JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 19
1990

Insertion of Tellurium into an Alkylpentacarbonylmanganese Complex and a Convenient New Route to Manganese Telluride

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The reaction between [Mn(CH_2Ph)(CO)$_5$] and TePEt$_3$ results in the insertion of tellurium into the Mn–CH_2 bond, producing the first known monomeric σ-bonded alkyltelluriomanganese complex [Mn(TeCH$_2$Ph)(CO)$_3$(PEt$_3$)$_2$] **2**; pyrolysis of **2** yields polycrystalline manganese telluride.

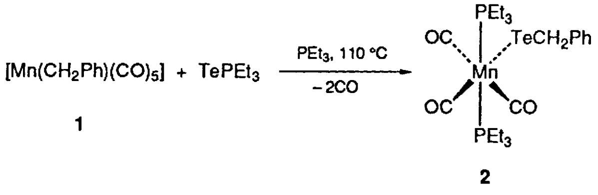
There is growing interest in the preparation of diluted magnetic group 12–16 semiconductors,[1] in particular manganese-doped mercury cadmium telluride (MCT). Research in this area has been hampered by a lack of suitable organometallic feedstocks for the low temperature growth of manganese-doped MCT. One way of addressing this problem may be to develop new bimetallic feedstocks which on decomposition produce pure metal alloys.[2] We now report the synthesis, characterisation and thermal decomposition of a novel alkyltelluriomanganese complex. This is the first report of tellurium insertion into a Mn–C bond and also the first example of a monomeric organomanganese complex with a Mn–Te σ bond.

The reaction of [Mn(CH_2Ph)(CO)$_5$] **1** with a stoichiometric amount of TePEt$_3$† in refluxing toluene (8 h) produces a dark red solution from which an air-stable red crystalline solid **2** can be isolated. The IR spectroscopic data in the carbonyl region‡ are characteristic of a *meridional* tricarbonyl complex,[5] whilst the ^1H NMR data clearly indicate the presence of triethylphosphine and benzyl groups in the ratio 2 : 1. Most importantly, the high frequency shift of the benzyl methylene resonance {relative to the parent compound, [Mn(CH_2Ph)(CO)$_5$] δ 2.36} and the observation of ^{125}Te satellites demonstrate unequivocally that tellurium has been inserted into the Mn–CH_2 bond of [Mn(CH_2Ph)(CO)$_5$], producing **2** as shown in Scheme 1.

An X-ray diffraction study§ establishes structure **2** for the complex (Fig. 1); each asymmetric unit contains two crystallographically independent monomeric molecules. The manganese atom is in a distorted octahedral environment; the *cis* L–Mn–L′ angles range from 86.2(2) to 95.7(3)° and the *trans* L–Mn–L′ angles from 166.2(3) to 175.4(2)°. The Mn–C and Mn–P distances are typical of manganese carbonyl phosphine complexes.[3,6] The Mn–Te bond length in **2** is very similar to that in the dimeric compound [{Mn(CO)$_3$(PEt$_3$)$_2$}$_2$(μ-Te$_2$)].[3]

The reaction of [Mn(CH_3)(CO)$_5$] with TePEt$_3$† in refluxing toluene (8 h) produces an intractable red oil which, on the basis of spectroscopic evidence‡ consists of a 2 : 1 mixture of the new compound [Mn(TeCH$_3$)(CO)$_3$(PEt$_3$)$_2$] **3** and the known compound [Mn(CH_3)(CO)$_3$(PEt$_3$)$_2$],[7] respectively. Further studies of these and related alkyltelluriomanganese complexes are in progress.

A small sample of **2** (0.15 g) was pyrolysed in a tube furnace at 300 °C for 45 min under a stream of H_2 gas. The resulting black/silver-grey deposit was identified by X-ray powder diffraction and X-ray photoelectron spectroscopy as polycrystalline MnTe: Importantly, no other crystalline phases were detected in the material and it was produced at a relatively low temperature. This is a significant result and



Scheme 1

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† The reaction was carried out in the presence of a two-fold excess of PEt$_3$ to inhibit dissociation of the phosphine telluride,[3] a convenient source for introducing elemental tellurium into organometallic reactions.[3,4]

‡ *Selected spectroscopic data* for **2**: IR (toluene), ν_{CO} 1990w, 1911vs, 1889s cm^{-1}; ^1H NMR (CDCl$_3$), δ 1.16 (overlapping dt, 18H, CH$_2$CH_3), 1.99 (overlapping dt, 12H, CH_2CH$_3$), 3.73 (s, 2H, $^2J_{TeH}$ 8.5 Hz, TeCH_2Ph), 7.27 (m, 5H, C$_6$H$_5$); ^{31}P{^{1}H} NMR (CDCl$_3$; ref. 85% H$_3$PO$_4$), δ 40.9 (s); ^{125}Te{^{1}H} NMR (CDCl$_3$; ref. 2 M Na$_2$TeO$_3$ in D$_2$O with the chemical shift taken to be +1723 ppm relative to neat TeMe$_2$ at 0 ppm), δ1121.7 ppm (s). Satisfactory elemental analysis was obtained. For **3**: IR (toluene), ν_{CO} 1991w, 1903vs, 1887vs cm^{-1}; ^1H NMR (CDCl$_3$), δ 1.14 (overlapping dt, 18H, CH$_2$CH_3), 1.51 (s, 3H, $^2J_{TeH}$ 10.2 Hz, TeCH_3), 1.97 (overlapping dt, 12H, CH_2CH$_3$).

§ *Crystal data* for **2**: $C_{22}H_{37}O_3P_2MnTe$, M = 594.0, triclinic, space group $P\bar{1}$, a = 9.263(2), b = 14.650(5), c = 20.265(7) Å, α = 91.27(3), β = 90.67(2), γ = 103.96(2)°; U = 2667.7(14) Å^3, Z = 4, D_c = 1.48 g cm^{-3}, Mo-Kα radiation, R = 0.047 for 8001 unique reflections with $I > 6\sigma(I)$ collected in the range $3.5° \leq 2\theta \leq 55°$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

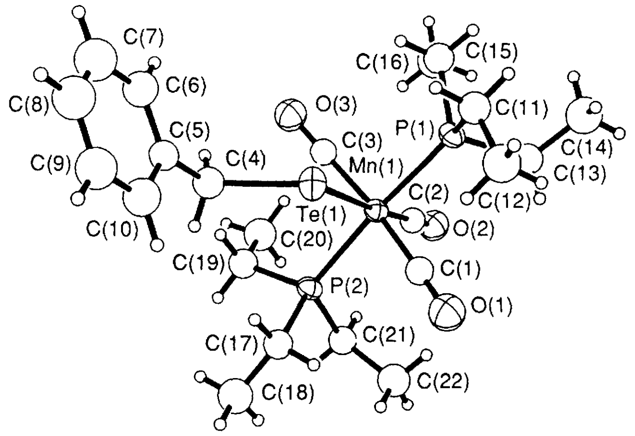

Fig. 1 Molecular structure of the complex **2**. Selected bond distances (Å) and angles (°) for one of the molecules in the unit cell: Mn(1)–Te(1) 2.705(1), Mn(1)–C(1) 1.807(6), Mn(1)–C(2) 1.773(6), Mn(1)–C(3) 1.813(6), Mn(1)–P(1) 2.308(2), Mn(1)–P(2) 2.313(2), Te(1)–C(4) 2.189(7), C(1)–O(1) 1.167(8), C(2)–O(2) 1.157(7), C(3)–O(3) 1.158(7), Mn(1)–Te(1)–C(4) 106.1(2), Te(1)–C(4)–C(5) 109.1(4); the molecular parameters for the two molecules are identical, but the conformation of the ethyl groups about P(2) and P(3) are different.

demonstrates that mixed manganese tellurium complexes may indeed be useful precursors to manganese-doped MCT.

We thank the Australian Government for partial support under the Generic Technology component of the Industry Research and Development Act 1986, Grant No. 15019.

Received, 4th June 1990; Com. 0/02492I

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