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Spectroscopic and structural characterisation of *fac*-$[Mn(CO)_3\{MeC(CH_2TeMe)_3\}]CF_3SO_3$: the first transition metal complex of a tritelluroether

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The preparation and crystal structure of the first complex of a multidentate telluroether, *fac*-$[Mn(CO)_3\{MeC(CH_2TeMe)_3\}]CF_3SO_3$ are described, and multinuclear NMR spectroscopic studies suggest that the telluroether is a significantly better σ-donor to Mn(I) compared to its selenoether analogue.

Since a range of ditelluroethers was reported by one of us[1,2] *ca.* 10 years ago the coordination chemistry of these ligands with a variety of transition metals has been studied in some detail, although much less so compared to analogous thio- and seleno-ether ligands.[3] Very few tri-, tetra- or higher polytelluroethers have been reported in the literature, reflecting difficulties in developing suitable synthetic routes to these sensitive compounds. Examples are limited to the tripodal $MeC(CH_2TeMe)_3$, spirocyclic $C(CH_2TePh)_4$ and one recently reported macrocyclic tritelluroether $[12]aneTe_3$ (1,5,9-tritelluracyclododecane) which was structurally characterised as its hexachloro derivative,[4] and no metal complexes of any of these have been reported. However, some years ago work by Schumann and Hoffmann and co-workers[5] using Me_2E led to the conclusion that for low valent centres metal–E bonding follows the series E = S < Se ≪ Te. This is also supported by our own recent work which shows that telluroether ligands are significantly better σ-donors to low-valent metal centres compared to the lighter Group 16 congeners.[6] In light of this we have begun a study of the coordination chemistry of $MeC(CH_2TeMe)_3$ and related multidentate telluroethers and we report here the preparation, full spectroscopic and structural characterisation of the first isolated tritelluroether complex, *fac*-$[Mn(CO)_3\{MeC(CH_2TeMe)_3\}]CF_3SO_3$.

The title compound is readily prepared as a yellow solid by treatment of *fac*-$[Mn(CO)_3(Me_2CO)_3]CF_3SO_3$ with $MeC(CH_2TeMe)_3$ at room temperature in Me_2CO solution, followed by evaporation to dryness and recrystallisation from CH_2Cl_2–light petroleum (bp 40–60 °C). The reaction was monitored by solution IR spectroscopy which showed the disappearance of the bands due to the tris(acetone) Mn(I) precursor and the appearance of strong bands at 2023 and 1947 cm^{-1} associated with the product, indicative of a *fac*-tricarbonyl unit (a_1 + e). Electrospray mass spectrometry (MeCN) shows peaks with the correct isotopic distribution for $[Mn(CO)_3\{MeC(CH_2TeMe)_3\}]^+$ as well as peaks associated with loss of CO ligands, and, together with microanalysis and ^1H and ^{13}C-$\{^1H\}$ NMR spectroscopy,† this supports the formulation $[Mn(CO)_3\{MeC(CH_2TeMe)_3\}]CF_3SO_3$ for the product. *fac*-$[Mn(CO)_3\{MeC(CH_2SeMe)_3\}]CF_3SO_3$ was prepared and characterised similarly for comparison [IR spectrum: ν(CO) 2039, 1962 cm^{-1}]. Yellow rod-like single crystals of the telluroether complex were obtained by vapour diffusion of light petroleum (bp 40–60 °C) into a solution of the complex in CH_2Cl_2. The crystal structure‡ shows that the cation and anion are both disordered across a crystallographic mirror plane. In the $[Mn(CO)_3\{MeC(CH_2TeMe)_3\}]^+$ cation (Fig. 1) the central Mn centre is coordinated to three mutually *fac* carbonyl ligands and all three Te donors from one tritelluroether ligand, Mn–Te(1) 2.601(1), Mn–Te(2) 2.6063(8), Mn–C(1) 1.795(6), Mn–C(2) 1.790(8) Å. However, the disorder leads to two alternative sites for each of the Te-bound Me groups, and hence it is not possible to establish which diastereoisomer (invertomer) occurs in the solid state. Similar Mn–Te and Mn–C bond distances have been observed for *fac*-$[MnCl(CO)_3\{o\text{-}C_6H_4(TeMe)_2\}]$,[6] *d*(Mn–Te) 2.598(1), 2.613(1), *d*(Mn–C) 1.795(6), 1.790(8) Å and the Te–Mn–Te angles in the title compound are very close to the 90° expected for a regular octahedron.

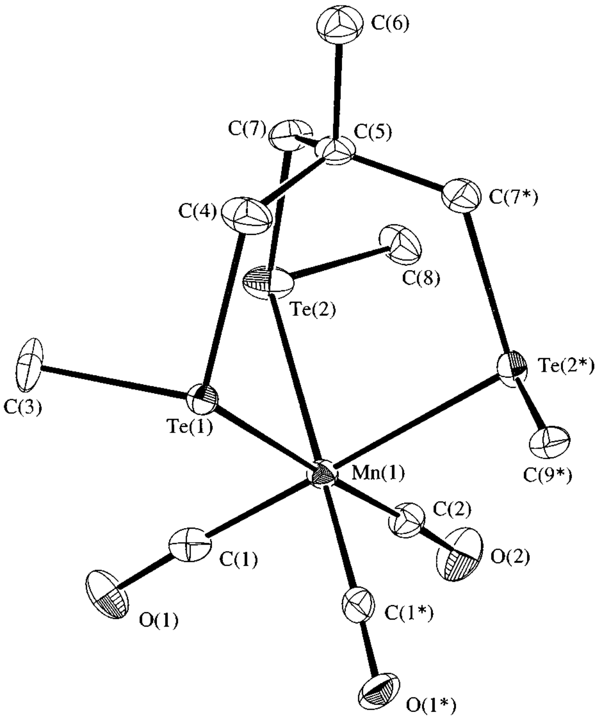

Fig. 1 View of the structure of $[Mn(CO)_3\{MeC(CH_2TeMe)_3\}]^+$ with the numbering scheme adopted. Ellipsoids are shown at the 40% probability level and H-atoms are omitted for clarity. The figure shows the *syn* arrangement established spectroscopically in solution, although we cannot be certain which isomer occurs in the solid state due to the disorder. Selected bond lengths (Å) and angles (°): Mn(1)–Te(1) 2.601(1), Mn(1)–Te(2) 2.6063(8), Mn–C(1) 1.795(6), Mn(1)–C(2) 1.790(8), C(1)–O(1) 1.153(6), C(2)–O(2) 1.157(9); Te(1)–Mn(1)–Te(2) 90.08(3), Te(2)–Mn(1)–Te(2*) 89.31(4).

The ^{125}Te-$\{^1H\}$ NMR spectrum ($CDCl_3$) of $[Mn(CO)_3\{MeC(CH_2TeMe)_3\}]CF_3SO_3$ shows a single resonance at δ 112, indicative of three equivalent Te donors and hence *fac*-tridentate coordination in solution [free $MeC(CH_2TeMe)_3$ δ(^{125}Te) 21]. Since pyramidal inversion at a coordinated Te donor atom is expected to be slow on the NMR timescale, this also implies that the ligand is in the *syn* configuration, with all three terminal Me groups pointing in the same direction giving a propeller-like arrangement. The ^{55}Mn (100% $I = 5/2$) NMR spectrum also shows a single strong resonance at δ −1509, $w_{1/2}$ *ca.* 1200 Hz [a very weak resonance at δ −1465 is attributed to a minor (<3%) quantity of the *anti* isomer]. This is *ca.* 800 ppm to low frequency of the ^{55}Mn NMR shifts for the most closely related neutral ditelluroether complexes *fac*-[MnX(CO)$_3${MeTe(CH$_2$)$_3$TeMe}]; X = Cl, δ −644, −594, −581 (invertomers); X = Br, δ −753, −690,[6] and also very considerably to low frequency compared to the tripodal selenoether analogue [Mn(CO)$_3${MeC(CH$_2$SeMe)$_3$}]CF$_3$SO$_3$ [δ(^{55}Mn) −721 (*syn*) and −672 (*anti*, <5% by ^{55}Mn NMR); δ(^{77}Se) 48 (*syn)*]. The δ(^{125}Te) : δ(^{77}Se) ratio for the tripodal species is therefore *ca.* 2.3 : 1 compared to the more usual 1.7–1.8 : 1[7] and this also supports the conclusion that there is a considerable increase in electron density at the Mn centre in the cationic tritelluroether complex compared to the other species. For the bidentate selenoether species [MnX(CO)$_3${MeSe(CH$_2$)$_3$SeMe}] shows[8] δ(^{55}Mn) −175, −190, −219 (X = Cl), −257, −317 (X = Br), *i.e.* the tripodal selenoether complex is only *ca.* 500 ppm to low frequency of these. The much larger shifts in both the ^{125}Te and ^{55}Mn NMR of [Mn(CO)$_3${MeC(CH$_2$TeMe)$_3$}]$^+$ may be attributed to the enhanced σ-donation from Te→Mn as a consequence of the positive charge on the Mn centre.

Acknowledgements

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Notes and references

† [Mn(CO)$_3${MeC(CH$_2$SeMe)$_3$}]CF$_3$SO$_3$: *fac*-[Mn(CO)$_3$(Me$_2$CO)$_3$]CF$_3$SO$_3$ (0.22 mmol) was stirred with MeC(CH$_2$SeMe)$_3$ (0.071 g, 0.22 mmol) in acetone (15 cm^3) under N$_2$ for 16 h. The solvent was removed *in vacuo* and CH$_2$Cl$_2$ (2 cm^3) was added to dissolve the residue. Ice cold light petroleum (bp 40–60 °C) was then added to precipitate a yellow powder which was filtered and dried *in vacuo* (yield: 47%) (Calc. for C$_{12}$H$_{18}$F$_3$MnO$_6$SSe$_3$: C, 22.5; H, 2.8. Found: C, 23.2; H, 3.0%). Electrospray mass spectrum (MeCN): *m*/*z* 491, [Mn(CO)$_3${MeC(CH$_2$SeMe)$_3$}]$^+$; 437, [Mn(CO){MeC(CH$_2$SeMe)$_3$}]$^+$; 407, [Mn{MeC(CH$_2$SeMe)$_3$}]$^+$. ^{1}H NMR spectrum: δ 2.70 (s, 6H, CH$_2$), 2.38 (s, 9H, SeMe), 1.27 (s, 3H, CCH$_3$). ^{13}C-{^{1}H} NMR spectrum: δ 215.4–217.7 (CO), 40.8 (C), 38.9 (CH$_2$), 34.7 (SeCH$_3$), 25.5 (C*C*H$_3$).

fac-[Mn(CO)$_3${MeC(CH$_2$TeMe)$_3$}]CF$_3$SO$_3$: this compound was prepared in the same way (yield: 78%) (Calc. for C$_{12}$H$_{18}$F$_3$MnO$_6$STe$_3$: C, 18.3; H, 2.3. Found: C, 18.9; H, 2.6%). Electrospray mass spectrum (MeCN): *m*/*z* 639, [Mn(CO)$_3${MeC(CH$_2$TeMe)$_3$}]$^+$; 583, [Mn(CO){MeC(CH$_2$TeMe)$_3$}]$^+$; 555, [Mn{MeC(CH$_2$TeMe)$_3$}]$^+$. ^{1}H NMR spectrum: δ 3.00 (br, 6H, CH$_2$), 2.06 (s, 9H, TeCH$_3$), 1.28 (s, 3H, CCH$_3$). ^{13}C-{^{1}H} NMR spectrum: δ 216.5–222.1 (CO), 39.5 (C), 31.8 (CH$_2$), 29.0 (C*C*H$_3$), −8.3 (TeCH$_3$).

‡ Crystal data for C$_{12}$H$_{18}$F$_3$MnO$_6$STe$_3$, M = 785.06, monoclinic, space group $P2_1/m$, a = 8.989(3), b = 10.033(2), c = 12.086(2) Å, β = 104.85(1)°, V = 1053.6(4) A^3, Z = 2, D_c = 2.474 g cm^{-3}, μ(Mo-Kα) = 48.47 cm^{-1}. A pale yellow rod (0.28 × 0.10 × 0.04 mm) was grown by diffusion of light petroleum into a solution of the compound in CH$_2$Cl$_2$. Data collection used a Rigaku AFC7S four-circle diffractometer, T = 150 K, Mo-Kα X-radiation (λ = 0.71073 Å), 1977 unique reflections (R_{int} = 0.026) of which 1603 with $F > 4\sigma(F)$ were used in all calculations. The structure was solved using heavy atom methods[9] and developed by iterative cycles of least-squares refinement[10] and difference Fourier synthesis. The cation and anion are both disordered across a crystallographic mirror plane, although we were able to model this very satisfactorily. In the cation Mn(1), Te(1), O(2), C(2) and C(4) lie on the plane, although there are two equally populated alternative positions for each of the terminal Me substituents. The disorder in the triflate anion also leads to two equally populated arrangements, such that S(1), F(1) and O(3) lie on the mirror plane and are common to both, with one 50% occupied triflate defined by S(1), O(3), O(4), O(5), F(1), F(2), F(3) and C(10), while the other is defined by S(1), O(3), O(4), O(5*), C(10*), F(1), F(2*) and F(3*). All non-hydrogen atoms were refined anisotropically and H atoms were included in fixed, calculated positions. Final R = 0.025, R_w = 0.034, S = 1.08 for 169 parameters. CCDC reference number 186/1345. See http://www.rsc.org/suppdata/dt/1999/823/ for crystallographic files in .cif format.

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