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Short communication

Pentafluorooxotellurate(VI) acid as a protic acid

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Abstract

The identification of the $[HM(CO)_3(PPh_3)_2][OTeF_5]$ (M = Fe, Ru, Os) complexes by NMR spectroscopic studies in solution illustrate the use of $HOTeF_5$ as a protic acid.

Keywords: Pentafluorooxotellurate(VI) acid; Protic acid; NMR spectroscopy

1. Introduction

Pentafluorooxotelluric acid ($HOTeF_5$) has been used extensively for the introduction of the $OTeF_5^-$ (teflate) ligand into Main Group and transition metal complexes [1]. Typical reactions involve halide–teflate [1] or methyl–teflate metathesis [2]. A driving force for these studies has been the opportunity for comparison between the highly electronegative teflate and fluoride ligands. Surprisingly then, since AHF is well established as a very strong protic acid [3], there have been no reports of the use of $HOTeF_5$ as an acid reagent. We are currently studying low-valent and organometallic transition metal fluoride complexes [4,5] and are investigating the fluoride–teflate analogy in these species [6]. Here, we report the use of $HOTeF_5$ as a proton source in reactions with $[M(CO)_3(PPh_3)_2]$ (M = Fe, Ru, Os).

2. Experimental details

Tricarbonylbis(triphenylphosphine)-iron [7], -ruthenium [8], -osmium [9] and $HOTeF_5$ [10] were prepared by literature methods. In typical experiments, the metal reagents (ca. 0.5 g, 0.75 mmol), a five-fold molar excess of $HOTeF_5$ (ca. 0.9 g, 3.8 mmol) and CD_2Cl_2 (ca. 0.5 cm^3) were loaded into pre-fluorinated 4 mm o.d. (0.5 mm wall thickness) FEP tubes and allowed to warm slowly to room temperature. When the reactions were judged to have finished (as evidenced by the absence of resonances attributable to the starting materials in the NMR spectra), the reaction vessels were either sealed or the solvent and excess $HOTeF_5$ removed under dynamic vacuum. The resulting solids were redissolved in CD_2Cl_2 and sealed for NMR investigation as described previously [6].

Table 1
NMR spectroscopic data for $[HM(CO)_3(PPh_3)_2][OTeF_5]$

M	^1H [a]	^{19}F [a,b]	$^2J_{FF}$ [c]	R	^{31}P [a]	$^2J_{PH}$ [c]
Fe	−7.85	ca. −39	180	ca. 0.1	55.4	30
		ca. −45	180			
Ru	−6.13	−37.1	178	0.075	33.6	15
		−45.5 [d]	178			
Os	−6.80	−39.1	179	0.099	−0.1	15
		−45.5	179			

[a] Chemical shifts in ppm relative to external standards.
[b] AB_4 patterns which could be simulated using these data.
[c] Coupling constants in Hz.
[d] $^1J_{TeF} = 3616$ Hz.

3. Results and discussion

The reactions of the yellow $[M(CO)_3(PPh_3)_2]$ (M = Fe, Ru, Os) with $HOTeF_5$ occur rapidly in dichloromethane at room temperature to produce yellow/green to dark green solutions. Removal of the solvent and excess teflic acid from the product of the reaction with M = Fe resulted in decomposition and the formation of an uncharacterisable mixture. However, NMR characterisation (see below) for the single product obtained prior to removal of the solvent was carried out in the presence of excess teflic acid. For M = Ru and Os, removal of the solvent and excess teflic acid gave dark green solids which were redissolved in CD_2Cl_2 for NMR characterisation.

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The ^1H, ^{19}F and ^{31}P NMR data for the products are summarised in Table 1. Protonation of the neutral five-coordinate metal complexes with protic acids (e.g. for M = Fe, conc. H_2SO_4 or CF_3CO_2H; for M = Ru or Os, HPF_6, HBF_4, $HClO_4$), yielding the $[HM(CO)_3(PPh_3)_2]^+$ cations, has been established for a number of years [11]. The ^1H NMR data for our complexes using $HOTeF_5$ as the proton source are in good agreement with the literature data, and give an alternative route to their preparation. For M = Ru, the cation is sufficiently solution-stable to allow natural-abundance ^{13}C NMR spectra to be recorded which confirmed the structure of these cations. In addition to the resonances associated with the phosphine ligands, two multiplets at δ 190.5 and 192.7 ppm can be assigned to metal-bound carbonyl ligands. In the $^{13}C\{^1H\}$ NMR spectra these resonances are both triplets, the magnitude of the couplings (8 and 13 Hz) being typical of *cis*-$^2J_{PC}$. In the fully coupled ^{13}C NMR spectra, these resonances are both doublets of triplets; assignment for the resonance at δ 190.5 ppm as CO *trans*-H ($^2J_{CH} = 24$ Hz) and that at δ 192.7 ppm as CO *cis*-H ($^2J_{CH} = 7$ Hz) could be made from the magnitude of the coupling constants.

The highly first-order nature, i.e. the low value for R [12] of the ^{19}F NMR spectra for the teflate anions (Table 1), suggests considerable hydrogen bonding between the cation and the anion. Similar strongly hydrogen-bonded teflate anions have been observed in the complexes $[(PS)H]^+$-$[OTeF_5]^-$ (PS = proton sponge; $R = 0.035$), $[lutH]^+$-$[OTeF_5]^-$ (lut = lutidine; $R = 0.042$) and $[pyH]^+$-$[OTeF_5]^-$ (py = pyridine; $R = 0.042$) [13] where an increase in R corresponds to an increase in hydrogen bonding between the anion and cation.

4. Conclusion

The reactions of $HOTeF_5$ with $M(CO)_3(PPh_3)_2$ (M = Fe, Ru, Os) readily give the previously characterised octahedral protonated cationic $[HM(CO)_3(PPh_3)_2]^+$ complexes hydrogen-bonded to the $[OTeF_5]^-$ anions, which illustrate the first use of $HOTeF_5$ as a protic acid.

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