avoid violent decomposition of the product. The products were characterised by a combination of multinuclear NMR techniques, IR and mass spectrometry and, for two complexes, by elemental analysis (the hydrolytic sensitivity of metal teflate complexes often precludes attempts to obtain accurate elemental analyses).

The IR data for the five complexes are similar and show the typical fingerprints for co-ordinated cp and $OTeF_5$ ligands. The ^{19}F NMR spectra (Table 1) all exhibit standard AB_4 patterns for co-ordinated teflate which range from first order (molybdenum, tungsten) to significantly second order (titanium, zirconium). These data, particularly the values of R, indicate variations in the degree of polarity in the metal–teflate interactions and may be compared with those of teflate derivatives which have very polar M–O interactions {*e.g.* $[Hpy][OTeF_5]$ (py = pyridine, $R = 0.042$),[19] $[Fe(cp)(CO)_2(OTeF_5)]$ ($R = 0.040$),[5] $[Re(CO)_5(OTeF_5)]$ ($R = 0.046$),[5] $[Ti(OTeF_5)_6]^{2-}$ ($R = 0.052$, 0.054),[7,11] $[Zr(OTeF_5)_6]^{2-}$ ($R = 0.055$),[11] $[Hf(OTeF_5)_6]^{2-}$ ($R = 0.056$)[11]} and those with slightly more covalent M–O interactions {*e.g.* $[Pt(PEt_3)_2(OTeF_5)_2]$ ($R = 0.067$),[3] $[Pt(PhCN)_2(OTeF_5)_2]$ ($R = 0.092$)[20]}. However, all of these complexes have very much more polar M–O interactions than those of the earlier reported teflate complexes of molybdenum and tungsten,[8,9] for which $\delta(F_A)$ is either coincident with $\delta(F_B)$ or occurs at a lower frequency. Throughout, these effects mirror the slight variations in the IR frequencies assignable to the ν(M–O) vibrations.

The ^1H NMR data add further examples of the co-ordination shifts associated with cp ligands bound to 'MX_2' metal fragments (Table 2). It can be seen that, for the Group 4 metals, the teflate and chloride ligands have a similar influence on the chemical shift for the protons on the cp ligands. This trend in ^1H NMR chemical shift has been rationalised[14] in terms of a stronger M–cp interaction which, including the teflate data, gives the series $F > Cl \approx OTeF_5 > Br > I$ which reflects the decreasing p_π–d_π halide–metal interaction $I > Br > Cl \approx OTeF_5 > F$. For the molybdenum and tungsten complexes the data cannot be compared in the same way since the only available data for the $[M(cp)_2X_2]$ (X = Cl, Br or I) species were recorded in liquid SO_2. However, the very-high-frequency chemical shifts for the protons on the cp ligands in the teflate complexes of these metals suggests a very strong M–cp interaction which, coupled with the established differences in the p_π–d_π (pseudo)halide–metal interaction for the fluoride and teflate ligands, may account for the failures to prepare either $[Mo(cp)_2F_2]$ or $[W(cp)_2F_2]$.

Table 1 Fluorine-19 NMR data for $[M(cp)_2(OTeF_5)_2]$ complexes

M	$\delta(F_A)$	$\delta(F_B)$	$^2J(F_AF_B)$/Hz	R*
Ti	−32.8	−45.3	187	0.053
Zr	−35.6	−47.0	188	0.058
Hf	−35.9	−46.8	188	0.061
Mo	−37.8	−44.6	180	0.094
W	−38.0	−45.5	179	0.085

* Degenerate AB_4 spectra can be analysed by the method of Harris and Packer[18] where the exact appearance of the spectra is dependent upon the parameter $R = J(AB)/\delta(AB)$, and where $J(AB)$ is the coupling constant between the axial and equatorial fluorines and $\delta(AB)$ is their chemical shift difference (both parameters in Hz).

Table 2 Proton NMR data (δ) for $[M(cp)_2X_2]$ complexes[a]

	X				
M	$OTeF_5$[b]	F	Cl	Br	I
Ti	6.69	6.51	6.70	6.83	7.00
Zr	6.59	6.52	6.62	6.69	6.82
Hf	6.50	6.48	6.52	6.59	6.69
Mo	7.88	—	5.4[c]	5.7[c]	5.7[c]
W	6.99	—	n.o.	5.5[c]	5.7[c]

[a] Recorded in tetrahydrofuran unless otherwise stated; n.o. = not observed. [b] In CD_2Cl_2. [c] In SO_2.

For the reactions involving $[Ti(cp)_2Cl_2]$, when an insufficient excess of $TeF_5(OH)$ had been added or the reaction was stopped by removal of the excess, additional, substantial resonances were seen in the NMR spectra. This second species is characterised by: δ(H) 6.62; $\delta(F_A)$ −31.8, $\delta(F_B)$ −45.9, $^2J_{FF}$ 190, $R = 0.037$; δ(Te) 578, $^1J(TeF_{ax})$ 3199, $^1J(TeF_{eq})$ 3497 Hz. These data strongly suggest a further $Ti(cp)_2$ teflate complex. The relative intensities of the resonances associated with this new complex and those for $[Ti(cp)_2(OTeF_5)_2]$, in the presence of an excess of $TeF_5(OH)$, decrease and increase respectively with time, which indicates that this new species is an intermediate in the formation of $[Ti(cp)_2(OTeF_5)_2]$, and it is assigned as the mixed-ligand complex $[Ti(cp)_2Cl(OTeF_5)]$.

The reaction of alkyl metal reagents with $TeF_5(OH)$ is a clean synthetic route to metal teflate complexes.[4,5] It is not surprising, therefore, that the reaction of $[Ti(cp)_2Me_2]$ with $TeF_5(OH)$ results in the elimination of methane, identified by its characteristic gas-phase IR spectrum, and the generation of $[Ti(cp)_2(OTeF_5)_2]$. If the reaction mixture is kept below 0 °C this is the cleanest synthetic route to this titanium complex. However, it should be noted that this is the first example of bis(methyl for teflate) substitution; the reactions of $CdMe_2$,[21] $HgMe_2$,[22] $[Os(CO)_4Me_2]$[4] and $SnMe_4$[23] with $TeF_5(OH)$ result only in the replacement of one methyl ligand. Unfortunately, this reaction is not applicable in all alkyl metal systems. The reactions of $[M(cp)(CO)_3Me]$ (M = Mo or W) with $TeF_5(OH)$ occur at very low temperatures with the elimination of methane and CO (identified by their gas-phase IR spectra) and the formation of paramagnetic metal-containing products which could not be characterised. These results suggest that, although M^{VI}–$OTeF_5$ and M^{IV}–$OTeF_5$ (M = Mo or W) complexes are stable, the metal(II) metal centres are too readily oxidised by the teflate ligand. Similar observations have been reported in attempts to prepare phosphorus(III) teflate species.[24]

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