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# Formation of thiolene *versus* dithiolene species from TTBEO. Crystal structures of [Au(ddtCO$_2$Et)(PPh$_3$)] and [Sn(ddtCO$_2$Et)$_2$Me$_2$] {TTBEO = 2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-en-8-one; ddtCO$_2$Et = 3-(ethoxycarbonylsulfanyl)-5,6-dihydro-1,4-dithiine-2-thiolate}

**Elena Cerrada,[a] J. Felipe García,[a] Mariano Laguna,*[a] Raquel Terroba[b] and M. Dolores Villacampa[a]**

[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*
[b] *Departamento de Química, Universidad de la Rioja, Obispo Bustamante 3, 26001 Logroño, Spain*

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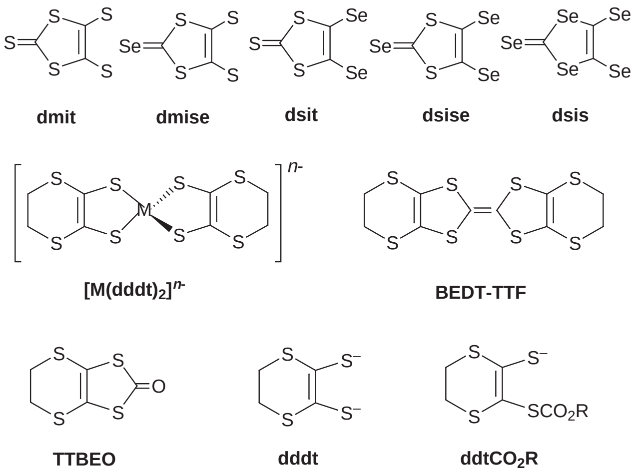
Thiolene gold(I) and tin(IV) complexes such as [Au(ddtCO$_2$R)L] [L = PPh$_3$, PPh$_2$Me or AsPh$_3$; R = Et or Me; ddtCO$_2$R = 3-(alkoxycarbonylsulfanyl)-5,6-dihydro-1,4-dithiine-2-thiolate] and [Sn(ddtCO$_2$R)$_2$Me$_2$] have been obtained from solutions of TTBEO {2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-en-8-one} with sodium ethoxide or methoxide and the corresponding halogeno-complexes [AuCl(L)] and SnMe$_2$Cl$_2$. Reaction of the same solutions with [N(PPh$_3$)$_2$]$_2$[ZnCl$_4$] and [ZnCl$_2$(N–N)] [N–N = 1,10=phenanthroline (phen) or 2,2′-bipyridine (bipy)] afforded the dithiolene complexes [N(PPh$_3$)$_2$]$_2$[Zn(dddt)$_2$], [Zn(dddt)(phen)] and [Zn(dddt)(bipy)] which are the transmetallating starting materials for the synthesis of dithiolene gold(I) and tin(IV) complexes [{Au$_2$(dddt)(AsPh$_3$)}$_n$], [Au$_2$(dddt)(PPh$_3$)$_2$], [Au$_2$(dddt)(PPh$_2$Me)$_2$] and [Sn(dddt)Me$_2$]. The results point to the existence of both thiolene ddtCO$_2$R$^-$ and dithiolene dddt$^{2-}$ species in TTBEO solutions with sodium alkoxide. The crystal structures of [Au(ddtCO$_2$Et)(PPh$_3$)] and [Sn(ddtCO$_2$Et)$_2$Me$_2$] confirm the presence of the ethoxycarbonylsulfanyl ligand.

## Introduction

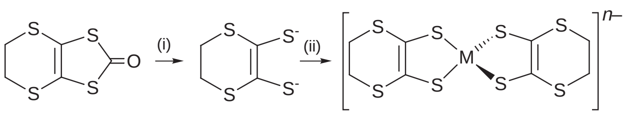
Metal bis(1,2-dithiolene) complexes have been widely studied over the past two decades[1,2] as precursors for molecular metals and superconductors. Owing to their nearly planar structures they show large third order optical non-linearities,[3,4] have good properties for optical data storage,[5,6] as well as unusual magnetic behaviour.[7,8] The most studied complexes are those containing the ligand 4,5-disulfanyl-1,3-dithiole-2-thiolate (C$_3$S$_5$, dmit), which gives some examples of superconductors even at ambient pressure as α-[EDT-TTF][Ni(C$_3$S$_5$)$_2$].[9] Conducting salts of dithiolene metal complexes tend to show one-dimensional structures and most of them become insulating at low temperatures. Ligands with one to five selenium atoms instead of sulfur in dmit derivatives, or ligands with a more extended sulfur framework, are the two strategies to prevent Peierls' transition to insulators by building up two- or three-dimensional structures. The former gives rise to a number of new ligands such as dmise (C$_3$S$_4$Se), dsit (C$_3$S$_3$Se$_2$), dsise (C$_3$S$_2$Se$_3$) and dsis (C$_3$Se$_5$)[10–13] and the latter to new ligands as dddt, 5,6-dihydro-1,4-dithiin-2,3-dithiolate, the [M(dddt)$_2$]$^{n-}$ complexes of which show a related structure to bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF). The latter is a donor organic molecule which forms superconductor salts[14,15] and some of the charge transfer salts with [M(dddt)$_2$] have been reported to present metallic behaviour at low temperatures.[16–28]



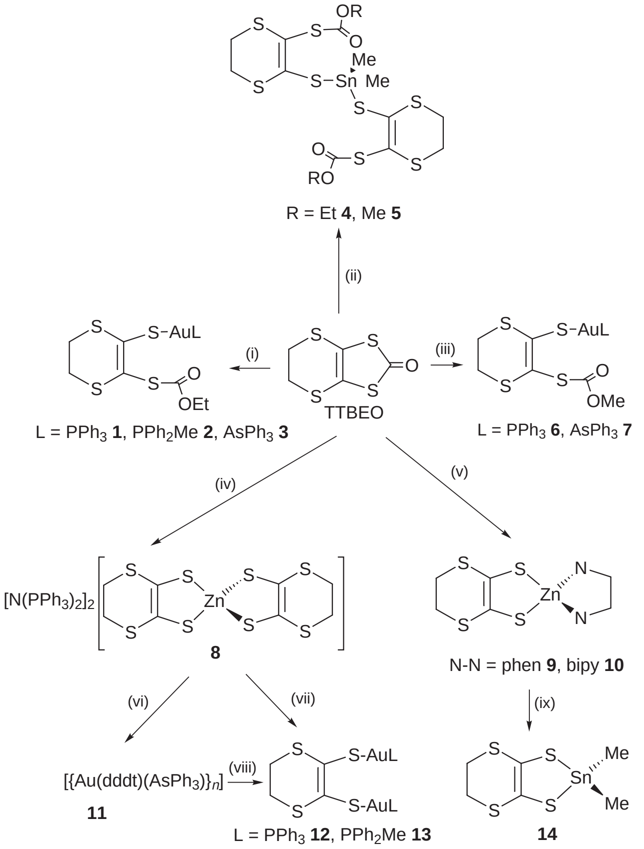
Continuing with our latest research in dithiolene gold chemistry and the role of dithiolene tin(IV) and zinc(II) complexes as transmetallating reagents,[29–31] in this work we select TTBEO {2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-en-8-one} as starting material for the synthesis of dddt complexes of gold(I), zinc(II) and tin(IV). Formation of monothiolene ddtCO$_2$R, 3-(alkoxycarbonylsulfanyl)-5,6-dihydro-1,4-dithiine-2-thiolate (R = Me or Et), derivatives occurs in competition with the more frequent dithiolene formation as evidenced by the crystal structures of [Au(ddtCO$_2$Et)(PPh$_3$)] and [Sn(ddtCO$_2$Et)$_2$Me$_2$]. Preparation of dddt$^{2-}$ derivatives with the same metallic centres gold(I) and tin(IV) is achieved by other preparative procedures involving transmetallation reactions through the zinc complex [N(PPh$_3$)$_2$]$_2$[Zn(dddt)$_2$] or [Zn(dddt)(N–N)] [N–N = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)].

## Results and discussion

The synthesis of dddt complexes by reaction of the suitable halogenometal complexes with dddt$^{2-}$ solutions prepared *in situ* from TTBEO and sodium ethoxide or methoxide (Scheme 1)



**Scheme 1** (i) NaOR (2 equivalents) or Na in ROH (R = Me or Et); (ii) $[MCl_4]^{n-}$.



**Scheme 2** (i) NaOEt–EtOH + [AuCl(L)]; (ii) NaOR–ROH + $SnMe_2Cl_2$; (iii) NaOMe–MeOH + [AuCl(L)]; (iv) NaOEt–EtOH + $[N(PPh_3)_2]_2[ZnCl_4]$; (v) NaOEt–EtOH + $[ZnCl_2(N–N)]$; (vi) $[AuCl(AsPh_3)]$; (vii) [AuCl(L)]; (viii) L; (ix) $SnMe_2Cl_2$.

has been described.[17–19] As stated above, attempts to prepare dinuclear dddt gold(I) complexes by a similar reaction, but using [AuCl(L)] (L = $PPh_3$, $PPh_2Me$ or $AsPh_3$) instead of $[MCl_4]^{n-}$ salts, gave mononuclear derivatives containing a $CO_2Et$ fragment attached to a sulfur atom [process (i), Scheme 2)]. Mononuclear thiolate complexes **1**–**3** $[Au(ddtCO_2Et)L]$ were collected in good yields as insoluble yellow solids in ethanol. The presence of one remaining ethyl carboxylate group was clearly shown by one absorption at ≈1725 $cm^{-1}$ in the IR spectra and confirmed by their $^1H$ NMR spectra showing the inequivalence of $CH_2$ protons of the ligand in agreement with its unsymmetrical nature and the presence of a triplet and a quartet corresponding to the ethoxy group. The positive-ion liquid secondary ion mass spectra ($LSIMS^+$) show the parent peaks at *m*/*z* (%): 712 (30) **1**, 650 (42) **2** and 756 (26) **3** in accordance with their formulation. Complexes **1** and **2** can be obtained by reaction of the triphenylarsine complex **3** with the appropriate phosphine in a 1 : 1 ratio.

When $SnMe_2Cl_2$ was added to solutions of TTBEO in sodium ethoxide complex **4** $[Sn(ddtCO_2Et)_2Me_2]$ was obtained [process (ii), Scheme 2]. Although a stoichiometric ratio Sn : TTBEO of 1 : 2 is present in the final compound, the best results were obtained when a 1 : 1 ratio was used. Others ratios gave oily mixtures from which it was impossible to crystallize complex **4**. Its IR spectrum shows an ester absorption at 1728 $cm^{-1}$ similar to those of complexes **1**–**3** and the $^1H$ NMR spectrum is in accordance with the formulation showing the methyl tin resonances as a singlet flanked by two pairs of tin satellites: $^2J(^{119}SnH) = 65.2$ and $^2J(^{117}SnH) = 62.5$ Hz. In addition to a triplet and a quartet corresponding to the ethyl group, it is worth nothing that the methylene protons of $SCH_2CH_2S$ appear in this case as a singlet at $\delta$ 3.31. Similar results were obtained when $SnMe_2Cl_2$ was added to solutions of TTBEO with sodium methoxide and complex **5** $[Sn(ddtCO_2Me)_2Me_2]$ was obtained. Also in this case the best yield was reached in the presence of an excess of the tin derivative. The spectroscopic properties of **5** are very close to those of **4** with the exception of an extra methyl resonance instead of the ethyl ones. The mass spectra of the tin complexes confirm their monomer nature and show the parent peaks $[M]^+$ at *m*/*z* (%) 656 (1) **4** and 628 (7) **5**.

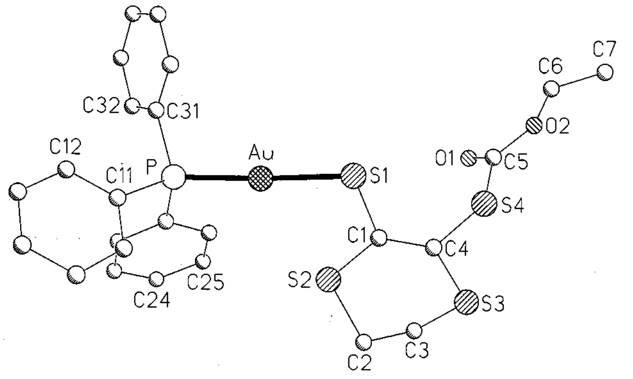


**Fig. 1** Molecule of complex **1** in the crystal with the atom numbering scheme; H atoms are omitted for clarity.

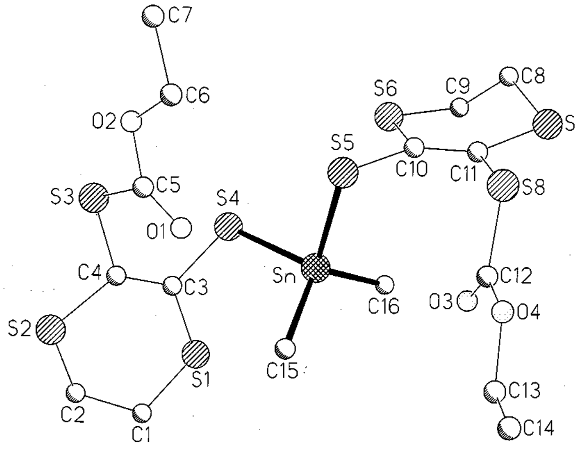


**Fig. 2** Molecule of complex **4** in the crystal with the atom numbering scheme; H atoms are omitted for clarity.

The presence of $ddtCO_2Et$ was confirmed by X-ray diffraction analysis of complexes **1** and **4** (Figs. 1 and 2) and a selection of bond distances and angles are listed in Tables 1 and 2. The former contains the gold atom in the usual linear co-ordination for gold(I) complexes, with S–Au–P angle of 176.85(12)°. Unlike other phosphine gold(I) thiolate complexes there are no intermolecular short gold–gold contacts in the lattice, probably because of the bulkiness of both the triphenylphosphine and the thiolate ligand with the carboxylate group, preventing further contacts between gold atoms. The Au–P bond length is 2.255(3)Å, very similar to those found in $[Au(SR)(PPh_3)]$ (R = Ph,[32] $C_6H_2Pr^i{}_3$-2,4,6[32], $C_{17}H_{15}NSO_2$[33] or $SC_6H_4SnBu^t{}_2Cl$[31]) derivatives, which lie in the range 2.2566(14)–2.260(3) Å. The Au–S distance is 2.299(3) Å which is in the range of those for the latter complexes [2.284(2)–2.3229(13)Å].

The tin atom in complex **4** is bonded to the sulfur atoms of two $ddtCO_2Et$ ligands in a slightly distorted tetrahedral arrangement with distances Sn–S(4) 2.455(2) and Sn–S(5) 2.440(2)Å and to the methyl groups with bond lengths Sn–C(15) 2.125(6) and Sn–C(16) 2.109(6) Å similar to those in other $Sn^{IV}$–C and $Sn^{IV}$–S compounds.[34–38]

**Table 1** Selected bond lengths (Å) and angles (°) for complex **1**

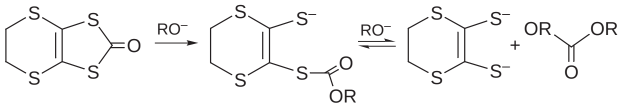
| | | | |
|---|---|---|---|
| Au–P | 2.255(3) | Au–S(1) | 2.299(3) |
| P–C(31) | 1.837(12) | S(1)–C(1) | 1.772(10) |
| S(2)–C(1) | 1.740(10) | S(2)–C(2) | 1.811(10) |
| S(3)–C(4) | 1.763(10) | S(3)–C(3) | 1.783(11) |
| S(4)–C(4) | 1.750(10) | S(4)–C(5) | 1.799(11) |
| O(1)–C(5) | 1.172(11) | O(2)–C(5) | 1.298(11) |
| O(2)–C(6) | 1.473(12) | C(1)–C(4) | 1.352(12) |
| C(2)–C(3) | 1.533(14) | C(6)–C(7) | 1.391(14) |
| P–Au–S(1) | 176.85(12) | C(1)–S(1)–Au | 103.2(3) |
| C(1)–S(2)–C(2) | 103.7(5) | C(4)–S(3)–C(3) | 103.3(5) |
| C(4)–S(4)–C(5) | 100.6(5) | C(5)–O(2)–C(6) | 116.5(9) |
| C(4)–C(1)–S(2) | 126.0(8) | C(4)–C(1)–S(1) | 119.7(8) |
| S(2)–C(1)–S(1) | 114.3(5) | C(3)–C(2)–S(2) | 111.5(8) |
| C(2)–C(3)–S(3) | 112.0(8) | C(1)–C(4)–S(4) | 122.4(8) |
| C(1)–C(4)–S(3) | 128.2(8) | S(4)–C(4)–S(3) | 109.4(5) |
| O(1)–C(5)–O(2) | 128.6(11) | O(1)–C(5)–S(4) | 125.9(9) |
| O(2)–C(5)–S(4) | 105.5(8) | C(7)–C(6)–O(2) | 108.1(10) |

**Table 2** Selected bond lengths (Å) and angles (°) for complex **4**

| | | | |
|---|---|---|---|
| Sn–C(16) | 2.109(6) | Sn–C(15) | 2.125(6) |
| Sn–S(5) | 2.440(2) | Sn–S(4) | 2.455(2) |
| S(1)–C(3) | 1.740(7) | S(1)–C(1) | 1.802(8) |
| S(2)–C(4) | 1.744(6) | S(2)–C(2) | 1.780(8) |
| S(3)–C(4) | 1.760(6) | S(3)–C(5) | 1.785(8) |
| S(4)–C(3) | 1.775(6) | S(5)–C(10) | 1.772(6) |
| S(6)–C(10) | 1.745(7) | S(6)–C(9) | 1.795(8) |
| S(7)–C(11) | 1.749(7) | S(7)–C(8) | 1.833(9) |
| S(8)–C(12) | 1.763(8) | S(8)–C(11) | 1.765(7) |
| O(1)–C(5) | 1.171(8) | O(2)–C(5) | 1.334(8) |
| O(2)–C(6) | 1.457(8) | O(3)–C(12) | 1.200(8) |
| O(4)–C(12) | 1.318(8) | O(4)–C(13) | 1.450(8) |
| C(1)–C(2) | 1.482(10) | C(3)–C(4) | 1.343(8) |
| C(8)–C(9) | 1.415(10) | C(10)–C(11) | 1.339(9) |
| C(16)–Sn–C(15) | 118.9(3) | C(16)–Sn–S(5) | 112.3(2) |
| C(15)–Sn–S(5) | 106.2(2) | C(16)–Sn–S(4) | 104.4(2) |
| C(15)–Sn–S(4) | 111.9(2) | S(5)–Sn–S(4) | 101.90(8) |
| C(4)–C(3)–S(1) | 126.2(5) | C(4)–C(3)–S(4) | 123.1(5) |
| S(1)–C(3)–S(4) | 110.6(4) | C(3)–C(4)–S(2) | 128.6(5) |
| C(3)–C(4)–S(3) | 121.7(5) | S(2)–C(4)–S(3) | 109.6(4) |
| O(1)–C(5)–O(2) | 127.2(8) | O(1)–C(5)–S(3) | 127.4(6) |
| O(2)–C(5)–S(3) | 105.4(6) | C(11)–C(10)–S(6) | 127.1(5) |
| C(11)–C(10)–S(5) | 123.0(6) | S(6)–C(10)–S(5) | 109.9(4) |
| C(10)–C(11)–S(7) | 127.5(6) | C(10)–C(11)–S(8) | 122.7(6) |
| S(7)–C(11)–S(8) | 109.7(4) | O(3)–C(12)–O(4) | 127.0(7) |
| O(3)–C(12)–S(8) | 125.9(6) | O(4)–C(12)–S(8) | 107.2(6) |

The ligands ddtCO$_2$Et in both complexes are quite similar. The sulfur atoms connected with the metal centres show sulfur–carbon distances ≈ 1.77 Å which are intermediate between single (1.81 Å) and double bonds (1.71 Å), indicating a slight degree of electron delocalization. The sulfur–carbon distances in the dithiacycle are slightly different depending on the character of the connected carbon atom. The shortest distances correspond to the sp$^2$ hybridized carbon [average 1.747(8) Å] compared with the sulfur–methylene carbon distances [average 1.801(9) Å]. The carbon–carbon distances of the planar $C_2S_4$ moieties [C(1)–C(4) 1.352(12) Å in **1** and C(3)–C(4) 1.343(8), C(10)–C(11) 1.339(9) Å in **4**] correspond to double bond values. The carboxylate groups show two different carbon–oxygen distances corresponding to double and single bonds. It is noteworthy that with the exception of the CO$_2$Et group all these distances are very similar to those shown by ddd$t^{2-}$ complexes as in [MoCp$_2$(dddt)][28] and one of the dddt ligands in [Au(dddt)$_2$].[18]

The reaction of TTBEO with sodium methoxide in methanol with gold halide complexes affords [Au(ddtCO$_2$Me)L] (L = PPh$_3$ **6** or AsPh$_3$ **7**) [process (iii), Scheme 2] only at 0 °C in an ice-bath, otherwise some impurities corresponding to [Au$_2$(dddt)L$_2$] complexes appear (see below). Complexes **6** and **7** show IR absorption at 1719 and 1730 cm$^{-1}$ respectively, assignable to $\nu$(C=O) and the $^1$H NMR spectra show singlets for the methoxy group and a multiplet at *ca.* $\delta$ 3.3 for methylene protons. Their LSIMS$^+$ mass spectra show the parent peaks at *m*/*z* (%) 698(37) **6** and 742(21) **7**.



**Scheme 3** Equilibrium in solution between TTBEO, ddtCO$_2$R$^-$ and dddt$^{2-}$.

As stated above in this way only ddtCO$_2$R$^-$ complexes of gold(I) and tin(IV) were obtained, but changing the strategy it was possible to obtain dddt complexes with these metals. Zinc complexes such as [N(PPh$_3$)$_2$]$_2$[ZnCl$_4$] and [ZnCl$_2$(N–N)] (N–N = phen or bipy) react with solutions of TTBEO with either ethoxide or methoxide in the corresponding alcohol, affording dddt$^{2-}$ complexes [N(PPh$_3$)$_2$]$_2$[Zn(dddt)$_2$] **8**, [Zn(dddt)(phen)] **9** and [Zn(dddt)(bipy)] **10** [processes (iv) and (v), Scheme 2]. The yields of these complexes are quite high and no evidence of monothiolate ddtCO$_2$R complexes was detected. The $^1$H NMR spectra are in accordance with their formulation, showing the methylene dddt resonances as singlets in addition to other resonances due to N(PPh$_3$)$_2$, phen or bipy. Although complexes **8** and **9** are slightly soluble in most of the common solvents, their LSIMS$^+$ mass spectra show the mononuclear species as the parent peak at *m*/*z* (%) 424(15) **9** and 400(10) **10** pointing to the mononuclear nature of these complexes. Owing to the dicationic nature of **8**, its mass spectrum does not show either the parent ion peak or related peaks, although it acts as a 2:1 electrolyte[39] in acetone solution, $\Lambda_M$ 159 ohm$^{-1}$ cm$^2$ mol$^{-1}$.

In order to show that these different behaviours are dependent on the metal complexes used we prepared only one solution of TTBEO with sodium ethoxide–ethanol or sodium methoxide–methanol and divided it in two equal parts; [AuCl(PPh$_3$)] or [N(PPh$_3$)$_2$]$_2$[ZnCl$_4$] were added, respectively. Complexes **1** or, respectively, **6** and **8** were obtained in more than 80% yield. These results point out that the two species mono-ddtCO$_2$R$^-$ and di-thiolene dddt$^{2-}$ should be present in solution and the equilibrium (Scheme 3) is displaced to one or other extreme depending on the products formed. Another possible explanation could be the presence of only ddtCO$_2$R$^-$ in solution which could remain after the co-ordination to gold(I) or tin(IV) or could evolve with subsequent removal of the CO$_2$R group after the co-ordination of the two sulfur sites to the more polarizing and Lewis acidic zinc(II) centre.

Zinc dddt$^{2-}$ complexes are the starting material to synthesize gold(I) and tin(IV) complexes of these ligands by transmetallation reactions as reported with other dithiolene derivatives.[29–31] So the reaction of [N(PPh$_3$)$_2$]$_2$[Zn(dddt)$_2$] with [AuCl(L)] (L = AsPh$_3$, PPh$_3$ or PPh$_2$Me) in acetone in 1:4 ratio afford insoluble dithiolene complexes [{Au$_2$(dddt)(AsPh$_3$)}$_n$] **11**, [Au$_2$(dddt)(PPh$_3$)$_2$] **12** or [Au$_2$(dddt)(PPh$_2$Me)$_2$] **13** respectively which were recovered by filtration [processes (vi) and (vii), Scheme 2]. The stoichiometry of the triphenylarsine complex, **11**, is different from those of the phosphine derivatives, **12** and **13**. Although the mass spectra of **11** cannot provide information because of its poor ionization we think that **11** could have a similar structure to those proposed for other dithiolene–arsine gold complexes[40] (dithiolene = $S_2C_6H_4$ or $S_2C_6H_3$Me) and therefore should be tetranuclear. In a similar way to the previous arsine complex **3**, the reaction of **11** with different phosphines such as PPh$_3$ and PPh$_2$Me renders complexes **12** and **13** in very good yields [process (viii), Scheme 2]. The mass spectra of the latter confirm the dinuclear nature with the presence of the base peak at *m*/*z* (%) 1098(41) **12** and 974(24) **13**. The $^1$H NMR spectra show singlets for the methylene protons of dddt and also singlets for the phosphorus in the $^{31}$P-{$^1$H} NMR spectra showing their equivalence in agreement with the proposed structure.

The preparation of tin(IV) dddt complexes can be achieved by a similar transmetallation reaction starting from [N(PPh$_3$)$_2$]$_2$[Zn(dddt)$_2$] and SnMe$_2$Cl$_2$ in 1 : 2 ratio in acetone. The fact that all the resulting reaction products are insoluble in acetone prevents a good separation. Better results were obtained using [Zn(dddt)(phen)] **9** as starting material with SnMe$_2$Cl$_2$ in 1 : 2 ratio in the same solvent. Both zinc complexes, the starting **9** and the reaction product [ZnCl$_2$(phen)], are insoluble in this medium and were recovered by filtration. From the solution complex [Sn(dddt)Me$_2$] **14** was obtained in a 70% yield. Its $^1$H NMR spectrum shows a singlet for the methylene protons of dddt and also a singlet for the methyl groups attached to Sn as confirmed by the presence of two pairs of satellites corresponding to $^{119}$Sn and $^{117}$Sn isotopomers. The mass spectrum shows the parent peak at *m*/*z* (%) 330(8).

## Conclusion

When TTBEO reacts with an excess of sodium ethoxide or methoxide in the corresponding alcohol and after the addition of different halogenometal complexes, monothiolene, ddtCO$_2$R, or dithiolene, dddt, derivatives could be obtained. So, with gold(I) complexes such as [AuCl(L)] and the tin(IV) derivative SnMe$_2$Cl$_2$ monothiolene complexes were obtained. On the contrary, with zinc complexes it was possible to obtain dithiolene derivatives which were used as transmetallation reagents for the synthesis of dddt derivatives of gold(I) and tin(IV). The synthesis of both ddtCO$_2$R and dddt complexes of gold(I) and tin(IV) by two different ways and their stability illustrates the importance of the synthetic pathway in inorganic synthesis. The different behaviour of TTBEO alkoxide solutions depending on the metal complexes used should be taken into account in order to understand some unsuccessful attempts to prepare dddt and related complexes.[41,42] Probably mono- and di-thiolene species should be formed in other ketone or thione degradations giving dithiolene derivatives.

## Experimental

The compounds TTBEO,[43] [AuCl(PPh$_3$)],[44] [AuCl(PPh$_2$Me)][44] and [AuCl(AsPh$_3$)][45] were obtained according to the literature procedures.

Infrared spectra were recorded on a Perkin-Elmer 559 or 883 spectrophotometer, over the range 4000–200 cm$^{-1}$, by using Nujol mulls between polyethylene sheets, $^1$H and $^{31}$P NMR spectra on a Varian UNITY 300 in CDCl$_3$ solutions; chemical shifts are quoted relative to SiMe$_4$ ($^1$H) and H$_3$PO$_4$ (external $^{31}$P). The C,H,N and S analyses were performed with a Perkin-Elmer 2400 microanalyser. Conductivities were measured in approximately $5 \times 10^{-4}$ mol dm$^{-3}$ acetone solutions, with a Philips PW 9509 apparatus. Mass spectra were recorded on a VG Autospec, by LSIMS$^+$ using 3-nitrobenzyl alcohol as matrix and a caesium gun. The melting points were measured in a Gallekamp apparatus and are uncorrected.

### Syntheses

**[Au(ddtCO$_2$Et)(L)] (L = PPh$_3$ 1, PPh$_2$Me 2 or AsPh$_3$ 3).** (a) To a suspension of TTBEO (0.021 g, 0.1 mmol) in 10 ml of ethanol was added a solution of 0.1 M NaOEt (0.4 mmol, 4 ml) under dinitrogen during 10 min and [AuCl(PPh$_3$)] (0.049 g, 0.1 mmol), [AuCl(PPh$_2$Me)] (0.043 g, 0.1 mmol) or [AuCl(AsPh$_3$)] (0.054 g, 0.1 mmol). After stirring for 24 h yellow solids precipitated, which were filtered off, washed with ethanol and dried *in vacuo*. Yields: **1**, 82; **2**, 64; **3**, 90%. IR (film): $\nu$(C=O) 1723 (**1**), 1720 (**2**), 1725 cm$^{-1}$ (**3**). $^1$H NMR (CDCl$_3$): **1**, $\delta$ 7.52–7.49 (m, 15 H, Ph), 4.26 (q, $^3J_{HH}$ = 6.7 Hz, 2 H, CH$_2$), 1.27 (t, 3 H, CH$_3$), 3.4 (m, 2 H, SCH$_2$CH$_2$S), 3.3 (m, 2 H, SCH$_2$CH$_2$S); **2**, 7.55–7.45 (m, 10 H, Ph), 4.23 (q, $^3J_{HH}$ = 7 Hz, 2 H, CH$_2$), 1.25 (t, 3 H, CH$_3$), 3.36 (m, 2 H, SCH$_2$CH$_2$S), 3.3 (m, 2 H, SCH$_2$CH$_2$S); **3**, 7.69–7.43 (m, 15 H, Ph), 4.25 (q, $^3J_{HH}$ = 7.1, 2 H, CH$_2$), 1.27 (t, 3 H, CH$_3$), 3.38 (m, 2 H, SCH$_2$CH$_2$S), 3.3 (m, 2 H, SCH$_2$CH$_2$S), 2.13 (d, $^3J_{HH}$ = 10.2 Hz, 3 H, CH$_3$). $^{31}$P-{$^1$H} NMR (CDCl$_3$): **1**, $\delta$ 35.6 (s); **2**, 18.3 (s). Mp 132 (**1**), 78 (decomp.) (**2**), 124 °C (**3**). (Found: C, 42.0; H, 3.35; S, 18.5. Calc. for C$_{25}$H$_{24}$AuO$_2$PS$_4$ **1**: C, 42.15; H, 3.3; S, 18.0. Found: C, 36.45; H, 3.05; S, 19.05. Calc. for C$_{20}$H$_{22}$AuO$_2$PS$_4$ **2**: C, 36.9; H, 3.4; S, 19.7. Found: C, 39.1; H, 3.2; S, 17.4. Calc. for C$_{25}$H$_{24}$AsAuO$_2$S$_4$ **3**: C, 39.7; H, 3.2; S, 16.9%) $\Lambda_M$/ohm$^{-1}$ cm$^2$ mol$^{-1}$ = 2 (**1**), 1 (**2**,**3**).

(b) To a solution of complex **3** (0.076 g, 0.1 mmol) in 15 ml of dichloromethane was added PPh$_3$ (0.029 g, 0.1 mmol) or PPh$_2$Me (0.020 g, 0.1 mmol). After 2 h of stirring at room temperature the solutions were concentrated and the addition of 15 ml of diethyl ether gave yellow solids **1** and **2**, which were filtered off and dried *in vacuo*.

**[Sn(ddtCO$_2$R)$_2$Me$_2$] (R = Et 4 or Me 5).** To a suspension of TTBEO (0.042 g, 0.2 mmol) in 10 ml of ethanol was added a solution of 0.1 M NaOEt (0.8 mmol, 8 ml) under dinitrogen during 10 min and SnCl$_2$Me$_2$ (0.042 g, 0.2 mmol). After 12 h of stirring the solution was filtered off through 1 cm of Celite, concentrated to dryness, dissolved in 15 ml of CH$_2$Cl$_2$, concentrated and the addition of 20 ml of *n*-hexane led to white solid **4**, which was filtered off and dried *in vacuo*. To a suspension of TTBEO (0.042 g, 0.2 mmol) in 10 ml of methanol was added a solution of 0.1 M NaOMe (0.8 mmol, 8 ml) under dinitrogen during 10 min and SnCl$_2$Me$_2$ (0.042 g, 0.2 mmol). After 12 h of stirring the solution was concentrated to gave a white solid (**5**). The solid was filtered off and dried *in vacuo*. Yields: **4**, 82, **5**, 79% (based on TTBEO). IR(film): $\nu$(C=O) 1728 (**4**), 1700 cm$^{-1}$ (**5**). $^1$H NMR (CDCl$_3$): **4**, $\delta$ 4.27 (q, $^3J_{HH}$ = 7, 2 H, CH$_2$), 1.29 (t, 3 H, CH$_3$), 3.31 (s, 8 H, SCH$_2$CH$_2$S) and 0.98 [s, $J$(119Sn–H) = 65.2 and $J$(117Sn–H) = 62.5 Hz, 6 H, CH$_3$]; **5**, 3.82 (s, 6 H, OMe), 3.31 (s, 8 H, SCH$_2$CH$_2$S) and 0.99 [s, $J$($^{119}$SnH) = 66 and $J$($^{117}$SnH) = 62 Hz, 6 H, CH$_3$]. Mp 120 (decomp.) (**4**), 96 °C (**5**). (Found: C, 29.2; H, 3.5; S, 39.0. Calc. for C$_{16}$H$_{24}$O$_4$S$_8$Sn **4**: C, 29.3; H, 3.7; S, 39.1. Found: C, 26.4; H, 2.9; S, 40.4. Calc. for C$_{14}$H$_{20}$O$_4$S$_8$Sn **5**: C, 26.8; H, 3.2; S, 40.8%).

**[Au(ddtCO$_2$Me)(L)] (L = PPh$_3$ 6 or AsPh$_3$ 7).** (a) To a suspension of TTBEO (0.021 g, 0.1 mmol) in 10 ml of methanol was added a solution of 0.1 M NaOMe (0.4 mmol; 4 ml) under dinitrogen during 10 min and [AuCl(PPh$_3$)] (0.049 g, 0.1 mmol) or [AuCl(AsPh$_3$)] (0.054 g, 0.1 mmol). After stirring for 1.5 h the yellow **6** and brown **7** solids obtained were filtered off, washed with methanol and dried *in vacuo*. Yields: **6**, 80; **7**, 65%. IR(film): $\nu$(C=O) 1719 (**6**), 1730 cm$^{-1}$ (**7**). $^1$H NMR (CDCl$_3$): **6**, $\delta$ 7.7–7.3 (m, 15 H, Ph), 3.74 (s, 3 H, OMe), 3.37 (m, 2 H, SCH$_2$CH$_2$S) and 3.28 (m, 2 H, SCH$_2$CH$_2$S); **7**, $\delta$ 7.7–7.1 (m, 15 H, Ph), 3.74 (s, OMe), 3.36 (m, 2 H, SCH$_2$CH$_2$S) and 3.22 (m, 2 H, SCH$_2$CH$_2$S). $^{31}$P-{$^1$H} NMR (CDCl$_3$) **6**, $\delta$ 38.4 (s). Mp 120 (**6**), 98 °C (**7**). (Found: C, 41.7; H, 2.85; S, 17.9. Calc. for C$_{24}$H$_{22}$AuO$_2$PS$_4$ **6**: C, 41.25; H, 3.15; S, 18.35. Found: C, 38.3; H, 2.35; S, 16.55. Calc. for C$_{24}$H$_{22}$AsAuO$_2$S$_4$ **7**: C, 38.8; H, 2.9; S, 17.3%). $\Lambda_M$/ohm$^{-1}$ cm$^2$ mol$^{-1}$ = 1 (**6**), 2 (**7**).

**[N(PPh$_3$)$_2$]$_2$[Zn(dddt)$_2$] 8.** To a suspension of TTBEO (0.104 g, 0.5 mmol) in 10 ml of ethanol was added a solution of 0.1 M NaOEt (2 mmol; 2 ml) under dinitrogen during 10 min and [N(PPh$_3$)$_2$]$_2$[ZnCl$_4$] (0.160 g, 0.25 mmol). After 12 h of stirring a yellow solid precipitated, which was filtered off, washed with water (2 × 10 ml) and dried with diethyl ether. Yield: 85%. $^1$H NMR (CDCl$_3$): $\delta$ 7.7–7.3 (m, 30 H, Ph) and 3.31 (s, 8 H, SCH$_2$CH$_2$S). Mp 116 °C. (Found: C, 63.5; H, 4.8; N, 2.0; S, 16.2. Calc. for C$_{80}$H$_{68}$N$_2$P$_4$S$_8$Zn: C, 63.9; H, 4.6; N, 1.7; S, 17.1%). $\Lambda_M$ = 159 ohm$^{-1}$ cm$^2$ mol$^{-1}$.

**[Zn(dddt)(N–N)] (N–N = phen 9 or bipy 10).** To a suspension of TTBEO (0.025 g, 0.25 mmol) in 10 ml of methanol was

**Table 3** Data collection and structure refinement for complexes **1** and **4**

| | **1** | **4** |
|---|---|---|
| Chemical formula | $C_{25}H_{24}AuO_2PS_4$ | $C_{16}H_{24}O_4S_8Sn$ |
| $M$ | 712.62 | 655.52 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 9.202(5) | 7.623(3) |
| $b$/Å | 11.495(6) | 20.585(4) |
| $c$/Å | 13.921(7) | 17.012(3) |
| $\alpha$/° | 70.85(4) | — |
| $\beta$/° | 87.05(4) | 90.53(4) |
| $\gamma$/° | 74.24(2) | — |
| $V$/Å$^3$ | 1337.6(12) | 2669.4(13) |
| $Z$ | 2 | 4 |
| $T$/K | 193(2) | 293(2) |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 5.892 | 1.603 |
| No. reflections measured | 4526 | 5826 |
| No. unique reflections | 4193 | 4687 |
| No. reflections observed [$F > 4\sigma(F)$] | 2897 | 2764 |
| $R$ [$F$, $F > 4\sigma(F)$] | 0.054 | 0.054 |
| $wR$ ($F^2$, all reflections) | 0.092 | 0.101 |
| No. reflections used | 4193 | 4686 |
| No. parameters | 298 | 264 |

added [$ZnCl_2$(phen)] (0.079 g, 0.25 mmol) or [$ZnCl_2$(bipy)] (0.073 g, 0.25 mmol). After 3 d of stirring complexes **9** and **10** precipitated as red and brown solids, which were filtered off and dried *in vacuo*. Yields: **9**, 75, **10**, 72%. $^1$H NMR ($CDCl_3$): **9**, $\delta$ 9.04 (m, 2 H, phen), 8.53 (m, 2 H, phen), 8.02 (s, 2 H, phen), 7.79 (m, 2 H, phen) and 3.03 (s, 4 H, $SCH_2CH_2S$); **10**, 8.66 (m, 2 H, bipy), 8.34 (m, 2 H, bipy), 7.79 (m, 2 H, bipy), 7.42 (m, 2 H, bipy), 3.04 (s, 4 H, $SCH_2CH_2S$) and 7.6–7.4 (m, bipy). Mp 193 (**9**), 214 °C (**10**). (Found: C, 44.65; H, 2.3; S, 31.0. Calc. for $C_{16}H_{12}N_2S_4Zn$ **9**: C, 45.1; H, 2.8; S, 30.1. Found: C, 41.55; H, 2.55; S, 30.8. Calc. for $C_{14}H_{12}N_2S_4Zn$ **10**: C, 41.8; H, 3.0; S, 31.9%).

**[$Au_2$(dddt)($AsPh_3$)] 11.** To a solution of [$N(PPh_3)_2$]$_2$[Zn(dddt)$_2$] (0.150 g, 0.1 mmol) in 20 ml of acetone was added [AuCl($AsPh_3$)] (0.108 g, 0.2 mmol). After stirring for 12 h complex **11** precipitated as a yellow solid, which was filtered off and dried *in vacuo*. Yield: 61%. $^1$H NMR ($CDCl_3$): $\delta$ 7.77–7.2 (m, 15 H, Ph), 2.72 (m, 2 H, $SCH_2CH_2S$) and 2.36 (m, 2 H, $SCH_2CH_2S$). Mp 108 °C (decomp.). (Found: C, 29.5; H, 2.1; S, 14.5. Calc. for $C_{22}H_{29}AsAuS_4$: C, 30.0; H, 2.15; S, 14.55%). $\Lambda_M = 2$ ohm$^{-1}$ cm$^2$ mol$^{-1}$.

**[$Au_2$(dddt)$L_2$] (L = $PPh_3$ 12 or $PPh_2Me$ 13).** To a solution of [$N(PPh_3)_2$]$_2$[Zn(dddt)$_2$] (0.150 g, 0.1 mmol) in 20 ml of acetone was added [AuCl($PPh_3$)] (0.098 g, 0.2 mmol) or [AuCl($PPh_2Me$)] (0.086 g, 0.2 mmol) and stirred for 2 h. Partial evaporation of the solvent by concentration and addition of 10 ml of diethyl ether afforded yellow solids **12** and **13**, which were filtered off and dried *in vacuo*. Yields: **12**, 60, **13**, 68%. $^1$H NMR ($CDCl_3$): **12**, $\delta$ 7.6–7.3 (m, 30 H, Ph) and 3.3 (s, 4 H, $SCH_2CH_2S$); **13**, 7.6–7.2 (m, 20 H, Ph), 3.3 (s, 4 H, $SCH_2CH_2S$) and 1.87 (d, $^3J_{HH} = 10$ Hz, 6 H, $CH_3$). $^{31}$P-{$^1$H} NMR ($CDCl_3$): **12**, $\delta$ 36.4 (s); **13**, 20.2 (s). Mp 159 (**12**), 145 °C (**13**) (Found: C, 43.7; H, 2.9; S, 11.6. Calc. for $C_{40}H_{32}Au_2P_2S_4$ **12**: C, 43.8; H, 2.95; S, 11.7. Found: C, 36.4; H, 2.9; S, 13.5. Calc. for $C_{30}H_{30}Au_2P_2S_4$ **13**: C, 36.95; H, 3.1; S, 13.15%). $\Lambda_M$/ohm$^{-1}$ cm$^2$ mol$^{-1}$ = 1 (**12**), 3 (**13**).

**[Sn(dddt)$Me_2$] 14.** To a solution of [Zn(dddt)(phen)] (0.021 g, 0.05 mmol) in 10 ml of acetone was added $SnCl_2Me_2$ (0.011 g, 0.05 mmol). After 3 h of stirring a white solid precipitated which was filtered off and dried *in vacuo*. Yield: 67%. $^1$H NMR ($CDCl_3$): $\delta$ 3.2 (s, 4 H, $SCH_2CH_2S$) and 1.0 [s, $J(^{119}SnH) = 60.6$ and $J(^{117}SnH) = 58.0$ Hz]. (Found: C, 21.5; H, 2.95; S, 38.5. Calc. for $C_6H_{10}S_4Sn$: C, 21.9; H, 3.1; S, 38.9%). $\Lambda_M$/ohm$^{-1}$ cm$^2$ mol$^{-1}$ = 5.

## Crystallography

Data for complexes **1** and **4** were collected on a Stoe-Siemens four-circle diffractometer using monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å), scan type $\theta$–$2\theta$. Data for **1** were measured at −100 °C and for **4** at room temperature. Cell constants were refined from setting angles of 48 reflections in the range $2\theta$ 15–27 for **1** and 15–34° for **4**. Absorption corrections were applied on the basis of $\psi$ scans. Structures were solved by the heavy-atom method and refined on $F^2$ using the program SHELXL 93.[46] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model except methyl hydrogens bonded to tin which were included as rigid groups. A system of restraints to light-atom displacement-factor components and local ring symmetry was used in **1**; no restraints in **4**. The significant residual electron density in **1** is in the heavy atom region; the distance of the maximum peak, 1.053 e Å$^{-3}$, to the nearest atom (Au) is 0.99 Å. Further details are given in Table 3.

CCDC reference number 186/1136.

See http://www.rsc.org/suppdata/dt/1998/3511/ for crystallographic files in .cif format.

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