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FULL PAPER

Transition metal complexes of 1,3-dihydrobenzo[*c*]tellurophene: synthesis, spectroscopy and crystal structures

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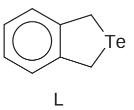
Reaction of 1,3-dihydrobenzo[*c*]tellurophene (L) with $[Cu(MeCN)_4]PF_6$ or $AgBF_4$ yielded $[CuL_4]PF_6$ and $[AgL_4]BF_4$ respectively, which adopt distorted tetrahedral structures at the metal centre, with the tellurophene ligated *via* a Te-based lone pair, Cu–Te 2.587(2)–2.596(2) Å; Ag–Te 2.7676(7)–2.8104(8) Å. With palladium(II) and platinum(II) chlorides the neutral species $[PdCl_2L_2]$ and $[PtCl_2L_2]$ were formed readily. Infrared, ^{125}Te-{^{1}H} and ^{195}Pt NMR spectroscopic studies showed that the former is the *trans* isomer, whereas the latter is the *cis* isomer. The ^{125}Te-{^{1}H} NMR spectra showed that in solution $[RhCl_3L_3]$ is a mixture of *mer* and *fac* isomers in approximately 3:2 ratio, whereas $RuCl_3$ reacted with L in EtOH and hypophosphorous acid to give *trans*-$[RuCl_2L_4]$ exclusively. The carbonyl derivatives *fac*-$[MnCl(CO)_3L_2]$, $[Mo(CO)_5L]$, *cis*-$[Mo(CO)_4L_2]$ and *fac*-$[Mo(CO)_3L_3]$ have also been characterised through IR spectroscopy, ^{1}H, ^{13}C-{^{1}H}, ^{55}Mn, ^{95}Mo and ^{125}Te-{^{1}H} NMR spectroscopy. For the molybdenum species $\delta(^{95}\mathrm{Mo})$ and $\delta(^{125}\mathrm{Te}\text{-}\{^1\mathrm{H}\})$ shift to high frequency with increasing substitution of the carbonyl ligands. The crystal structure of $[Mo(CO)_4L_2]$ confirms the *cis* geometry and shows the Mo–CO bond lengths *trans* to L are about 0.10 Å shorter than those *trans* to CO. The ^{1}H NMR spectra of these complexes typically reveal AB quartets for the methylene protons, indicative of co-ordination through a Te-based lone pair in each case. The ^{125}Te-{^{1}H} NMR studies reveal a high frequency co-ordination shift except for the copper and silver species which show $\delta(^{125}\mathrm{Te}\text{-}\{^1\mathrm{H}\})$ to low frequency of that for free L.

Introduction

We have recently initiated a programme aimed at the preparation of cyclic telluroethers. During the course of this work we isolated 1,3-dihydrobenzo[*c*]tellurophene, L, as an unexpected product of one of our reactions. This compound has previously been prepared by treatment of *a*,*a*′-dichloro-*o*-xylene with Te and NaI in 2-methoxyethanol to give 2,2-diiodo-1,3-dihydrobenzo[*c*]tellurophene.[1] Subsequent treatment of this with $NaBH_4$ in MeOH gives L.[2] There is interest in deducing whether tellurophenes such as L bind to metal centres *via* the arene unit or *via* a lone pair on the Te atom. However, a survey of the literature revealed that reported compounds of L are limited to two organorhodium examples.[3,4] We have therefore investigated the co-ordinating properties of L with a variety of metal ions across the transition series, including low-valent carbonyl derivatives of Mo^0 and Mn^I, platinum group metal halides and Group 11 centres. We report here the results of this study, including characterisation of the products by IR and multinuclear NMR spectroscopy (^{1}H, ^{13}C-{^{1}H}, ^{55}Mn, ^{63}Cu, ^{95}Mo, ^{109}Ag, ^{125}Te-{^{1}H} and ^{195}Pt-{^{1}H}), and the single crystal structures of $[CuL_4]PF_6\cdot MeNO_2$, $[AgL_4]BF_4\cdot MeNO_2$ and $[Mo(CO)_4L_2]$.



L

Results and discussion

1,3-Dihydrobenzo[*c*]tellurophene (L) was isolated in low yield as a by-product of an attempted preparation of 2,11-ditellura[3.3]orthocyclophane. The procedure involved treatment of *a*,*a*′-dichloro-*o*-xylene with two molar equivalents of KTeCN in dmso solution. The product isolated from this reaction was very unstable, however a solution of this and a solution of *a*,*a*′-dichloro-*o*-xylene in thf–EtOH were simultaneously added dropwise to a suspension of $NaBH_4$ in thf–EtOH over *ca.* 20 h. Following usual work-up, the resulting solid was purified by flash chromatography on silica with light petroleum as eluent, giving a small amount of yellow solid. Proton, ^{13}C-{^{1}H} and ^{125}Te-{^{1}H} NMR spectroscopy identified the product as L, although a FAB mass spectrum of the crude product showed peaks with the correct isotopic distribution for L (*m*/*z* 234) as well as low intensity peaks consistent with the 2,11-ditellura[3.3]orthocyclophane (*m*/*z* 462), the original target compound. We are not certain at which point in the reaction L is produced, but it is known that the analogous selenium compound, 2,11-diselena[3.3]orthocyclophane, is converted into 1,3-dihydrobenzo[*c*]selenophene in high yield when heated to 600 °C,[5] and since telluroethers are known to be susceptible to elimination reactions even at room temperature it is possible that a similar process occurred in the tellurium reaction. Further work is underway to establish if this is the case. Compound L was also synthesized by the literature method[1,2] to establish with certainty that it was the product of our reaction.

A 4:1 ratio of L and either $[Cu(MeCN)_4]PF_6$ or $AgBF_4$ reacts rapidly in dry, degassed CH_2Cl_2 solution at room temperature to afford $[CuL_4]PF_6$ and $[AgL_4]BF_4$ respectively in high yield as cream coloured solids. The silver derivative is rather photosensitive, and therefore the reaction was conducted in a foil-wrapped vessel and the product stored similarly. The IR spectra show peaks consistent with the presence of L and free PF_6^- or BF_4^- as expected, and in the case of the copper complex there are no peaks associated with either free or co-ordinated MeCN. The electrospray mass spectrum of that complex shows peaks with the correct isotopic distributions corresponding to $[CuL_2(MeCN)]^+$ and $[CuL_2]^+$. However, since the spectrum was recorded in MeCN solvent, the inclusion of MeCN in the products observed is likely to arise from ligand exchange during the experiment (also see IR discussion above).

Multinuclear NMR data for all of the new complexes are

Table 1 NMR Spectroscopic data[a]

Compound	$\delta(^{125}Te-\{^1H\})$	$\delta(^{95}Mo)$
L	374	
$[CuL_4]PF_6$	278	
$[AgL_4]BF_4$	230	
trans-$[PdCl_2L_2]$[b]	Unstable	
cis-$[PtCl_2L_2]$[b]	588	
fac-$[RhCl_3L_3]$	592	
mer-$[RhCl_3L_3]$	581, 620 (1:2)	
trans-$[RuCl_2L_4]$	596	
fac-$[MnCl(CO)_3L_2]$	472	
$[Mo(CO)_5L]$	418	−1731
cis-$[Mo(CO)_4L_2]$	468	−1550
fac-$[Mo(CO)_3L_3]$	532	−1320

[a] Spectra were recorded in CH_2Cl_2–$CDCl_3$ unless otherwise stated. [b] Solution in dmf.

Table 2 Selected bond lengths (Å) and angles (°) for $[CuL_4]^+$

Te(1)–Cu(1)	2.596(2)	Te(1)–C(11)	2.14(1)
Te(1)–C(18)	2.15(1)	Te(2)–Cu(1)	2.596(2)
Te(2)–C(21)	2.18(1)	Te(2)–C(28)	2.16(1)
Te(3)–Cu(1)	2.587(2)	Te(3)–C(31)	2.14(1)
Te(3)–C(38)	2.16(1)	Te(4)–Cu(1)	2.590(2)
Te(4)–C(41)	2.17(2)	Te(4)–C(48)	2.17(1)
Cu(1)–Te(1)–C(11)	99.3(4)	Cu(1)–Te(1)–C(18)	101.5(4)
C(11)–Te(1)–C(18)	83.0(6)	Cu(1)–Te(2)–C(21)	102.9(4)
Cu(1)–Te(2)–C(28)	105.0(4)	C(21)–Te(2)–C(28)	83.5(5)
Cu(1)–Te(3)–C(31)	92.9(4)	Cu(1)–Te(3)–C(38)	106.2(4)
C(31)–Te(3)–C(38)	85.1(5)	Cu(1)–Te(4)–C(41)	101.7(4)
Cu(1)–Te(4)–C(48)	97.6(3)	C(41)–Te(4)–C(48)	83.1(5)
Te(1)–Cu(1)–Te(2)	109.90(7)	Te(1)–Cu(1)–Te(3)	107.51(7)
Te(1)–Cu(1)–Te(4)	109.65(7)	Te(2)–Cu(1)–Te(3)	106.51(7)
Te(2)–Cu(1)–Te(4)	112.35(7)	Te(3)–Cu(1)–Te(4)	110.77(7)

presented in Table 1. The ^1H NMR spectra typically show AB quartets for the methylene protons. Indeed this is true for all of the complexes of L described in this work except for $[CuL_4]PF_6$ and $[AgL_4]BF_4$ which show singlets for the methylene groups, indicative of significant ligand dissociation in solution, as might be expected for labile d^{10} centres. The $^{125}Te-\{^1H\}$ NMR spectra of $[CuL_4]PF_6$ and $[AgL_4]BF_4$ each show a singlet to low frequency of free L (δ 374). We have observed similar low frequency shifts for other complexes of Cu^I and Ag^I, $[M(L–L)_2]^+$, where L–L is a bidentate selenoether or telluroether ligand.[6]

The complex $[CuL_4]PF_6$ shows no ^{63}Cu NMR resonance at room temperature, although on addition of free L a resonance appears at δ −28 ($w_{\frac{1}{2}}$ *ca.* 1500 Hz). This contrasts with $[Cu(TeMe_2)_4]^+$ which showed a broad signal at room temperature which sharpened upon addition of $TeMe_2$,[7] indicating that the latter is slightly less dissociated in solution. In view of the large quadrupole moment associated with ^{63}Cu, copper resonances tend to be seen only for species with near cubic symmetry. Therefore, in the presence of free L the near tetrahedral $[CuL_4]^+$ species is dominant in solution.

At room temperature $[AgL_4]BF_4$ shows a sharp ^{109}Ag NMR resonance at δ +1030, consistent with tetrahedral $[AgL_4]^+$ dominating in solution. This compares well with $[Ag(MeTeCH_2CH_2CH_2TeMe)_2]^+$ which shows $\delta(^{109}Ag)$ +1053.[6]

The geometry adopted by the copper(I) complex was established by a crystal structure determination which shows (Fig. 1, Table 2) a slightly distorted tetrahedral arrangement of the four telluroethers around the central Cu, giving Cu–Te(1) 2.596(2), Cu–Te(2) 2.596(2), Cu–Te(3) 2.587(2), Cu–Te(4) 2.590(2) Å. The angles subtended at Cu lie within the range 106.51(7)–112.35(7)°. The Cu–Te bond distances are slightly longer than those observed for $[Cu\{o-C_6H_4(TeMe)_2\}_2]^+$: 2.5299(8) and 2.5598(7) Å.[6]

Table 3 Selected bond lengths (Å) and angles for $[AgL_4]^+$

Te(1)–Ag(1)	2.773(1)	Te(1)–C(11)	2.160(7)
Te(1)–C(18)	2.143(8)	Te(2)–Ag(1)	2.8104(8)
Te(2)–C(21)	2.146(8)	Te(2)–C(28)	2.146(8)
Te(3)–Ag(1)	2.8068(9)	Te(3)–C(31)	2.154(7)
Te(3)–C(38)	2.149(8)	Te(4)–Ag(1)	2.7676(7)
Te(4)–C(41)	2.143(7)	Te(4)–C(48)	2.154(8)
Ag(1)–Te(1)–C(11)	101.9(2)	Ag(1)–Te(1)–C(18)	99.8(2)
C(11)–Te(1)–C(18)	84.2(3)	Ag(1)–Te(2)–C(21)	98.1(2)
Ag(1)–Te(2)–C(28)	94.9(2)	C(21)–Te(2)–C(28)	82.9(3)
Ag(1)–Te(3)–C(31)	89.7(2)	Ag(1)–Te(3)–C(38)	102.9(2)
C(31)–Te(3)–C(38)	84.0(3)	Ag(1)–Te(4)–C(41)	98.1(2)
Ag(1)–Te(4)–C(48)	94.4(2)	C(41)–Te(4)–C(48)	84.7(3)
Te(1)–Ag(1)–Te(2)	107.05(2)	Te(1)–Ag(1)–Te(3)	107.22(3)
Te(1)–Ag(1)–Te(4)	118.07(3)	Te(2)–Ag(1)–Te(3)	103.34(2)
Te(2)–Ag(1)–Te(4)	111.42(2)	Te(3)–Ag(1)–Te(4)	108.67(3)

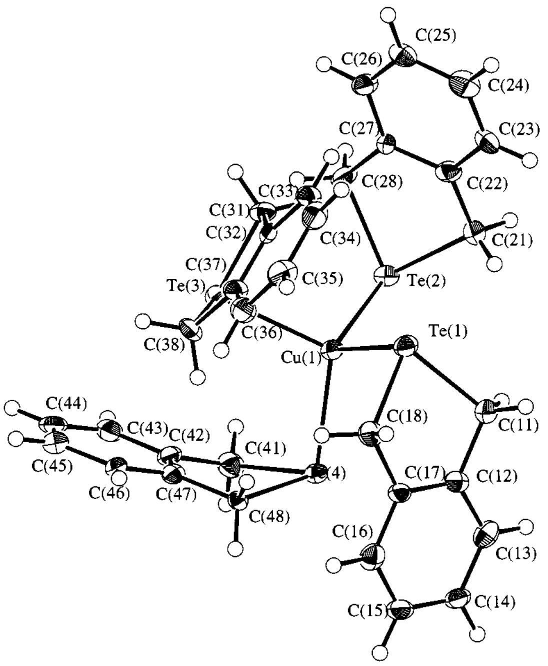


Fig. 1 View of the structure of $[CuL_4]^+$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

The silver(I) species $[AgL_4]^+$ (Fig. 2, Table 3) shows a very similar structural arrangement with Ag–Te(1) 2.773(1), Ag–Te(2) 2.8104(8), Ag–Te(3) 2.8068(9), Ag–Te(4) 2.7676(7) Å, and Te–Ag–Te angles in the range 103.34(2)–118.07(3)°. The increase in M–Te distance of approximately 0.18 Å is consistent with the increase in ionic radius from Cu^I *vs.* Ag^I. The only other silver(I) telluroether structure which has been reported is that of $[\{Ag(MeTeCH_2CH_2CH_2TeMe)_2\}_n][BF_4]_n$ which adopts an infinite polymeric structure, with d(Ag–Te) = 2.789(2), 2.785(2), 2.837(2) and 2.820(2) Å.[8] These distances are very similar to the Ag–Te distances in $[AgL_4]^+$.

We found that L is a sensitive compound which decomposes readily when stored at room temperature and in the presence of O_2. We were able to circumvent this problem by storing L as its copper(I) complex, $[CuL_4]PF_6$. This is a convenient synthon for other complexes of L through transmetallation using a less labile centre. Thus, the neutral metal(II) species $[PdCl_2L_2]$ and $[PtCl_2L_2]$ are readily prepared either by direct reaction of L with $[PdCl_2(MeCN)_2]$ or $PtCl_2$ respectively, or by transmetallation using $[CuL_4]PF_6$ and either $PdCl_2$ or $PtCl_2$ respectively in MeCN. The products are stable as solids, although both are unstable in MeCN, $MeNO_2$ or dmf, the palladium species in particular rapidly turning black, and this hindered our attempts to obtain $^{125}Te-\{^1H\}$ NMR data. The IR spectrum of $[PdCl_2L_2]$ shows a single Pd–Cl stretching vibration at 349 cm^{-1}, indicative of the *trans* isomer. This contrasts with the spectrum of $[PtCl_2L_2]$ which shows two peaks at 307 and 283 cm^{-1}, suggest-

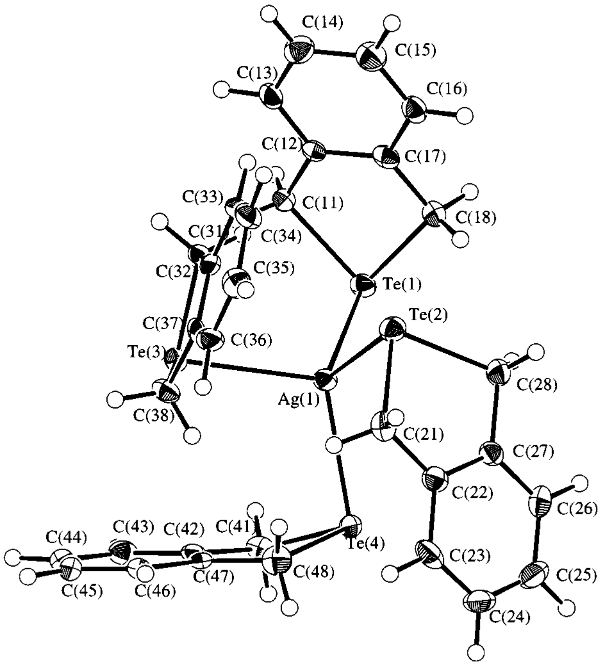


Fig. 2 View of the structure of $[AgL_4]^+$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

ing that this species is the *cis* isomer. Similar behaviour has been observed for dichlorobis(telluracyclopentane)metal complexes: ν(Pd–Cl) 333; ν(Pt–Cl) 299, 282 cm^{-1}.[9] Both the ^{125}Te-{^{1}H} and ^{195}Pt NMR spectra of $[PtCl_2L_2]$ show singlets (with satellites), also indicative of a single isomer in solution. The ^{125}Te-{^{1}H} shift is 214 ppm to high frequency of free L, contrasting with the situation for the copper(I) and silver(I) derivatives discussed above. The ^{195}Pt NMR shift of δ −4296 and the magnitude of the $^1J_{PtTe}$ coupling constant of 660 Hz are also indicative of a *cis*-dichloro complex.[9–11] Dichlorobis(telluracyclopentane)platinum exists in solution as a mixture of *cis* and *trans* isomers [*trans*, δ(^{195}Pt) −3715, $^1J_{PtTe} = 321$; *cis*, δ(^{195}Pt) −4251, $^1J_{PtTe} = 665$ Hz].[9]

Treatment of $RhCl_3{\cdot}3H_2O$ with three molar equivalents of L in EtOH yields the neutral rhodium(III) complex $[RhCl_3L_3]$ as an orange solid. This formulation is confirmed by IR and ^{1}H NMR spectroscopy and microanalytical data. The IR spectrum shows several peaks in the range 200–400 cm^{-1} attributed to Rh–Cl stretching vibrations. Evidence for the geometric isomers present comes from the ^{125}Te-{^{1}H} NMR spectrum which shows three doublets to high frequency of free L; the one at δ 592 is attributed to the *fac* isomer, with $^1J_{RhTe} = 90$ Hz. There are then two doublets at δ 581 and 620, both with $^1J_{RhTe} = 70$ Hz, and with relative intensities 1 : 2. These are ascribed to the *mer* isomer. The coupling constants are in line with those observed for *fac*- and *mer*-trichlorotris(tellurocyclopentane)-rhodium.[9] The *fac* and *mer* isomers are present in solution in an approximately 2 : 3 ratio, and since isomerisation is expected to be slow for a low spin d^6 metal centre it is likely that this represents the composition of the solid. Two rhodium(III) complexes of L have been described previously, $[Rh(Cp^*)L][CF_3SO_3]_2$ and $[Rh(Cp^*)Cl_2L]$, and the $^1J_{RhTe}$ coupling constants observed for these (65.9 and 108 Hz respectively) are comparable to those for our rhodium(III) species. Some related rhodium(III) complexes involving dibenzotellurophene have also been reported.[3,4]

The yellow-brown ruthenium(II) compound $[RuCl_2L_4]$ is generated through reaction of $RuCl_3$ with L in EtOH solution in the presence of hypophosphorous acid (H_3PO_2). The ^{125}Te-{^{1}H} NMR spectrum of this species shows a single resonance to high frequency of free L, confirming the product to be the *trans*-dichloro isomer exclusively in solution. The UV/VIS spectra (dmf solution) recorded for these platinum group metal complexes are typical of square planar Pd^{II} and Pt^{II} and octahedral Ru^{II} and Rh^{III}.[9–12]

We have recently shown that bidentate thio-, seleno- and telluro-ethers (L–L) react readily with $[MnCl(CO)_5]$ to yield the neutral manganese(I) compounds $[MnCl(CO)_3(L–L)]$, which exist both in solution and in the solid state as *fac*-tricarbonyl derivatives. Manganese-55 NMR and solution IR studies on these species have provided strong evidence for an increase in σ donation along the series S < Se < Te, consistent with theoretical predictions.[13] The compound $[MnCl(CO)_5]$ also reacts with two molar equivalents of the monodentate tellurophene L to yield *fac*-$[MnCl(CO)_3L_2]$. The solution IR spectrum ($CHCl_3$) shows three strong CO stretching vibrations as expected for a molecule with local C_s symmetry, and the positions of these bands (2018, 1942 and 1903 cm^{-1}) are in accord with those for *fac*-$[MnCl(CO)_3$(ditelluroether)] [ditelluroether = $MeTe(CH_2)_3TeMe$, $PhTe(CH_2)_3TePh$ or *o*-$C_6H_4(TeMe)_2$].[13] The ^{125}Te-{^{1}H} NMR spectrum shows a high frequency co-ordination shift and a single tellurium environment is consistent with this geometry. The ^{55}Mn NMR spectrum shows a broad resonance at δ −600 ($w_{\frac{1}{2}}$ *ca.* 2200 Hz). This is typical of a manganese(I) species with the formula *fac*-$[MnCl(CO)_3L_2]$. Thus for example δ(^{55}Mn) for *fac*-$[MnCl(CO)_3(TeMe_2)_2]$ occurs at −637 ($w_{\frac{1}{2}}$ *ca.* 1600).[13]

Crystals of $[MnCl(CO)_3L_2]$ were also obtained by cooling (5 °C) a solution of the complex in $MeNO_2$, although the crystal quality, and hence the data quality, were rather poor. The donor set at Mn^I was identified, but some of the C atoms associated with the tellurophene were poorly located, and the arene rings distorted from planarity. A detailed discussion is therefore not appropriate, although it was established that the Mn^I is octahedrally co-ordinated through three mutually *fac* carbonyls, a Cl and two telluroethers, as shown in solution by NMR and IR spectroscopy.

The mono- and di-substituted molybdenum(0) carbonyl species $[Mo(CO)_5L]$ and $[Mo(CO)_4L_2]$, were prepared by treatment of $[Mo(CO)_5(thf)]$ and $[Mo(CO)_4(nbd)]$ respectively with L. The geometries were confirmed as C_{4v} and C_{2v} respectively by IR spectroscopy. Treatment of $[Mo(CO)_3(MeCN)_3]$ with three molar equivalents of L gave the trisubstituted analogue *fac*-$[Mo(CO)_3L_3]$, although spectroscopic studies revealed that this material was contaminated with some of the disubstituted derivative. However the ^{125}Te-{^{1}H} and ^{95}Mo NMR shifts of the *fac* isomer were easily identified. Moreover, this series of compounds allows us to determine the trends in δ(^{125}Te-{^{1}H}) and δ(^{95}Mo) upon sequentially replacing a CO ligand by L at Mo^0. Thus, δ(^{95}Mo) shifts to high frequency by approximately 200 ppm each time a CO ligand is replaced by L {δ(^{95}Mo) for $[Mo(CO)_6]$ −1856[14]}. This is the same trend seen for molybdenum carbonyl compounds involving other ligands such as phosphines and thioethers, and reflects the increasing electron density on Mo^0; δ(^{125}Te-{^{1}H}) also shifts in the same sense.

A search of the Cambridge Crystallographic Database revealed that there are no structurally characterised examples of molybdenum carbonyl telluroethers. A single crystal structure determination on $[Mo(CO)_4L_2]$ (Fig. 3, Table 4) confirms that the telluroethers occupy mutually *cis* positions in the distorted octahedral molecule, with Mo–Te(1) 2.814(1), Mo–Te(2) 2.820(2), Mo–C(1) 1.96(1), Mo–C(2) 2.05(1), Mo–C(3) 1.95(1), Mo–C(4) 2.04(1) Å. Thus, the Mo–CO distances *trans* to the telluroether ligands are approximately 0.10 Å shorter than those *trans* to other CO ligands. This trend is also seen for a range of *cis*-$[Mo(CO)_4(PR_3)_2]$ compounds.[15] The Te(1)–Mo–Te(2) angle of 96.43(4)° is several degrees larger than any of the other angles involving mutually *cis* ligands in this compound. The crystal structure therefore confirms retention of the solution state geometry deduced from the multinuclear NMR studies.

These results show that L co-ordinates readily to a wide range of transition metal fragments and that co-ordination through a Te-based lone pair is the preferred mode. In this sense

Table 4 Selected bond lengths (Å) and angles (°) for $[Mo(CO)_4L_2]$

Te(1)–Mo(1)	2.814(1)	Te(1)–C(11)	2.15(1)
Te(1)–C(18)	2.17(1)	Te(2)–Mo(1)	2.820(2)
Te(2)–C(21)	2.14(1)	Te(2)–C(28)	2.13(1)
Mo(1)–C(1)	1.96(1)	Mo(1)–C(2)	2.05(1)
Mo(1)–C(3)	1.95(1)	Mo(1)–C(4)	2.04(1)
O(1)–C(1)	1.16(1)	O(2)–C(2)	1.14(2)
O(3)–C(3)	1.17(1)	O(4)–C(4)	1.13(1)
Mo(1)–Te(1)–C(11)	111.9(5)	Mo(1)–Te(1)–C(18)	102.1(4)
C(11)–Te(1)–C(18)	82.1(5)	Mo(1)–Te(2)–C(21)	103.3(4)
Mo(1)–Te(2)–C(28)	103.5(3)	C(21)–Te(2)–C(28)	83.0(5)
Te(1)–Mo(1)–Te(2)	96.43(4)	Te(1)–Mo(1)–C(1)	172.9(4)
Te(1)–Mo(1)–C(2)	88.3(4)	Te(1)–Mo(1)–C(3)	85.7(4)
Te(1)–Mo(1)–C(4)	90.9(3)	Te(2)–Mo(1)–C(1)	90.4(4)
Te(2)–Mo(1)–C(2)	90.4(4)	Te(2)–Mo(1)–C(3)	177.3(4)
Te(2)–Mo(1)–C(4)	89.0(3)	C(1)–Mo(1)–C(2)	89.7(5)
C(1)–Mo(1)–C(3)	87.5(6)	C(1)–Mo(1)–C(4)	91.1(5)
C(2)–Mo(1)–C(3)	91.4(5)	C(2)–Mo(1)–C(4)	178.9(5)
C(3)–Mo(1)–C(4)	89.3(5)	Mo(1)–C(1)–O(1)	179(1)
Mo(1)–C(2)–O(2)	179(1)	Mo(1)–C(3)–O(3)	175(1)
Mo(1)–C(4)–O(4)	177.2(9)		

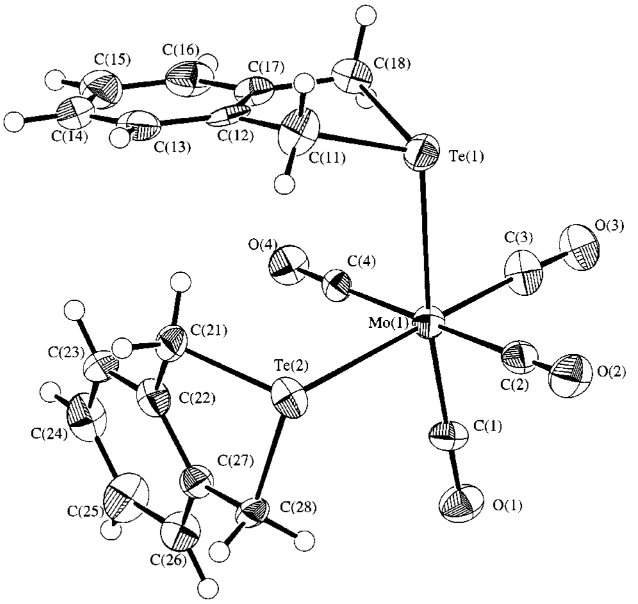


Fig. 3 View of the structure of $[Mo(CO)_4L_2]$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

L behaves rather like an acyclic monodentate telluroether, showing similar trends in ^{125}Te NMR chemical shifts upon co-ordination.

Experimental

Infrared spectra were measured as CsI discs using a Perkin-Elmer 983G spectrometer over the range 200–4000 cm^{-1} or in solution using a Perkin-Elmer 1600 FTIR spectrometer, UV/VIS spectra in solution using quartz cells (1 cm path length) on a Perkin-Elmer Lambda 19 spectrophotometer. Mass spectra were run by positive electrospray (ES) using a VG Biotech Platform, or by fast atom bombardment (FAB) using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70-250-SE normal geometry double focusing mass spectrometer. The ^1H NMR spectra were recorded using a Bruker AM300 spectrometer operating at 300 MHz, $^{13}C\text{-}\{^1H\}$, ^{55}Mn, ^{63}Cu, ^{95}Mo, ^{109}Ag, $^{125}Te\text{-}\{^1H\}$ and ^{195}Pt NMR spectra in 10 mm outside diameter tubes containing *ca.* 10% deuteriated solvent, using a Bruker AM360 spectrometer operating at 90.6, 89.27, 95.5, 23.4, 16.75, 113.6 and 77.7 MHz and are referenced to $SiMe_4$, external aqueous $KMnO_4$, external $[Cu(MeCN)_4]BF_4$ in MeCN, external aqueous Na_2MoO_4, external 9.1 mol dm^{-3} solution of $AgNO_3$ in D_2O (containing Fe^{3+} as relaxation agent), external neat Me_2Te and external aqueous $Na_2[PtCl_6]$ respectively. The ^{109}Ag NMR spectrum was recorded from a solution containing the free radical TEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl). Microanalyses were performed by the University of Strathclyde microanalytical service.

Preparations

$[CuL_4]PF_6$. The compounds $[Cu(MeCN)_4]PF_6$ (27 mg, 0.724 mmol) and L (72 mg, 1.55 mmol) were added to anhydrous CH_2Cl_2 (35 cm^3). The mixture was refluxed for 30 min whereupon the yellow solution was filtered and concentrated *in vacuo* to *ca* 5 cm^3. The solution was treated with Et_2O to afford a cream precipitate which was filtered off and dried *in vacuo*. Recrystallisation by vapour diffusion from nitromethane and Et_2O at 4 °C afforded cream prismatic crystals. Yield: 66 mg, 80%. IR (CsI disc): 2920m, 2853w, 1571w, 1483m, 1447s, 1409w, 1363m, 1281w, 1180w, 1084m, 1032w, 940w, 839s, 811w, 793m, 751w, 735m, 694w, 619w and 558m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.21–7.08 (16 H, m, *o*-C_6H_4) and 4.16 (16 H, s, CH_2). $^{13}C\text{-}\{^1H\}$ NMR (90.5 MHz, $CDCl_3$): δ 143.0, 128.3, 127.2 (*o*-C_6H_4) and 16.44 (CH_2). Electrospray mass spectrum (MeCN): $m/z = 570$, 529; calc. for $[^{63}Cu(^{130}TeC_8H_8)_2(MeCN)]^+$ m/z 572, $[^{63}Cu(^{130}TeC_8H_8)]^+$ m/z 531 (Found: C, 34.2; H, 3.0. Calc. for $C_{32}H_{32}CuF_6PTe_4$: C, 34.3; H, 2.9%).

$[AgL_4]BF_4$. A solution of L (410 mg, 1.77 mmol) in dry, deoxygenated CH_2Cl_2 (5 cm^3) was added to a slurry of $AgBF_4$ (83 mg, 0.426 mmol) in dry, deoxygenated CH_2Cl_2 and the mixture stirred for 1 h at room temperature under N_2. The resulting colourless solution was filtered and then treated with Et_2O to afford a photosensitive cream precipitate which was filtered off and dried *in vacuo*. Recrystallisation by vapour diffusion from nitromethane and Et_2O at 4 °C afforded cream prismatic crystals. Yield: 377 mg, 79%. IR (CsI disc): 3067w, 2913w, 1668 (br) w, 1572w, 1489m, 1437m, 1362s, 1285w, 1057s, 796s, 731m, 629w and 519w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.15–7.06 (16 H, m, *o*-C_6H_4) and 4.24 (16 H, s, CH_2). $^{13}C\text{-}\{^1H\}$ NMR (90.5 MHz, $CDCl_3$): δ 143.31, 128.07, 126.92 (*o*-C_6H_4) and 15.20 (CH_2) (Found: C, 33.5; H, 2.9. Calc. for $C_{32}H_{32}AgBF_4Te_4$: C, 33.5; H, 3.0%).

$[PdCl_2L_2]$. *Method 1.* A solution of $[CuL_4]PF_6$ (82 mg, 0.072 mmol) in deoxygenated MeCN (5 cm^3) was added to a slurry of $PdCl_2$ (25 mg, 0.141 mmol) in deoxygenated MeCN (20 cm^3) and the mixture rapidly stirred for 3 h at room temperature, giving an orange precipitate. The mixture was concentrated *in vacuo* and the precipitate filtered off and dried *in vacuo*. Yield: 46 mg, 49%.

Method 2. A solution of L (113 mg, 0.488 mmol) in deoxygenated MeCN (10 cm^3) was added to a solution of $[Pd(MeCN)_2Cl_2]$ (61 mg, 0.235 mmol) in MeCN (50 cm^3) and the mixture allowed to stand for 2 h at room temperature. An orange precipitate was formed which was filtered off and dried *in vacuo*. Yield: 59 mg, 39%. IR (CsI disc): 2964w, 2918w, 1634 (br), 1569m, 1481m, 1445m, 1357s, 1282w, 1261w, 1125s, 1097s, 801s, 738m, 613m, 532m, 423w, 349m, 296w, 275w, 246m, 221m and 192w cm^{-1}. UV/VIS spectrum (dmf): $\nu_{max} = 25770$ ($\varepsilon_{mol} = 11590$) and 31350 cm^{-1} (7720 dm^3 mol^{-1} cm^{-1}). ^1H NMR [300 MHz, $(CD_3)_2SO$]: δ 7.23–7.11 (8 H, m, *o*-C_6H_4) and 4.70–4.25 (8 H, br, m, CH_2) (Found: C, 29.7; H, 2.5. Calc. for $C_{16}H_{16}Cl_2PdTe_2$: C, 30.0; H, 2.5%).

$[PtCl_2L_2]$. A solution of $[CuL_4]PF_6$ (108 mg, 0.095 mmol) in deoxygenated MeCN (10 cm^3) was added to a slurry of $PtCl_2$ (50 mg, 0.188 mmol) in deoxygenated MeCN (40 cm^3) and the mixture stirred for 2 h at room temperature, giving a yellow precipitate. The mixture was concentrated *in vacuo* and the precipitate filtered off and dried *in vacuo*. Yield: 109 mg, 79%. IR (CsI disc): 2921w, 1634 (br) w, 1568m, 1481m, 1442m, 1356s, 1281w, 1181w, 1130m, 1091m, 942w, 817w, 788s, 731m, 613w,

Table 5 Crystallographic data

	$[CuL_4]PF_6{\cdot}MeNO_2$	$[AgL_4]BF_4{\cdot}MeNO_2$	$[Mo(CO)_4L_2]$
Formula	$C_{33}H_{35}CuF_6NO_2PTe_4$	$C_{33}H_{35}AgBF_4NO_2Te_4$	$C_{20}H_{16}MoO_4Te_2$
M	1196.56	1182.72	671.48
a/Å	11.111(7)	10.855(4)	9.573(6)
b/Å	15.865(4)	15.958(5)	12.967(4)
c/Å	21.346(5)	21.198(5)	16.806(4)
β/°	100.99(3)	98.60(3)	98.86(4)
U/Å^3	3693(2)	3630(1)	2059(1)
μ(Mo-Kα)/cm^{-1}	37.93	37.56	34.29
Unique observed reflections	6748	6639	3805
R_{int} (based on F^2)	0.022	0.069	0.066
Observed reflections with $[I_o > 2\sigma(I_o)]$	4988	4735	3072
R	0.063	0.031	0.069
R'	0.071	0.034	0.080

Details in common: monoclinic, space group $P2_1/n$; $Z = 4$; $R = \Sigma(|F_{obs}|_i - |F_{calc}|_i)/\Sigma|F_{obs}|_i$; $R' = [\Sigma w_i(|F_{obs}|_i - |F_{calc}|_i)^2/\Sigma w_i|F_{obs}|_i^2]^{\frac{1}{2}}$.

532 (br) w, 425w, 307w, 283w and 193w cm^{-1}. UV/VIS spectrum (dmf): $\nu_{max} = 26100$ ($\varepsilon_{mol} = 329$) and 33600 cm^{-1} (6600 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 7.35–7.21 (8 H, m, o-C_6H_4) and 4.60–4.30 (8 H, br, m, CH_2) (Found: C, 26.8; H, 1.6. Calc. for $C_{16}H_{16}Cl_2PtTe_2$: C, 26.3; H, 2.2%).

$[RhCl_3L_3]$. A solution of L (137 mg, 0.591 mmol) in degassed EtOH (10 cm^3) was added to a solution of $RhCl_3{\cdot}3H_2O$ (51 mg, 0.194 mmol) in degassed EtOH (25 cm^3) giving an orange precipitate. The mixture was stirred for 1 h whereupon it was concentrated *in vacuo*. The orange precitipate was filtered off and dried *in vacuo*. Yield: 109 mg, 62%. IR (CsI disc): 2963w, 2920w, 1638 (br) w, 1569m, 1481m, 1441m, 1357s, 1124 (sh), 1094s, 794s, 735m, 614w, 530 (br) w, 424w, 334w and 293w cm^{-1}. UV/VIS spectrum (dmf): $\nu_{max} = 28090$ ($\varepsilon_{mol} = 21830$) and 32980 cm^{-1} (18580 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20–7.06 (12 H, m, o-C_6H_4) and 5.31–3.73 (12 H, m, CH_2) (Found: C, 31.6; H, 2.8. Calc. for $C_{24}H_{24}Cl_3RhTe_3$: C, 31.9; H, 2.7%).

$[RuCl_2L_4]$. A solution of L (175 mg, 0.755 mmol) in degassed EtOH (10 cm^3) was added to a solution of $RuCl_3{\cdot}xH_2O$ (50 mg, 0.191 mmol) in degassed EtOH (40 cm^3) and water (15 cm^3). The mixture was brought to reflux whereupon hypophosphorous acid (2 cm^3 of 50% wt. in water) was gradually added. The mixture was then refluxed for 45 min. A yellow-brown precipitate formed upon cooling, and this was filtered off and dried *in vacuo*. Yield: 629 mg, 30%. IR (CsI disc): 2922m, 2851w, 1658 (br) w, 1567w, 1443m, 1357s, 1097s, 814w, 788m, 771w, 536 (br) w and 305w cm^{-1}. UV/VIS spectrum (dmf): $\nu_{max} = 19840$ ($\varepsilon_{mol} = 676$) and 28600 cm^{-1} (3070 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11–7.01 (16 H, m, o-C_6H_4) and 5.10–3.84 (16 H, m, CH_2) (Found: C, 35.8; H, 3.2. Calc. for $C_{32}H_{32}Cl_2RuTe_4$: C, 35.0; H, 2.9%).

$[MnCl(CO)_3L_2]$. A solution of L (122 mg, 0.526 mmol) in degassed $CHCl_3$ (5 cm^3) was added to a solution of $[MnCl(CO)_5]$ (60 mg, 0.260 mmol) in degassed $CHCl_3$ (35 cm^3). The mixture was stirred for 16 h at room temperature. The solution was concentrated *in vacuo* to afford a yellow precipitate which was filtered off, washed with cold light petroleum (bp 40–60 °C) and dried *in vacuo*. Recrystallisation from nitromethane at 4 °C afforded yellow prismatic crystals. Yield: 122 mg, 74%. IR (CsI disc): 3050w, 2918w, 2018s, 1942s, 1903s, 1648 (br) w, 1570w, 1481w, 1445w, 1356s, 1261w, 1126m, 1096m, 1017m, 801m, 750w, 735w, 668w, 610w, 533w, 428w, 253w and 204w cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (8 H, br, m, o-C_6H_4) and 4.79–4.26 (8 H, br, m, CH_2). ^{13}C-{^{1}H} NMR (90.56 MHz, $CDCl_3$–CH_2Cl_2): δ 221.4, 219.1 (CO), 142.1, 128.7, 127.4 (o-C_6H_4), 20.6, 19.2 (CH_2) (Found: C, 35.5; H, 2.7. Calc. for $C_{19}H_{16}MnO_3Te_2$: C, 35.8; H, 2.5%).

$[Mo(CO)_5L]$. A solution of $[Mo(CO)_5(thf)]$, prepared by photolysing $[Mo(CO)_6]$ (60 mg, 0.227 mmol) in degassed thf (35 cm^3) with 5 drops of toluene, was added to a solution of L (53 mg, 0.227 mmol) in degassed thf (5 cm^3) *via* a syringe. The mixture was stirred for 2 h at room temperature, then concentrated *in vacuo* and hexane added to afford a brown solid. This solid was removed by filtration and the resulting yellow solution evaporated to dryness affording a yellow solid which was dried *in vacuo*. Yield: 84 mg, 79%. IR (CsI disc): 3058w, 2963w, 2963w, 2927w, 2849w, 2069s, 1998s, 1917s, 1575m, 1485m, 1445m, 1409m, 1356m, 1261m, 1099 (br) m, 1037m, 939w, 906w, 866w, 798s, 736m, 604s, 584s and 528w cm^{-1}. FAB mass spectrum: found m/z = 470, 444, 386 and 358; calculated for $[^{98}Mo(CO)_5(^{130}TeC_8H_8)]^+$ 472, $[^{98}Mo(CO)_4(^{130}TeC_8H_8)]^+$ 444, $[^{98}Mo(CO)_2(^{130}TeC_8H_8)]^+$ 388 and $[^{98}Mo(CO)(^{130}TeC_8H_8)]^+$ 360. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.08 (4 H, m, o-C_6H_4), 4.93–4.36 (4 H, m, CH_2). ^{13}C-{^{1}H} NMR (90.56 MHz, $CDCl_3$–CH_2Cl_2): δ 210.5, 206.8 (CO), 142.1, 128.1, 127.3 (o-C_6H_4) and 19.3 (CH_2) (Found: C, 33.3; H, 1.9. Calc. for $C_{13}H_8MoO_5Te$: C, 33.4; H, 1.7%).

$[Mo(CO)_4L_2]$. A solution of L (171 mg, 0.738 mmol) in degassed $CHCl_3$ (5 cm^3) was added to a solution of [Mo(CO)(nbd)] (89 mg, 0.365 mmol) in degassed $CHCl_3$ (35 cm^3). The mixture was stirred for 22 h at room temperature. The solvent was removed *in vacuo* to afford a yellow-brown powder. Ether was added and the solid filtered off and dried *in vacuo*. Recrystallisation from slow evaporation of CH_2Cl_2 afforded brown needle-like crystals. Yield: 136 mg, 61%. IR (CsI disc): 3062w, 2929w, 2012s, 1914s, 1881s, 1838s, 1639 (br) w, 1570w, 1481m, 1446m, 1403m, 1356m, 1180w, 1129 (br) m, 941w, 797m, 748m, 734m, 616m, 580m, 425w, 384m and 272w cm^{-1}. FAB mass spectrum: found m/z = 671 and 557; calculated for $[^{98}Mo(CO)_4(^{130}TeC_8H_8)_2]^+$ 673 and $[^{98}Mo(^{130}TeC_8H_8)_2]^+$ 561. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.10 (8 H, m, o-C_6H_4) and 4.73–4.30 (8H, m, CH_2). ^{13}C-{^{1}H} NMR (90.56 MHz, $CDCl_3$–CH_2Cl_2): δ 216.0, 210.3 (CO), 142.8, 128.0, 127.0 (o-C_6H_4), 18.6 (CH_2) (Found: C, 35.9; H, 2.6. Calc. for $C_{20}H_{16}MoO_4Te_2$: C, 35.8; H, 2.40%).

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 5. The crystals were grown by vapour diffusion of diethyl ether into solutions of the complexes in $MeNO_2$ (Cu and Ag) or CH_2Cl_2 (Mo). Data collection used a Rigaku AFC7S four-circle diffractometer operating at 150 K, using graphite monochromated Mo-Kα X-radiation ($\lambda = 0.71073$ Å). No significant crystal decay or movement was observed.

$[CuL_4]PF_6{\cdot}MeNO_2$ and $[AgL_4]BF_4{\cdot}MeNO_2$. The structures were solved by heavy atom Patterson methods[16] and developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms.[17] In both cases a $MeNO_2$ solvent molecule was also identified in the asymmetric unit. All non-H atoms were refined anisotropically and H atoms placed in fixed, calculated positions with $d(C-H) = 0.96$ Å. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses.

[Mo(CO)$_4$L$_2$]. The structure was solved and developed as above. ψ-Scans did not give a satisfactory absorption correction and therefore the model was taken to isotropic convergence and DIFABS[18] applied to the raw data. Other details as above.

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