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THE SYNTHESIS OF SOME ALKYLTELLURIDE-MANGANESE(I) COMPLEXES, AND AN ASSESSMENT OF THEIR SUITABILITY FOR MOCVD APPLICATIONS

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Abstract—Tellurium does not insert directly into the Mn—C bond of $RMn(CO)_5$ (R = Me or $PhCH_2$). However, reactions between $RMn(CO)_5$ ($R = Me, PhCH_2$) and $TePR'_3$ ($R' = Me, Et$) result in Te insertion accompanied by CO substitution to produce $RTeMn(CO)_3(PR'_3)_2$ complexes. These complexes are formed by initial substitution to give $RMn(CO)_3(PR'_3)_2$ followed by Te insertion. The crystal structure of the complex with $R = PhCH_2$ and $R' = Et$ has been determined from X-ray diffraction data. Crystal data: $C_{22}H_{37}O_3P_2MnTe$; $M = 594.0$; $P\bar{1}$, $a = 9.263(2)$, $b = 14.650(5)$, $c = 20.265(7)$Å, $\alpha = 91.27(3)$, $\beta = 90.67(2)$, $\gamma = 103.96(2)°$, $U = 2667.7(14)$ Å^3; $D_{calc} = 1.479$ ($Z = 4$), $D_{meas} = 1.480(5)$ mg m^{-3}, $\mu = 1.687$ mm^{-1} for Mo-K_α radiation ($\lambda = 0.7107$ Å), final $R = 3.11$, $R_w = 5.46$, from 7788 observed reflections (12974 collected). The geometry about manganese is slightly distorted octahedral with a *trans*-arrangement of the phosphine groups and a *meridional* placement of the carbonyls. Pyrolysis of $PhCH_2TeMn(CO)_3(PEt_3)_2$ at 300°C in a hydrogen stream gives a film of MnTe. Treatment of $Mn(CO)_5Br$ with LiTeR yields the dimeric products $[Mn(CO)_4(\mu\text{-}TeR)]_2$ (R = Me, Et, Pr^i, CH_2SiMe_3, $Si(SiMe_3)_3$, and Ph). For most of these complexes, two conformations have been detected by multinuclear NMR spectroscopy. Variable temperature ^1H NMR spectroscopy shows that the conformers interconvert for $R = Me$ and CH_2SiMe_3. The mass spectra of $[Mn(CO)_4(\mu\text{-}TeR)]_2$ (R = Me, Et, Pr^i) show gas phase fragmentation to Mn_xTe_y species. Pyrolysis of two of these complexes (R = Me, Et) in a hydrogen atmosphere produced a film containing MnTe. Addition of PEt_3 to a solution of $[Mn(CO)_4(\mu\text{-}TeMe)]_2$ results in bridge cleavage to yield $MeTeMn(CO)_3(PEt_3)_2$, but the reaction is slow and other unidentified products are formed. A similar reaction occurs when $R = CH_2SiMe_3$. The formation of $MeTeMn(CO)_3(PEt_3)_2$ was also achieved from the reaction between $BrMn(CO)_3(PEt_3)_2$ and LiTeMe. The Hg—Mn complex $MeHgMn(CO)_5$ was obtained by treatment of $[Mn(CO)_5]^-$ with MeHgCl. This complex readily disproportionates to Me_2Hg and $Hg[Mn(CO)_5]_2$. Pyrolysis of $MeHgMn(CO)_5$ at 300°C gives a film of manganese with no retention of mercury.

In the production of semiconductor materials by metal organic chemical vapour deposition (MOCVD),[1] further developments will depend on several factors. Chemistry will play a key role through the discovery and use of new chemical feedstocks[2] that meet the demand for low temperature growth. Of particular current interest are a range of volatile multimetal compounds that can deposit two metals simultaneously. So far, most attention has been directed at the possible growth of III–V semiconductors using single source precursors[3] containing, for example, both Ga and As or In and P. One of our major interests in this area relates to the possible use of single source compounds containing a dopant element directly linked to a semiconductor element. A particular focus is compounds that incorporate Mn—Te bonds.

A fairly limited range of manganese–tellurium complexes has been reported in the literature.[4] The known complexes that incorporate neutral alkyl- or aryl-tellurium ligands are of the types $Mn(CO)_4X(TeR_2)$,[5] $Mn(CO)_3X(TeR_2)_2$,[6,7] $Mn(NO)_3(TeR_2)$,[6] $Mn(SO_3Cl)_2(TeR_2)$,[8] $[CpMn(CO)_2]_2(\mu\text{-}TeR_2)$,[9] and $[Mn(CO)_3(\mu\text{-}Br)]_2(\mu\text{-}Te_2R_2)$.[10] Some other complexes contain bridging telluride ligands, and these include a few binuclear species of formula $[Mn(CO)_4(\mu\text{-}TeR)]_2$,[6,11] $Mn_2(CO)_8(\mu\text{-}PR_2)(\mu\text{-}TeR')$,[12] and $[CpMn(CO)_2(\mu\text{-}TeR)]_2$.[13] In a variety of polynuclear complexes, "naked" Te atoms act as bridging groups.[14] There are also a few complexes that contain the more exotic tellurium ligands $Te{=}\overline{CN(R)CH_2CH_2N}(R)$[15] and $\mu\text{-}Te{=}CH_2$.[16] None of these complexes has been assessed for MOCVD applications. Given our success in the use of $MeMn(CO)_5$ to incorporate manganese into II–VI semiconductors by MOCVD,[17] we decided to investigate some alkyltellurium—manganese carbonyl complexes of similar composition. In this paper, we report our investigations with Mn–(TeR) complexes. A preliminary account of some aspects of this work has been published.[18] Further studies with Mn–(TeR_2) complexes will be described in a subsequent paper.

EXPERIMENTAL

All reactions and manipulations were carried out under argon or nitrogen using standard Schlenk and dry-box techniques. The solvents used in reactions were rigorously dried and purified.[19] They were distilled under nitrogen from an appropriate drying agent as required.

Methyllithium (1.5 molar solution in tetrahydrofuran; 1.4 molar solution in diethyl ether) and trimethylsilylmethyllithium (1.0 molar solution in pentane) were purchased from Aldrich. Other organo-lithium reagents were prepared as solutions in diethyl ether from lithium and bromoethane,[20] 1-chloro-1-methylethane, or bromobenzene.[21] The reagent $Si(SiMe_3)_4$ was prepared from silicon tetrachloride, chlorotrimethylsilane, and lithium; it was treated with methyl lithium to form $LiSi(SiMe_3)_3(THF)_3$.[22]

Tellurium powder (60 mesh) was purchased from Aldrich and was heated under vacuum before use. Triethylphosphine, trimethylphosphine, and $Mn_2(CO)_{10}$ were obtained from Strem Chemicals. $Mn(CO)_5Br$ was prepared by treatment of $Mn_2(CO)_{10}$ with bromine in dichloromethane;[23] the compound was purified by repeated sublimations at 50–60°C/0.1 mm or recrystallization from dichloromethane–hexane at −15°C until the IR spectrum showed no evidence of unchanged $Mn_2(CO)_{10}$. The preparations of $MeMn(CO)_5$ and $PhCH_2Mn(CO)_5$ were adapted from a procedure described in the patent literature.[24] This involved the initial reduction of $Mn_2(CO)_{10}$ with $NaK_{2.8}$,[25] and subsequent treatment of the $[Mn(CO)_5]^-$ anion with MeI or $PhCH_2Br$. The complex *mer-trans*-$BrMn(CO)_3(PEt_3)_2$ was prepared from $BrMn(CO)_5$ following the general procedure described in the literature.[26]

Microanalyses were performed by Chemical and Micro Analytical Services Pty. Ltd., North Essendon, Victoria, Australia. Infrared spectra were recorded as solutions in KBr cells on a Perkin–Elmer 1600 series spectrometer over the range 4000–400 cm^{-1}. Nuclear magnetic resonance (NMR) spectra were recorded on Brüker AC-200 (^1H and ^{13}C) or AM-300 (other nuclei) spectrometers. Spectra were recorded in deuterated chloroform or benzene, with the residual solvent peak being used as an internal reference. The ^{31}P and ^{125}Te chemical shifts are relative to external H_3PO_4 and $TeMe_2$. Mass spectra were recorded on a VG TRIO-1 GC-MS instrument. Vapour pressures were calculated from mass loss recorded on a Cahn R-100 series microbalance using the Knudsen effusion method.[27] Analyses by X-ray powder diffraction and X-ray photoelectron spectroscopy were performed at CSIRO, Division of Materials Science and Technology, Clayton.

The attempted reaction of $RMn(CO)_5$ *complexes with* Te

Tellurium metal was added to a solution of $MeMn(CO)_5$ in hexane. No reaction was evident when the mixture was refluxed for several days. Similarly, a mixture of Te, $PhCH_2Mn(CO)_5$, and toluene remained essentially unchanged after 3 h at 95°C. The $PhCH_2Mn(CO)_5$ decomposed when the temperature of this mixture was raised to 110°C. Attempts to activate the tellurium *in situ* by ultrasound irradiation were not effective.

The reaction of $PhCH_2Mn(CO)_5$ *with* $TePEt_3$

Triethylphosphine (0.66 ml, 0.53 g, 4.5 mmol) was injected into a Schlenk flask containing a suspension of tellurium powder (0.24 g, 1.9 mmol) in toluene (20 ml), and the mixture was stirred until all metal had dissolved. In a second Schlenk flask, a solution of $PhCH_2Mn(CO)_5$ (0.56 g, 1.9 mmol) in toluene was prepared. This was delivered by cannula to the $TePEt_3$ solution, and the reaction mixture was refluxed. Within a few hours, the colour of the solution was bright red. Infrared monitoring of the reaction mixture indicated that no $PhCH_2Mn(CO)_5$ remained after 8 h; refluxing was stopped after this time. Removal of solvent under reduced pressure left a dark red oil. This was extracted with toluene and the extract was filtered through Celite. Toluene was evaporated under reduced pressure from the filtrate, and the residue was redissolved in pentane. About half of the solvent was removed under reduced pressure, and the remaining solution was cooled to -78°C (acetone/dry ice bath). When crystals had formed, the cold mother liquor was removed through a cannula. The crystals were washed twice with cold pentane and dried in a gentle stream of nitrogen. The product was recrystallized from pentane by repetition of the above procedure. This gave red crystals of *mer-trans*-$\mathrm{PhCH_2TeMn(CO)_3(PEt_3)_2}$ (0.33 g, 29% yield), m.p. 58–59°C. Found: C, 44.2; H, 6.3; O, 8.0. Calc. for $\mathrm{C_{22}H_{37}MnO_3P_2Te}$: C, 44.5; H, 6.3; O, 8.1%. Spectroscopic results: IR (toluene) ν(CO) at 1990 w, 1911 s, 1889 s $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.27 (m, 5H, $\mathrm{C_6H_5}$), 3.73 [s with Te satellites, ^2J(Te-H) = 17 Hz, 2H, $\mathrm{CH_2Te}$], 1.99 (overlapping *d* of q, 12H, $\mathrm{CH_2}$ of $\mathrm{PEt_3}$), 1.16 (overlapping *d* of t, 18H, $\mathrm{CH_3}$ of $\mathrm{PEt_3}$); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 146.4, 128.2, 127.8, and 124.3 (4 × s, $\mathrm{C_6H_5}$), 20.9 (m, $\mathrm{CH_2}$ of $\mathrm{PEt_3}$), 8.05 (s, $\mathrm{CH_3}$ of $\mathrm{PEt_3}$), -7.62 (s, $\mathrm{CH_2}$ of benzyl); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 40.9 (s); ^{125}Te{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 1122 (s).

The reaction of $\mathrm{PhCH_2Mn(CO)_5}$ *with* $\mathrm{TePMe_3}$ *at* 110°C

Similar reaction conditions were used—Te (0.14 g, 1.1 mmol) in toluene (40 ml), $\mathrm{PMe_3}$ (0.30 ml, 2.8 mmol), and $\mathrm{PhCH_2Mn(CO)_5}$ (0.20 g, 0.70 mmol). Infrared monitoring indicated that the reaction was complete after refluxing for 6 h. Toluene was removed under reduced pressure, and the dark coloured oily residue was extracted with pentane. The red pentane solution was chromatographed twice on alumina with pentane as eluent. A major red band was collected, and pentane was removed under reduced pressure. This left a viscous red oil. Attempts to obtain crystals of the compound from a solution in pentane at -20°C were not successful. The ^{1}H NMR spectrum of the oil ($\mathrm{CD_2Cl_2}$ solution) indicated the presence of small amounts of impurities. The product was characterized spectroscopically as *mer-trans*-$\mathrm{PhCH_2TeMn(CO)_3(PMe_3)_2}$ (0.12g, 34%). Spectroscopic data: IR (pentane) 2001 m, 1922 s, 1906 s $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.27 (m, 5H, $\mathrm{C_6H_5}$), 3.80 (s, with Te satellites, ^2J(Te-H) = 18 Hz, 2H, $\mathrm{CH_2Te}$), 1.66 (*d*, ^2J(P-H) = 8 Hz, 18H, $\mathrm{PMe_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 146.5, 128.3, 127.9, and 124.9 (4 × s, $\mathrm{C_6H_5}$), 20.7 (m, $\mathrm{PMe_3}$), -7.85 (s, $\mathrm{CH_2}$ of benzyl); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 12.4 (s); ^{125}Te{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 629.7 (s); MS (*m*/*z*), 512 ([P]$^+$), 426 ([P-3CO]$^+$), 352 ([P-3CO-$\mathrm{PMe_3}$]$^+$), 312, ([$\mathrm{MnTe_2}$]$^+$), 274 ([$\mathrm{PhCH_2TeMn}$]$^+$), 258 ([$\mathrm{Te_2}$]$^+$), 219 ([$\mathrm{PhCH_2Te}$]$^+$), 130 ([Te]$^+$).

The reaction of $\mathrm{PhCH_2Mn(CO)_5}$ *with* $\mathrm{TePMe_3}$ *at* 95°C

The above reaction was repeated at 95°C for 6h. A major yellow product was isolated by chromatography. This was identified spectroscopically as *mer-trans*-$\mathrm{PhCH_2Mn(CO)_3(PMe_3)_2}$ (50% yield) m.p. 95°C. Spectroscopic results: IR (pentane) 1993 w, 1913 s, 1889 s $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.08 (m, 4H, $\mathrm{C_6H_5}$), 6.84 (t, 1H, $\mathrm{C_6H_5}$), 1.84 (t, ^3J(P-H) = 7 Hz, 2H, $\mathrm{CH_2Ph}$), 1.32 (*d*, ^2J(P-H) = 8 Hz, 18H, $\mathrm{PMe_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 156.0 (t, J(P-C) = 4 Hz, $\mathrm{C_6H_5}$), 127.8, 126.9, and 121.4 (3 × s, $\mathrm{C_6H_5}$), 19.3 (m, $\mathrm{PMe_3}$), 13.6 (t, J(P-C) = 8 Hz, $\mathrm{CH_2}$ of benzyl); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 23.2 (s). MS (*m*/*z*), 382 ([P]$^+$), 291 ([P-$\mathrm{CH_2Ph}$]$^+$), 263 ([P-$\mathrm{CH_2Ph}$-CO]$^+$), 235 ([P-$\mathrm{CH_2Ph}$-2CO]$^+$), 207 ([$\mathrm{Mn(PMe_3)_2}$]$^+$), 91 ([$\mathrm{CH_2Ph}$]$^+$), 55 ([Mn]$^+$).

The reaction of $\mathrm{MeMn(CO)_5}$ *with* $\mathrm{TePEt_3}$

Similar reaction conditions were used—Te (0.38 g, 3.0 mmol) in toluene (30 ml), $\mathrm{PEt_3}$ (1.00 ml, 0.79 g, 6.7 mmol), and $\mathrm{MeMn(CO)_5}$ (0.62 g, 3.0 mmol) in toluene (20 ml), reflux 8 h. Workup gave a red oil which contained a mixture of products [IR and NMR evidence indicates this is predominantly a 2 : 1 mixture of *mer-trans*-$\mathrm{MeTeMn(CO)_3(PEt_3)_2}$ and the known[28] compound *mer-trans*-$\mathrm{MeMn(CO)_3(PEt_3)_2}$]. The red oil was dissolved in dichloromethane (5 ml), and the solution was flash-chromatographed on Florisil with a 3 : 1 mixture of hexane and dichloromethane as eluent and a head pressure of argon. This separated a major red band from a yellow band which was rejected. Removal of solvent from the red eluate gave a red solid, which was characterized spectroscopically as *mer-trans*-$\mathrm{MeTeMn(CO)_3(PEt_3)_2}$, m.p. 54°C. IR (toluene) ν(CO) at 1990 w, 1911 s, 1897 vs $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.97 (overlapping *d* of q, 12H, $\mathrm{CH_2}$ of $\mathrm{PEt_3}$), 1.51 (s with Te satellites, ^2J(Te-H) = 20 Hz, 3H, TeMe), 1.14 (overlapping *d* of t, 18H, $\mathrm{CH_3}$ of $\mathrm{PEt_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$) δ 20.7 (m, $\mathrm{CH_2}$ of $\mathrm{PEt_3}$), 5.75 (s, $\mathrm{CH_3}$ of $\mathrm{PEt_3}$), -37.4 (s, TeMe). MS (*m*/*z*), 520 ([P]$^+$), 436 ([P-3CO]$^+$), 421 ([P-3CO-Me]$^+$), 375 ([P-TeMe]$^+$), 291 ([$\mathrm{Mn(PEt_3)_2}$]$^+$). The compound could not be obtained analytically pure (Found: C, 39.4; H, 6.6. Calc. for $\mathrm{C_{16}H_{33}MnO_3PTe}$: C, 37.1; H, 6.4%), and the yield obtained was variable (generally <25% after chromatography).

The formation of LiTeR *compounds*

A solution of LiTeMe was prepared by the literature procedure.[29] Methyllithium (3.3 cm^3 of a 1.5 M solution in tetrahydrofuran, 5.0 mmol) was injected dropwise into a flask containing a suspension of tellurium powder (0.62 g, 4.9 mmol) in tetrahydrofuran (40 ml). The solution was stirred for 30 min at room temperature. During this time, the tellurium dissolved to give initially a deep red ($MeTe_2Li$) and finally a pale yellow (MeTeLi) solution.

The other LiTeR compounds were prepared in identical manner from Te and the appropriate LiR (R = Et, ^{i}Pr, CH_2SiMe_3, $Si(SiMe_3)_3$,[30] Ph[29])

The reaction of $Mn(CO)_5Br$ *with* LiTeMe

A solution of $Mn(CO)_5Br$ (1.46 g, 5.31 mmol) in tetrahydrofuran (20 ml) was transferred by cannula to a yellow solution of MeTeLi. Immediately, there was evolution of CO and a colour change to red. The reaction mixture was stirred for 5 min at room temperature. Solvent was then removed under reduced pressure, and the red gelatinous residue was extracted with pentane to give a deep red solution. Evaporation of solvent in a vacuum gave a dark red solid. This was characterized as $Mn_2(CO)_8(\mu\text{-}TeMe)_2$ (0.65 g, 52%) m.p. 110°C. A small amount of the product was purified by sublimation at 80°C and 10^{-3} mm Hg. Found; C, 19.1; H, 0.9. Calc. for $C_{10}H_6Mn_2O_8Te_2$; C, 19.4; H, 1.0%. IR (hexane) $\nu(CO)$ at 2048 s, 1990 s, 1964 s cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.00 (s, 3H, CH_3), 1.90 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ −27.8, −27.5, 211.3, 219.6. $^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ −964 (s), −974 (s). MS, *m/z*; 620 ($[P]^+$, 5%); other fragment peaks are shown in Table 1.

The formation of other $[Mn(CO)_4(\mu\text{-}TeR)]_2$ *complexes.* These complexes were prepared in similar manner from $Mn(CO)_5Br$ (1.15 g, 4.1 mmol) and the appropriate LiTeR in tetrahydrofuran.

R = Et; red–brown solid (0.53g, 43%) m.p. 82°C, sublimes at 90°C/0.1 mm Hg. Found; C, 22.2; H, 1.45. Calc. for $C_{12}H_{10}Mn_2O_8Te_2$; C, 22.2; H, 1.6%. IR (hexane) $\nu(CO)$ at 2046 m, 1987 m, 1962 m cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.9 (m, 4H, CH_2), 1.3 (t, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −17.4, −8.2, −8.6. $^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ −806 (s), −818 (s). MS (*m/z*), 648 (P^+).

R = Pr^i; brown solid (0.62g, 45%) m.p. 180°C, sublimes at 145°C/0.1 mm Hg. IR (hexane) $\nu(CO)$

Table 1. Mass spectral data for the complexes $[Mn(CO)_4(\mu\text{-}TeR)]_2$

			R group (% rel. int.)		
ion	Me	Et	Pr^i	CH_2SiMe_3	Ph
$[P]^+$	620 (5)	648 (2)	676 (2)	764 (–)[a]	744 (5)
$[P\text{-}CO]^+$	592 (10)	620 (1)	648 (8)	736 (–)	716 (10)
$[P\text{-}2CO]^+$	—	—	—	—	—
$[P\text{-}3CO]^+$	536 (10)	564 (5)	592 (2)	—	660 (5)
$[P\text{-}4CO]^+$	508 (22)	536 (20)	564 (25)	652 (2)	632 (4)
$[P\text{-}5CO]^+$	480 (6)	508 (6)	523 (–)	624 (–)	—
$[P\text{-}6CO]^+$	452 (4)	480 (4)	—	—	—
$[P\text{-}7CO]^+$	424 (15)	452 (10)	480 (8)	—	—
$[Mn_2Te_2R_2]^+$	396 (38)	424 (46)	452 (60)	540 (3)	—
$[Mn_2Te_2]^+$	366 (41)	366 (57)	366 (78)	366 (5)	366 (15)
$[MnTe_2]^+$	311 (11)	311 (15)	311 (18)	—	311 (4)
$[Te_2]^+$	256 (4)	—	256 (8)	—	—
$[Mn_2Te]^+$	240 (12)	240 (17)	240 (21)	—	—
$[MnTe]^+$	185 (15)	185 (15)	185 (15)	—	—
$[TeR_2]^+$	160 (13)	189 (–)	216 (3)	304 (4)	284 (15)
$[TeR]^+$	145 (15)	159 (3)	173 (18)	—	207 (8)
$[Te]^+$	130 (5)	130 (7)	130 (12)	—	130 (2)
$[Mn_2]^+$	110 (13)	110 (12)	—	—	—
$[MnCO]^+$	83 (9)	83 (5)	83 (55)	—	—
$[MnR]^+$	70 (20)	—	—	—	—
$[Mn]^+$	55 (100)	55 (100)	55 (100)	—	55 (5)
$[R_2]$	—	—	—	—	154 (100)
$[R]^+$	—	—	—	—	77 (35)
$[R\text{-}CH_2]^+$				73 (100)	

[a] Signifies peak detected but relative intensity < 1%.

at 2045 m, 1986 m, 1962 m cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 3.8 (m, 2H, CH), 2.1 (*d*, 12H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 26.8, 26.7, 8.5, 8.4 ^{125}Te{^{1}H} NMR (CDCl$_3$) δ -630 (s), -636 (s). MS (*m*/*z*), 676 (P$^+$).

R = CH$_2$SiMe$_3$; red crystals (0.72g, 46%) m.p. 123–126°C. Found; C, 24.9; H, 3.0. Calc. for $C_{16}H_{22}Mn_2O_8Si_2Te_2$; C, 25.2; H, 2.9%.IR (hexane) ν(CO) at 2046 s, 1989 vs, 1961 s cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 1.97 (s with Te satellites, *J*(Te-H) = 20 Hz, 2H, CH$_2$), 1.82 (s with Te satellites, *J*(Te-H) = 17 Hz, 2H, CH$_2$), 0.09 (s, 9H, SiMe$_3$), 0.07 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ -19.1 (CH$_2$), -18.3 (CH$_2$), -0.75 (SiMe$_3$). ^{125}Te{^{1}H} NMR (C$_6$D$_6$) δ -927 (s). MS (*m*/*z*), 764 (P$^+$).

R = Si(SiMe$_3$)$_3$; dark red–black crystals (0.17g, 10%). This complex could not be obtained analyticaly pure. IR (hexane) ν(CO) at 2049 m, 1991 vs, 1965 s cm^{-1}. ^{1}H NMR (C$_6$D$_6$) δ 0.27 (s, SiMe$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 2.85 (s, SiMe$_3$) ^{125}Te{^{1}H} NMR (C$_6$D$_6$) δ -1996 (s). MS (*m*/*z*), 592 (Mn$_2$Te$_2$(CO)$_8$$^+$).

R = Ph; red solid (0.69g, 45%) m.p. 170°C dec. IR (hexane) ν(CO) at 2055 m, 2004 m, 1992 m, 1963 m cm^{-1}. ^{1}H NMR (acetone-*d*$_6$) a broad unresolved multiplet was observed near δ 7.2 (C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 129.4, 130.0, 137.9 ^{125}Te{^{1}H} NMR (CDCl$_3$) δ -592 (s). MS (*m*/*z*), 744 (P$^+$).

The formation of MeTeMn(CO)$_3$(PEt$_3$)$_2$ *from* BrMn(CO)$_3$(PEt$_3$)$_2$ *and* LiTeMe

The complex *mer*, *trans*-BrMn(CO)$_3$(PEt$_3$)$_2$ (0.50g, 1.1 mmol) was added to a solution of LiTeMe (1.9 mmol) in THF (60 ml), and the mixture was stirred at room temperature for 4 days. Removal of solvent under reduced pressure left a dark red oily residue. This was extracted with pentane and chromatographed on alumina. A major red band developed upon elution with benzene. This was collected, and solvent was removed under reduced pressure. The red oily residue was dissolved in hexane (1 ml), and the solution was left at -20°C for 3 days. A dark red solid deposited. The mother liquor was removed, and the solid was dried in a vacuum. This gave MeTeMn(CO)$_3$(PEt$_3$)$_2$ (0.090 g, 16%). The spectroscopic properties are given above in the description of the reaction of CH$_3$Mn(CO)$_5$ with TePEt$_3$.

Attempted bridge cleavage of [Mn(CO)$_4$(μ-TeR)]$_2$ *complexes with tertiary phosphines*

The following reactions were conducted in NMR tubes so that the progress of the reactions could be monitored. A drop of PEt$_3$ (0.05 ml) was added to a solution of [Mn(CO)$_4$(μ-TeMe)]$_2$ (0.012 g) in *d*$_8$-toluene. The ^{1}H and ^{31}P NMR spectra indicated that very little reaction had occurred when the reaction solution was left for 5 days at room temperature; very small amounts of MeTeMn(CO)$_3$(PEt$_3$)$_2$ and some unidentified products were indicated. The solution was then heated at 70°C for 12 h. The NMR spectra established that almost half of the starting material had been consumed, and that the amount of MeTeMn(CO)$_3$(PEt$_3$)$_2$ had increased; several other products were also indicated.

A similar experiment was conducted with [Mn(CO)$_4$(μ-TeCH$_2$SiMe$_3$)]$_2$ and PEt$_3$ in *d*$_6$-benzene. Very little reaction had occurred in 5 days at room temperature. After 24 h at 90°C, almost all of the starting material had disappeared, and five SiMe$_3$ signals were evident in the ^{1}H NMR spectrum; the ^{31}P NMR spectrum was also complex. No attempts were made to repeat these experiments on a preparative scale.

Preparation of MeHgMn(CO)$_5$

Two methods were used. One was based on a literature preparation[31] in which Me$_3$SnMn(CO)$_5$ is treated with MeHgCl in acetone. In the other, a purple solution of NaK$_{2.8}$[Mn(CO)$_5$] (5.2 mmol) in tetrahydrofuran was added to a colourless solution of MeHgCl (1.4 g, 5.6 mmol) in the same solvent. The resultant brown solution was stirred for 5 min and then poured onto ice to give a white flocculant precipitate in a dirty brown solution. (In this and the previously published procedure, the yield of product seems critically dependent on how quickly the reaction is quenched). The resultant mixture was filtered, and the residue was extracted with acetone. Solvent was removed under reduced pressure from the clear yellow acetone extract, and this left MeHgMn(CO)$_5$ as a white solid (0.72 g, 30%) m.p. 94°C. The product could be purified by sublimation at 45°C 10^2 mmHg. Spectroscopic properties: IR (hexane) ν(CO) at 2082 w, 1979 vs, cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 1.1 (s with Hg satellites, *J*(Hg-H) = 180 Hz, HgMe).

Crystal structure of mer-trans-PhCH$_2$TeMn(CO)$_3$(PEt$_3$)$_2$

A preliminary report of this structure is included in ref. 18. Orange–red acicular crystals of the complex were grown from hexane at -20°C, and a representative crystal was selected. Intensity measurements were made on a Nicolet R3m/V automatic diffractometer. The crystal data and results are summarized in Table 2. Three standard reflections were monitored every 197 reflections and showed no significant intensity variation. Intensity

Table 2. Summary of crystal structure data for the complex *mer-trans*-$PhCH_2Mn(CO)_3(PEt_3)_2$

Crystal data	
Empirical formula	$C_{22}H_{37}MnO_3P_2Te$
Crystal size (mm)	$0.25 \times 0.14 \times 0.14$
Crystal system	triclinic
Space group	$P\bar{1}$
a(Å)	9.263(2)
b(Å)	14.650(5)
c(Å)	20.265(7)
α(deg)	91.27(3)
β(deg)	90.67(2)
γ(deg)	103.96(2)
V(Å^3)	2667.7(14)
Z	4
Formula weight	594.0
D_{calc} (mg m^{-3})	1.479
D_{obs} (mg m^{-3})	1.480(5)
Abs. coeff. (mm^{-1})	1.687
F(000)	1200
Data collection	
Diffractometer used	Nicolet R3m/V
Radiation	Mo-K_α ($\lambda = 0.71073$Å)
Temperature (K)	293
Monochromator	highly oriented graphite crystal
2θ range (°)	3.5–55.0
Scan type	ω
ω-scan range (degree)	1.3
Scan rate (degree min^{-1})	variable; 2.00-15.00 in ω
Index ranges	$-12 \leqslant h \leqslant 12$; $-19 \leqslant k \leqslant 19$; $0 \leqslant l \leqslant 26$
Independent reflections	12218
Observed reflections	7788 [$F > 6.0\sigma(F)$]
Absorption correction	face-indexed numerical
Min/max transmission	0.7066/0.8405
Solution and refinement	
System used	Nicolet SHELXTL PLUS (MicroVAX 2000)
Solution	Patterson methods
Refinement method	full-matrix least squares
Quantity minimized	$\Sigma w(F_0 - F_c)^2$
Hydrogen atoms	riding model, single variable isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0096F^2$
Final R indices (obs. data)	$R = 3.11\%$, $R_w = 5.46\%$
R indices (all data)	$R = 6.01\%$, $R_w = 15.29\%$
Goodness of fit	0.51

data were corrected for Lorentz, polarization, and absorption.[32] Atomic scattering factors for neutral atoms were taken from ref. 33 and were corrected for anomolous dispersion using published values from ref. 33. Final refinement was by full-matrix least-squares employing anisotropic thermal parameters for all non-hydrogen atoms and a single variable isotropic thermal parameter [which refined to 0.086(2)] for hydrogen. Hydrogen atoms were positioned in geometrically idealized positions (C—H 0.96 Å).

Pyrolysis of $PhCH_2Mn(CO)_3(PEt_3)_2$ *and* $[Mn(CO)_4(\mu\text{-}TeR)]_2$, R = Me, Et

A Lindberg furnace fitted with a pyrolysis tube was pre-heated to 300°C. Under a stream of argon, a silica boat containing $PhCH_2Mn(CO)_3(PEt_3)_2$

(0.15 g) was manipulated into the hot zone of the pyrolysis tube. The gas stream was switched to hydrogen (flow rate 0.2 l min^{-1}), and pyrolysis was continued for 30 min. The pyrolysis tube was cooled in an argon stream, and the black–silver–grey deposit in the silica boat was then analysed. The material was identified by X-ray powder diffraction and X-ray photoelectron spectroscopy as polycrystalline MnTe. No other crystalline phases were detected.

A similar procedure was used in the pyrolysis of the $[Mn(CO)_4(\mu\text{-}TeR)]_2$ complexes; the furnace temperature was 300°C for R = Me and 200°C for R = Et. Analysis of the pyrolysis residue by X-ray powder diffraction and X-ray photoelectron spectroscopy revealed Mn and Te, but no well defined MnTe phases.

RESULTS AND DISCUSSION

Insertion of Te *into* Mn—C *bond*

There are some examples of the direct insertion of chalcogens into transition metal to carbon bonds, and one of these is represented in eq. (1).[34]

$$(RC_5H_4)_2ZrR'_2 + 2E \longrightarrow (RC_5H_4)_2Zr(ER')_2$$

$$(R = H, Me;\ R' = Me, Ph;\ E = S, Se, Te) \quad (1)$$

The rate of insertion depends on the chalcogen, decreasing in the order S > Se > Te.

We attempted a similar insertion of tellurium into the manganese–carbon bond of $RMn(CO)_5$ ($R = Me$ or $PhCH_2$). The two reactants were stirred in hydrocarbon solvents at temperatures between 25–110°C. No reaction occurred at temperatures below about 100°C; above this temperature, the $RMn(CO)_5$ decomposed.

The use of $TePR_3$ compounds provides an alternative method of introducing tellurium into organometallic compounds. The phosphine tellurides are readily prepared by treating tellurium metal in toluene with an excess of the tertiary phosphine [eq. (2)].[35,36]

$$Te + PR_3 \rightleftharpoons TePR_3 \quad (2)$$

An excess of phosphine is needed to inhibit dissociation of the phosphine telluride. Steigerwald and Rice[35] have treated $Mn_2(CO)_{10}$ with two equivalents of $TePEt_3$ and obtained the dinuclear complex $[(Et_3P)_2(CO)_3Mn]_2(\mu-Te_2)$; presumably, this is formed by the sequential insertion of two tellurium atoms into the Mn—Mn bond. The need for excess phosphine results in the substitution of some carbonyls by triethylphosphine.

Transition metal–tellurium bonds are also formed when $Ni(COD)_2$ or $Co_2(CO)_8$ is treated with $TePEt_3$; the products obtained in these cases are large clusters of the type $(Et_3P)_8Ni_9Te_6$[37] and $(Et_3P)_6Co_6Te_8$.[38] These results encouraged us to attempt to insert Te into the Mn—C bond of $RMn(CO)_5$ complexes by reaction with $TePR_3$ compounds. Initially, the benzyl complex $PhCH_2Mn(CO)_5$ was treated with a toluene solution containing $TePEt_3$ and a 2.5 excess of PEt_3. Monitoring of the solution by infrared spectroscopy revealed the formation of some *cis*-$PhCH_2COMn(CO)_4(PEt_3)$.[39] The reaction was repeated under more forcing conditions (-refluxing toluene for 8 h), and this produced a dark red solution from which red crystals of $PhCH_2TeMn(CO)_3(PEt_3)_2$ were isolated in reasonable yield. Spectroscopic data (see experimental section) are consistent with a *meridional* -tricarbonyl, *trans*-bis(triethylphosphine) stereochemistry. In the NMR spectrum, the high frequency shift of the benzyl methylene resonance [δ 3.73; *cf.* δ 2.36 for the parent compound $PhCH_2Mn(CO)_5$] and the observation of ^{125}Te satellites demonstrate unequivocally that Te has been inserted into the Mn—CH_2 bond of $PhCH_2Mn(CO)_5$. The single resonance in the ^{31}P NMR spectrum indicates a *trans*-arrangement of the PEt_3 groups. Satisfactory elemental analyses were obtained.

This is the first report of Te insertion into a Mn—C bond and also the first example of a monomeric organomanganese complex with a Mn—Te σ-bond. A similar class of compounds has been reported for the chalcogen species $(RE)Mn(CO)_3(PMe_3)_2$ ($E = S, Se$; $R = H, SnMe_3$)[40,41] which were isolated from the reaction of $[Mn(CO)_4(\mu\text{-}ER)]_2$ with PMe_3. The geometry of the complex was established by an X-ray diffraction study. Each asymmetric unit in the crystal structure contains two crystallographically independent monomeric molecules. The molecular parameters for the two molecules are very similar, but the conformations of the ethyl groups about the phosphorus atoms are different. Figure 1 shows the molecular structure of molecule 2; the structure of molecule 1 was presented and discussed briefly in ref. 18. Atomic coordinates are given in Table 3 and selected bond distances and angles are presented in Table 4. The manganese atom is in a distorted octahedral environment; the *cis* L—Mn—L′ angles range from 80.2(1) to 97.8(1)° and the *trans* L—Mn—L′ angles from 167.8(2) to 176.5(2)°. The main distortion is a slight bending of the two carbonyls that are *cis* to the tellurium towards the tellurium atom. The Mn—C and Mn—P distances are typical of manganese carbonyl phosphine complexes.[35,42] Comparison of the Mn—Te bond length

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for the complex $PhCH_2TeMn(CO)_3(PEt_3)_2$ with ESD values in parentheses

	x	y	z	*U*(eq)
Te(1)	3000.1(3)	3565.4(2)	3584.3(2)	45.7(1)
Mn(1)	5509.0(6)	4043.5(4)	2872.3(3)	32.2(2)
P(1)	4121.6(11)	4304.3(8)	1974.3(5)	37.9(3)
P(2)	7066.0(11)	3889.3(8)	3742.5(5)	36.5(3)
O(1)	5730(5)	5989(3)	3394(2)	77(2)
O(2)	8138(4)	4409(3)	2034(2)	66(1)
O(3)	4675(4)	1973(2)	2612(2)	65(1)
C(1)	5658(5)	5246(3)	3180(2)	44(1)
C(2)	7101(5)	4280(3)	2361(2)	41(1)
C(3)	5003(5)	2767(3)	2709(2)	43(1)
C(4)	3189(5)	2344(4)	4150(3)	54(2)
C(5)	1740(5)	1940(3)	4467(2)	47(2)
C(6)	764(6)	1158(4)	4199(3)	65(2)
C(7)	−577(8)	786(6)	4498(4)	91(3)
C(8)	−1000(8)	1191(6)	5030(4)	87(3)
C(9)	−42(8)	1963(5)	5312(3)	85(3)
C(10)	1321(7)	2343(4)	5032(3)	71(2)
C(11)	2314(5)	4620(4)	2079(3)	57(2)
C(12)	2386(7)	5521(5)	2468(3)	77(3)
C(13)	5156(6)	5260(4)	1476(3)	57(2)
C(14)	4417(7)	5543(5)	873(3)	80(3)
C(15)	3537(6)	3313(4)	1377(3)	60(2)
C(16)	4799(8)	2986(5)	1044(3)	83(3)
C(17)	6586(5)	4286(3)	4558(2)	50(2)
C(18)	7579(8)	4211(5)	5134(3)	73(2)
C(19)	7308(6)	2699(4)	3879(3)	59(2)
C(20)	8123(7)	2323(4)	3312(3)	78(3)
C(21)	9012(5)	4554(4)	3666(3)	55(2)
C(22)	9242(6)	5619(4)	3675(3)	67(2)
Te(2)	2448.9(3)	8850.6(3)	1985.9(2)	51.2(1)
Mn(2)	−77.6(6)	8459.8(4)	1244.4(3)	31.7(2)
P(3)	−1279.5(12)	9318.0(8)	1918.9(5)	38.0(3)
P(4)	993.1(12)	7612.0(8)	504.5(5)	37.0(3)
O(4)	1242(5)	10215(3)	536(2)	67(1)
O(5)	−2837(4)	7887(3)	452(2)	65(1)
O(6)	−807(5)	6828(3)	2129(2)	67(1)
C(23)	743(5)	9535(3)	803(2)	42(1)
C(24)	−1748(5)	8127(3)	761(2)	41(1)
C(25)	−531(5)	7462(3)	1790(2)	43(1)
C(26)	1810(6)	8399(5)	2979(3)	63(2)
C(27)	3155(5)	8626(3)	3423(2)	45(1)
C(28)	3876(7)	9541(4)	3615(3)	63(2)
C(29)	5079(7)	9718(5)	4057(3)	76(2)
C(30)	5609(7)	8978(5)	4285(3)	80(3)
C(31)	4936(7)	8090(5)	4095(3)	73(2)
C(32)	3730(6)	7913(4)	3666(3)	57(2)
C(33)	−2521(6)	8638(4)	2529(3)	59(2)
C(34)	−3763(6)	7871(4)	2230(4)	78(2)
C(35)	−230(6)	10283(3)	2447(3)	56(2)
C(36)	734(7)	11110(4)	2106(4)	78(2)
C(37)	−2512(6)	9885(3)	1447(3)	52(2)
C(38)	−3305(6)	10526(4)	1826(3)	66(2)
C(39)	3015(5)	7843(4)	430(2)	52(2)
C(40)	3811(6)	8828(4)	234(3)	67(2)
C(41)	384(5)	7717(3)	−354(2)	47(2)
C(42)	974(7)	7159(4)	−886(3)	65(2)
C(43)	557(6)	6338(3)	627(3)	54(2)
C(44)	−1074(7)	5852(4)	525(3)	72(2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

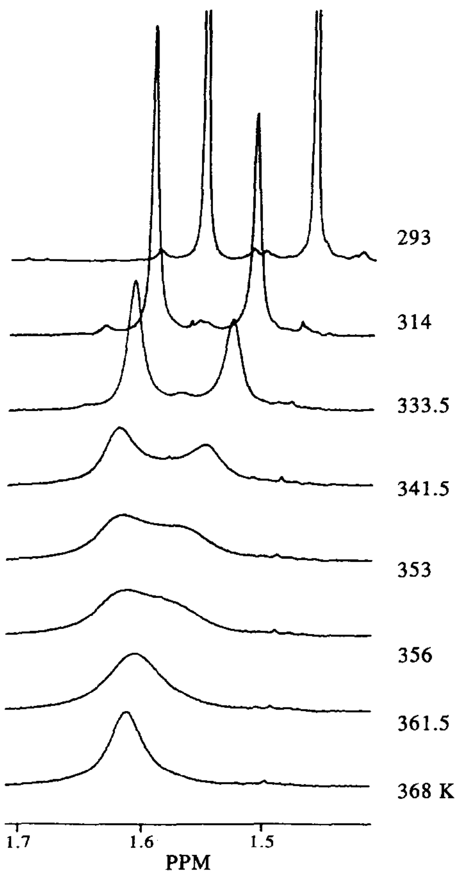


Fig. 1. The variable temperature ^1H NMR spectra of a solution of $[Mn(CO)_4(\mu\text{-}TeMe)]_2$ in d_8-toluene. The temperature (K) is shown to the right of each spectrum.

of *mer-trans*-$PhCH_2TeMn(CO)_3(PEt_3)_2$ with that of the dimeric compound $[(Et_3P)_2(CO)_3Mn]_2(\mu-Te_2)$[35] [2.7175(11)] shows them to be very similar.

In an attempt to obtain a complex of greater volatility, we modified the experimental procedure in two ways. First, we repeated the reaction but with a 1 : 1 ratio of $PhCH_2Mn(CO)_5$ and $TePEt_3$, and only a small excess of PEt_3. The aim of this experiment was to encourage the formation of $PhCH_2TeMn(CO)_4(PEt_3)$. Unfortunately, only *mer-trans*-$PhCH_2TeMn(CO)_3(PEt_3)_2$, unchanged $PhCH_2Mn(CO)_5$, and elemental Te could be isolated from the reaction mixture. Monitoring of the reaction by infrared spectroscopy provided no evidence of the formation of a tetracarbonyl species during the course of the reaction.

We also investigated the reaction of $TePMe_3$ with $PhCH_2Mn(CO)_5$ in the presence of excess PMe_3. This resulted in the formation of *mer-trans*-$PhCH_2$ $TeMn(CO)_3(PMe_3)_2$. Unfortunately, it was not possible to remove traces of impurities from this product, and it was isolated as a red oil which could not be crystallized. The infrared and ^1H NMR spectroscopic data (see experimental) are similar to those observed for the analogous PEt_3 complex. In contrast to the PEt_3 derivative, the mass spectrum of this complex did show a parent ion. Repetition of this reaction at a somewhat lower temperature (95–100°C) gave $PhCH_2Mn(CO)_3(PMe_3)_2$ rather than the Te-insertion product. Treatment of $PhCH_2Mn(CO)_3(PMe_3)_2$ in refluxing toluene with Te does give $PhCH_2TeMn(CO)_3(PMe_3)_2$. This, coupled with the earlier observation that Te does not insert directly into the Mn—C bond of $PhCH_2Mn(CO)_5$ in refluxing toluene, indicates that the formation of $PhCH_2TeMn(CO)_3(PR_3)_2$ complexes from $PhCH_2Mn(CO)_5$ occurs *via* the substituted intermediate $PhCH_2Mn(CO)_3(PR_3)_2$.

A related investigation with $MeMn(CO)_5$ was undertaken. Treatment of $MeMn(CO)_5$ with a stoichiometric amount of $TePEt_3$ in refuxing toluene (8 h) produces a dark red oil. Spectroscopic results (see experimental) indicate that this consists of a 2 : 1 mixture of the new compound *mer-trans*-$MeTeMn(CO)_3(PEt_3)_2$ and the known compound *mer-trans*-$MeMn(CO)_3(PEt_3)_2$.[43] The reaction was monitored by infrared spectroscopy, and $\nu(CO)$ stretches corresponding to the formation of *cis*-$MeCOMn(CO)_4(PEt_3)$, *cis*-$MeMn(CO)_4(PEt_3)$,[39] and a *meridional* tricarbonyl complex were observed in solution within a few hours. The $\nu(CO)$ stretches for the tetracarbonyl complexes disappeared after approximately 8 h. However, since the $\nu(CO)$ frequencies for *mer-trans*-$MeTeMn(CO)_3(PEt_3)_2$ and *mer-trans*-$MeMn(CO)_3(PEt_3)_2$ are very similar, it was impossible to determine the sequence in which these products are formed. However, in line with our comments above, we propose initial formation of $MeMn(CO)_4(PEt_3)$ or $MeCOMn(CO)_4(PEt_3)$, then $MeMn(CO)_3(PEt_3)_2$, followed by Te insertion. Prolonged reaction times result in decomposition of the insertion product and the deposition of elemental tellurium.

The low volatility of these compounds detracts from their possible usefulness in conventional MOCVD applications. Nonetheless, a small sample of *mer-trans*-$PhCH_2TeMn(CO)_3(PEt_3)_2$ was pyrolysed by direct insertion into a tube furnace at 300°C for 30 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. A qualitative analysis of the volatile by-products indicated the presence of PEt_3 and unidentified hydrocarbons; no volatile organo-tellurium residues were produced.

Table 4. Selected bond distances and bond angles for the complex $PhCH_2TeMn(CO)_3(PEt_3)_2$

Bond distances (Å)			
Molecule 1		Molecule 2	
Mn(1)—Te(1)	2.704(1)	Mn(2)—Te(2)	2.701(1)
Te(1)—C(4)	2.188(6)	Te(2)—C(26)	2.177(5)
Mn(1)—P(1)	2.307(1)	Mn(2)—P(4)	2.307(2)
Mn(1)—P(2)	2.315(1)	Mn(2)—P(3)	2.307(2)
Mn(1)—C(1)	1.829(5)	Mn(2)—C(23)	1.833(4)
Mn(1)—C(2)	1.781(4)	Mn(2)—C(24)	1.780(4)
Mn(1)—C(3)	1.836(5)	Mn(2)—C(25)	1.822(5)
C(1)—O(1)	1.148(6)	C(23)—O(4)	1.143(6)
C(2)—O(2)	1.154(5)	C(24)—O(5)	1.157(5)
C(3)—O(3)	1.141(6)	C(25)—O(6)	1.149(6)
Bond angles (deg).			
Molecule 1		Molecule 2	
Mn(1)—Te(1)—C(4)	106.0(1)	Mn(2)—Te(2)—C(26)	106.5(1)
Te(1)—Mn(1)—P(1)	89.8(1)	Te(2)—Mn(2)—P(4)	89.9(1)
Te(1)—Mn(1)—P(2)	94.3(1)	Te(2)—Mn(2)—P(3)	94.3(1)
Te(1)—Mn(1)—C(1)	86.2(1)	Te(2)—Mn(2)—C(23)	86.4(1)
Te(1)—Mn(1)—C(2)	175.4(1)	Te(2)—Mn(2)—C(24)	176.5(2)
Te(1)—Mn(1)—C(3)	80.2(1)	Te(2)—Mn(2)—C(25)	81.4(1)
P(1)—Mn(1)—P(2)	175.0(1)	P(3)—Mn(2)—P(4)	175.5(1)
P(1)—Mn(1)—C(1)	90.4(2)	P(4)—Mn(2)—C(23)	89.5(2)
P(2)—Mn(1)—C(1)	87.1(2)	P(3)—Mn(2)—C(23)	89.2(2)
P(1)—Mn(1)—C(2)	88.2(1)	P(4)—Mn(2)—C(24)	88.2(2)
P(2)—Mn(1)—C(2)	87.9(1)	P(3)—Mn(2)—C(24)	87.7(2)
P(1)—Mn(1)—C(3)	91.8(1)	P(4)—Mn(2)—C(25)	91.0(2)
P(2)—Mn(1)—C(3)	91.7(1)	P(3)—Mn(2)—C(25)	91.2(2)
C(1)—Mn(1)—C(2)	97.8(2)	C(23)—Mn(2)—C(24)	96.6(2)
C(1)—Mn(1)—C(3)	166.2(2)	C(23)—Mn(2)—C(25)	167.8(2)
C(2)—Mn(1)—C(3)	95.8(2)	C(24)—Mn(2)—C(25)	95.6(2)

Metathesis involving $BrMn(CO)_5$ *and* RTeLi

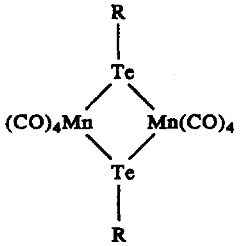
In principle, the reactions between $BrMn(CO)_5$ and RTeLi should give $RTeMn(CO)_5$. We have investigated several reactions of this type [R = Me, Et, Pr^i, CH_2SiMe_3, Ph, and $Si(SiMe_3)_3$] and find that the only isolable manganese product is the dinuclear complex $[Mn(CO)_4(\mu\text{-}TeR)]_2$. Presumably, this is formed *via* $RTeMn(CO)_5$ with the subsequent loss of CO [eq.(3)].

$$BrMn(CO)_5 + RTeLi \longrightarrow LiBr + \{RTeMn(CO)_5\}$$

$$\longrightarrow 1/2\,[Mn(CO)_4(\mu - TeR)]_2 + CO \quad (3)$$

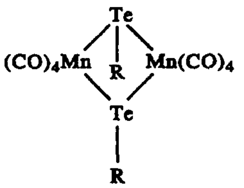
The complex $[Mn(CO)_4(\mu - TePh)]_2$ has been prepared before from the reaction between $Mn_2(CO)_{10}$ and $TePh_2$,[11] and the analogous complexes with $Te(SnMe_3)$ and TeH bridging groups are also known.[6] The R = $SnMe_3$ derivative was formed from $Mn(CO)_5Br$ and $(Me_3Sn)_2Te$, and treatment of this with HCl yielded the μ-TeH complex. We had hoped that use of the very bulky $Si(SiMe_3)_3$ group would inhibit formation of the dimeric μ-TeR complex. Although the yield of the dimeric complex was low, we found no evidence for a monomeric species of formula $(Me_3Si)_3SiTeMn(CO)_5$. There may be some inhibition of dimer formation, but clearly the monomeric intermediate is inherently unstable and finds other pathways for decomposition.

The infrared and NMR spectra of the $[Mn(CO)_4(\mu\text{-}TeR)]_2$ complexes show some interesting features. In the infrared spectrum, we observe three bands in the terminal carbonyl region. This is one less than would be expected for an octahedral *cis*-disubstituted tetracarbonyl manganese centre. It corresponds to the reported spectra[6] for the oligomeric tricarbonyl species $[Mn(CO)_3(\mu\text{-}ER)]_n$, E = S or Se. However, mass spectral data on our tellurium complexes strongly supports the tetracarbonyl formulation. We therefore attribute the observed infrared spectrum to insufficient resolution of some of the carbonyl stretching frequencies. Previous investigations[6] on the selenium complex $[Mn(CO)_4(\mu\text{-}SeMe)]_2$ provide infrared evidence for the existence of two isomers with different orientations of the alkyl group and the lone pair on the selenium atoms. However, the ^{1}H NMR spectrum of this complex revealed only one methyl environment at room temperature. Our investigation of the ^{1}H, ^{13}C, and ^{125}Te NMR spectra of $[Mn(CO)_4(\mu\text{-}TeMe)]_2$ clearly distinguishes two TeMe environments, and this is consistent with the co-existence of two conformers in solution. The isomers of C_{2h} and C_{2v} symmetry are shown in (1) and (2), respectively. The ratio of the isomers in solution at 20°C is about 5 : 4. Variable temperature ^{1}H NMR spectroscopy on solutions of $[Mn(CO)_4(\mu\text{-}TeMe)]_2$ in toluene shows convergence of the two methyl resonances at 361 K and emergence of a single peak at slightly higher temperatures (see Fig. 2). Similar effects were observed for $[Mn(CO)_4(\mu\text{-}TeCH_2SiMe_3)]_2$ with convergence of the trimethylsilyl signals at 343 K. In the ^{125}Te NMR spectrum of this complex, only one Te signal was evident. NMR spectroscopic data for the other alkyltellurato complexes $[Mn(CO)_4(\mu\text{-}TeR)]_2$ (R = Et, Pr^{i}) are less complete, but again there is evidence for two isomers. However, only one Te signal is evident in the ^{125}Te NMR spectra of $[Mn(CO)_4(\mu\text{-}TeR)]_2$ [R = Si(SiMe$_3$)$_3$, Ph], indicating the presence of just one stable isomer, or the rapid interconversion of different configurations [unlikely for R = Si(SiMe$_3$)$_3$], or accidental degeneracy of the resonances.



Anti

(1)



Syn

(2)

Examination of the mass spectra of the complexes $[Mn(CO)_4(\mu\text{-}TeR)]_2$ indicates that the initial fragmentation is a stepwise loss of eight carbonyls to leave the $[Mn_2(TeR)_2]$ skeleton (see Table 1). In most cases, this fragments further to form Mn_2Te_2, $MnTe_2$, Mn_2Te, MnTe and Mn. Formation of the manganese tellurides is an encouraging sign if these complexes were able to be used in MOCVD applications. Vapour pressure measurements indicated that these complexes had very low vapour pressures. The methyltellurato complex $[Mn(CO)_4(\mu\text{-}TeMe)]_2$ was the most volatile, but we determined a vapour pressure of only 1mm Hg at 128°C. Pyrolyses of the complexes $[Mn(CO)_4(\mu\text{-}TeMe)]_2$ and $[Mn(CO)_4(\mu\text{-}TeEt)]_2$ were carried out at 300°C and 200°C, respectively in a stream of hydrogen. Analysis of the deposit showed that it contained MnTe.

Possible alternative routes to $RTeMn(CO)_3(PR'_3)_2$

It seemed reasonable to expect that treatment of $[Mn(CO)_4(\mu\text{-}TeR)]_2$ complexes with tertiary phosphines would result in bridge cleavage to give $RTeMn(CO)_4(PR_3')$ or $RTeMn(CO)_3(PR'_3)_2$. The reaction of $[Mn(CO)_4(\mu\text{-}TeMe)]_2$ with PEt_3 was monitored by ^{1}H NMR spectroscopy. There was evidence of the formation of $MeTeMn(CO)_3(PEt_3)_2$, but the reaction was exceedingly slow at room temperature. On warming the reaction mixture, the rate of disappearance of $[Mn(CO)_4(\mu\text{-}TeMe)]_2$ was accelerated but the formation of a range of products was indicated. Similar reactions between $[Mn(CO)_4(\mu\text{-}TeCH_2SiMe_3)]_2$ and PEt_3 also gave a range of products.

Treatment of $BrMn(CO)_3(PR'_3)_2$ with LiTeR′ provides another possible route to the complexes $RTeMn(CO)_3(PR'_3)_2$. The reaction between $BrMn(CO)_3(PEt_3)_2$ and LiTeMe did give some $MeTeMn(CO)_3(PEt_3)_2$ which could be isolated as a red solid after chromatography on alumina. NMR spectroscopy on solutions of the red solid indicated that the complex decomposed slowly in solution even when protected from the air. As a consequence, it proved impossible to obtain analytically pure samples of this complex by recrystallization or chromatography.

The formation and pyrolysis of $MeHgMn(CO)_5$

The complex $MeHgMn(CO)_5$ has been prepared previously from $Me_3SnMn(CO)_5$ and MeHgCl. We found it more convenient to prepare the complex from $Mn_2(CO)_{10}$ by initial cleavage with sodium–potassium alloy and subsequent treatment of the $[Mn(CO)_5]^-$ anion with MeHgCl. In each case, reasonable yields of $MeHgMn(CO)_5$ are obtained only if side-reactions are suppressed. One such reaction that yields the insoluble complex $ClHgMn(CO)_5$ is shown in eq. (4).

$$MeHgMn(CO)_5 + MeHgCl \longrightarrow ClHgMn(CO)_5 + Me_2Hg \quad (4)$$

In the mass spectrum of $MeHgMn(CO)_5$, the peak of highest m/z value was found to be $Hg[Mn(CO)_5]_2$. This indicates that $MeHgMn(CO)_5$ disproportionates in the gas phase according to eq. (5)

$$2\,MeHgMn(CO)_5 \rightleftharpoons Hg[Mn(CO)_5]_2 + Me_2Hg \quad (5)$$

$MeHgMn(CO)_5$ is sufficiently volatile to be sub-

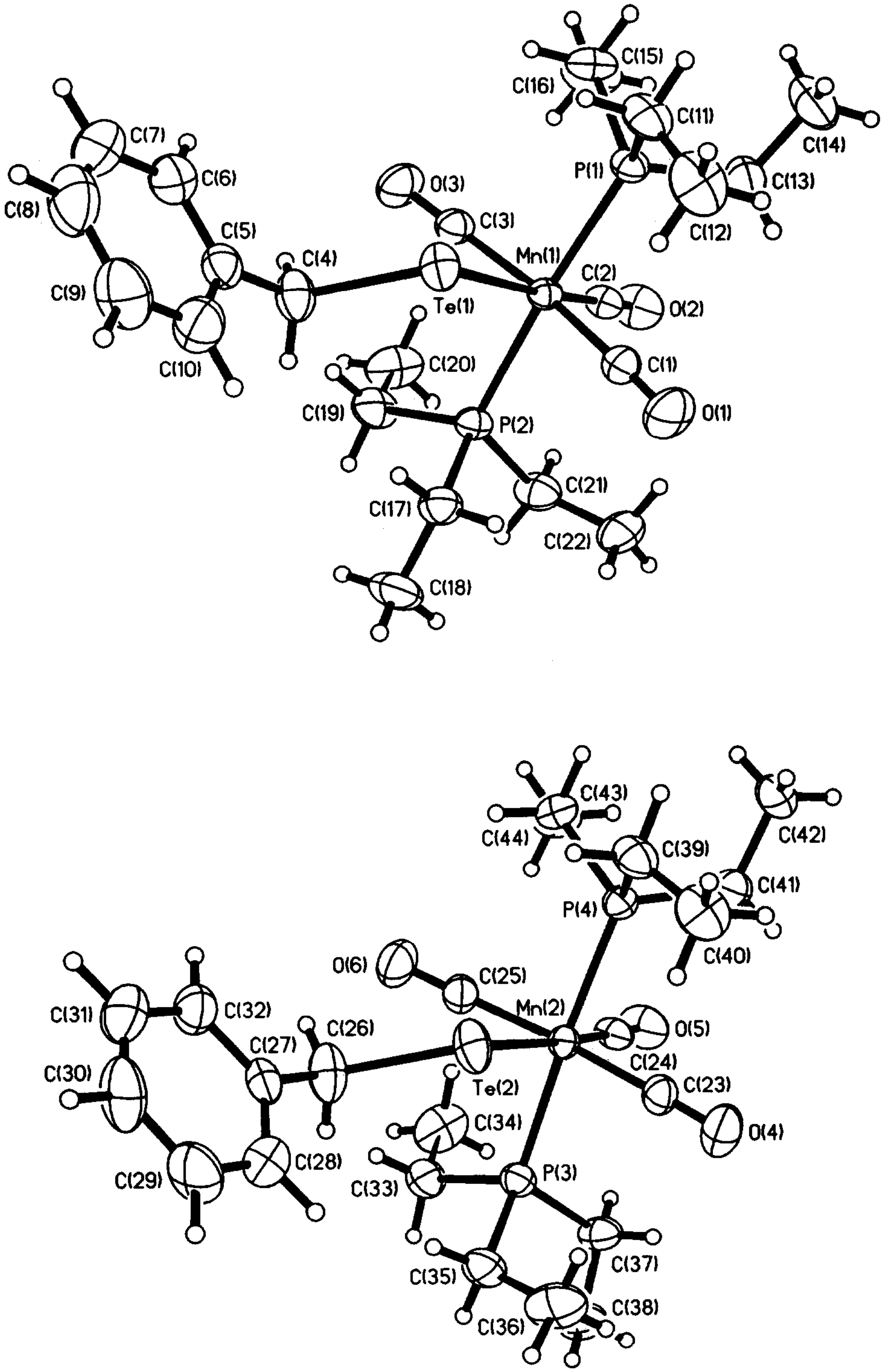


Fig. 2. A view of the molecular structure of *mer-trans*-PhCH$_2$Mn(CO)$_3$(PEt$_3$)$_2$. Molecule 2, transformed through $\bar{x}$, $\bar{y}$, $\bar{z}$ for easy comparison with molecule 1.

limed at 45°C under vacuum. We determined that its vapour pressure is 1 mm Hg at 77°C. Pyrolysis of the compound at 300°C in a hydrogen stream produced a metal film which was found to be pure manganese by EDX analysis.

CONCLUSIONS

Although Te will not insert directly into the Mn—C bond of the alkyl- or aryl-manganese carbonyl complexes RMn(CO)$_5$, complexes incorporating the RTeMn unit have been prepared by several other routes. Products of formula $RTeMn(CO)_3(PR'_3)_2$ and $[Mn(CO)_4(\mu\text{-}TeR)]_2$ have been obtained. These complexes deposit MnTe when heated in a hydrogen stream, but their very low volatilities limit their usefulness for conventional MOCVD applications. The alkylmercury complex $MeHgMn(CO)_5$ can be obtained, but it disproportionates readily. When heated in a hydrogen stream, a mercury-free deposit of manganese is obtained. The thermal decomposition of the manganese–tellurium complexes establishes that single source compounds of this type may be useful in MOCVD applications, but complexes of greater volatility will need to be discovered.

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