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Organochalcogenido-bridged dimeric 2-methylallylpalladium complexes: synthesis, structure and their transformation into palladium chalcogenides

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Organochalcogenido-bridged dimeric 2-methylallylpalladium complexes of the type $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}C_4H_7)_2]$ (**1**) [ER = SBu^t (**1a**), SPh (**1b**), SC_6F_5 (**1c**), SePh (**1d**), TePh (**1e**)] have been prepared. The structure of the SBu^t bridged complex has been established by single crystal X-ray diffraction analysis. The four-membered Pd_2S_2 ring adopts a non-planar conformation with the two η^3-2-MeC_3H_4 (η^3-C_4H_7) in a *syn* configuration. The thermal behaviour of these complexes has been investigated by thermogravimetric analysis. These complexes yield Pd_4E (E = S or Se) or Pd_3Te_2 at moderately low temperatures.

Introduction

Platinum group metal chalcogenides (M_xE_y; M = Pd or Pt; E = S, Se, Te) have found extensive applications in catalysis[1–4] and materials science. Examples of the latter include manufacture of semiconductors and solar cells,[5] lithographic films/plates with high resolution,[6] optical disc recording films,[7] *etc.* The continuing drive for scaling down of the dimensions of these devices has motivated research into the design and development of organometallic precursor chemistry. This has led to an ever increasing number of organometallic precursor molecules which show lower growth temperatures and cleaner depositions.

The lability of an allyl group in allylpalladium compounds is well documented.[8,9] This has been exploited in the deposition of palladium films from allylpalladium compounds, such as $[Pd(\eta^3\text{-allyl})_2]$ (allyl = C_3H_5, C_4H_7), $[CpPd(\eta^3\text{-}C_3H_5)]$, at moderately low temperatures.[10] Recently we have reported organochalcogenide bridged allylpalladium complexes for the first time.[9] We thought that these complexes could serve as potential candidates for the preparation of palladium chalcogenides by either MOCVD or bulk pyrolysis. In this paper we report thermal studies on these compounds leading to the formation of metal rich chalcogenides, and the X-ray structure of one of them, $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$.

Experimental

The complexes $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2]$,[11] $Pb(ER)_2$ and $Hg(TePh)_2$[12] were prepared by literature methods, while $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}C_4H_7)_2]$ complexes were prepared by our earlier method.[9] All preparations were carried out in a nitrogen atmosphere. Elemental analyses (C, H, Pd) were carried out by the Analytical Chemistry Division of this Research Centre. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker DPX 300 NMR spectrometer. Thermogravimetric analyses (TGA) were carried out on a Setaram 92-16-18 instrument. The TG curves were recorded at a heating rate of 10 °C min^{-1} under a flow of argon. The plot of mass loss as a function of temperature was recorded. X-Ray powder diffraction data were collected on a Philips X-ray diffractometer (Model PW 1729) using Cu-Kα radiation. SEM photographs were taken on a JEOL JSM-T330A instrument.

1 Pyrolysis of $[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_4H_7)_2]$ (1b) in refluxing xylene

A xylene solution (40 ml) of $[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_4H_7)_2]$ (504 mg, 1.17 mmol) was refluxed with stirring for 45 min under a nitrogen atmosphere. A black powder separated which was filtered, washed with diethyl ether and dried in vacuum (yield 166 mg, 80%). The XRD pattern of this black powder agrees well with the pattern reported for Pd_4S. Analysis found: C, 1.8; H, 0.0; Pd 89%; calc. for Pd_4S: Pd, 93%.

2 Pyrolysis of $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$ (1a)

This was carried out in a manner similar to that described above, and gave Pd_4S in 82% yield. The XRD pattern corresponds to Pd_4S. Analysis found: C, 10.8; H, 2.0; Pd, 79%, calc. for Pd_4S: Pd 93%.

3 Pyrolysis of $[Pd_2(\mu\text{-}SC_6F_5)_2(\eta^3\text{-}C_4H_7)_2]$ (1c)

This was carried out in a similar manner and gave Pd_4S in 69% yield. The XRD pattern compares well with Pd_4S. Analysis found: C, 4.2; H, 0.0%.

4 Pyrolysis of $[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$ (1d)

This was carried out in a similar manner. The black powder obtained (185 mg, 85%) exhibited an XRD pattern corresponding to Pd_4Se. Analysis found: C, 0.5%; H, 0.0%; Pd, 80%, calc. for Pd_4Se: Pd, 84%.

5 Pyrolysis of $[Pd_2(\mu\text{-}TePh)_2(\eta^3\text{-}C_4H_7)_2]$ (1e)

Since the complex $[Pd_2(\mu\text{-}TePh)_2(\eta^3\text{-}C_4H_7)_2]$ decomposes at room temperature, this was not isolated. In a typical experiment a xylene solution (25 ml) of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2]$ (236 mg, 0.6 mmol) was treated with solid $Hg(TePh)_2$ (366 mg, 0.6 mmol) at 0 °C under a nitrogen atmosphere. After stirring for 30 minutes at 0 °C and then allowing to stand at room temperature for another 0.5 h, the solution was filtered and the filtrate was refluxed for 25 min. A black shining powder formed which was filtered, washed with diethyl ether and dried *in vacuo* (yield 60 mg). The XRD pattern of this black powder agrees well with that of Pd_3Te_2. Analysis found: C, 0.7%, H, 0.0%: Pd, 51%, calc. for Pd_3Te_2: 55%.

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Table 1 Crystal data and structure refinement details for $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$

Chemical formula	$C_{16}H_{32}Pd_2S_2$
Formula weight	501.34
Crystal system, Space group	Orthorhombic, $C222_1$
Unit cell dimensions:	
a/Å	12.369(3)
b/Å	13.674(2)
c/Å	12.3800
V/Å^3	2093.8(7)
Z	4
D_c/mg m^{-3}	1.590
Absorption coefficient, μ/mm^{-1}	1.908
Index ranges	$-10<h<14$, $-10<k<16$, $0<l<14$
Reflections collected/unique	2053/1845 [$R_{int}=0.0173$]
Data/restraints/parameters	1845/0/108
Final R indices [$I>2\sigma(I)$]	$R1=0.0184$, $wR2=0.0448$
R indices (all data)	$R1=0.0213$, $wR2=0.0470$

Crystallography

X-Ray data on yellow crystals of $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$ (**1a**) ($0.15\times0.10\times0.10$ mm) were collected at room temperature (295 ± 1 K) on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo-Kα radiation ($\lambda=0.71073$ Å) employing the ω–2θ scan technique. The unit cell parameters (Table 1) were determined from 25 reflections measured by a random search routine and indexed by the method of short vectors followed by least squares refinement. The intensity data were corrected for Lorentz-polarization and absorption effects. The structure was solved using SHELXS 86[13] and refined using SHELXL 93[14] computer programs. The non-hydrogen atoms were refined anisotropically.

CCDC reference number 1145/210. See http://www.rsc.org/suppdata/jm/a9/a908133j/ for crystallographic files in .cif format.

Results and discussion

Organochalcogenide bridged 2-methylallylpalladium complexes were prepared by transmetallation reactions (eqn. 1, 2):[9]

$$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2] + Pb(ER)_2 \rightarrow \underset{\textbf{1a–d}}{[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}C_4H_7)_2]} + PbCl_2$$

$$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2] + Hg(TePh)_2 \rightarrow \underset{\textbf{1e}}{[Pd_2(\mu\text{-}TePh)_2(\eta^3\text{-}C_4H_7)_2]} + HgCl_2$$

These samples **1a–1d** gave satisfactory microanalyses. Except for **1c** [(^{1}H NMR in $CDCl_3$ δ 1.99 (s, Me), 2.86 (br, *anti* CH), 3.47 (br, *syn* CH); analysis found (calcd.): C, 32.8 (33.3), H, 2.0 (2.0%)] which is reported in this work, the ^{1}H NMR spectra of the other samples were in agreement with our reported data.[9] The phenyltellurato bridged compound decomposes on standing in solution within a few minutes, hence further characterisation data could not be obtained.

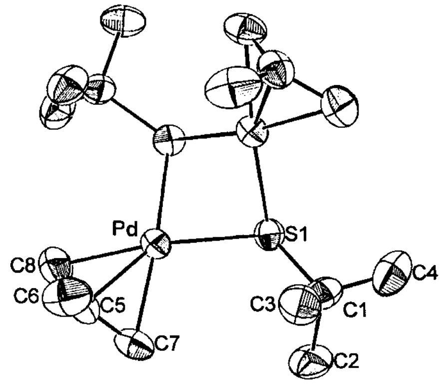

Fig. 1 Crystal and molecular structure of $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$.

Table 2 Selected bond lengths (Å) and angles (°) for $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]^a$

Bond lengths			
Pd–C(5)	2.140(3)	Pd–Pd#1	3.1447(6)
Pd–C(8)	2.150(11)	Pd–S(1)	2.361(2)
Pd–C(7)	2.163(9)	Pd–S(1)#1	2.351(2)
S(1)–C(1)	1.851(4)	Pd#1–S(1)	2.351(2)
Bond angles			
C(5)–Pd–C(8)	39.5(4)	C(1)–S(1)–Pd	114.3(3)
C(5)–Pd–C(7)	36.4(4)	S(1)–Pd–S(1)#1	78.09(3)
C(7)–Pd–C(8)	66.6(2)	Pd–S(1)–Pd#1	83.74(3)
C(7)–C(5)–C(8)	115.8(5)	S(1)–Pd–C(5)	137.3(3)
C(7)–C(5)–Pd	72.7(5)	S(1)–Pd–C(7)	106.8(3)
C(8)–C(5)–Pd	70.6(5)	S(1)–Pd–C(8)	171.4(4)
C(6)–C(5)–Pd	115.7(2)	S(1)#1–Pd–C(5)	140.1(3)
C(5)–C(7)–Pd	70.9(4)	S(1)#1–Pd–C(7)	174.6(3)
C(5)–C(8)–Pd	69.9(4)	S(1)#1–Pd–C(8)	108.3(3)
C(1)–S(1)–Pd	117.5(4)		
Dihedral angles			
S(1)–Pd–S(1)#1/C(7)–C(5)–C(8): 68.3°			
C(7)–Pd–C(8)/C(7)–C(5)–C(8): 73.1°			
S(1)–Pd–S(1)#1/S(1)–Pd#1–S(1)#1: 118.5°			

^{a}#1 $x, -y, -z+1$.

Structure of $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$ (1a)

The crystal and molecular structure of $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$ was established by X-ray diffraction. An ORTEP plot of the molecule together with the crystallographic numbering scheme is depicted in Fig. 1. Selected bond lengths, angles and dihedral angles are given in Table 2.

The two palladium atoms are held together by two bridging thiolato groups and the resulting four membered Pd_2S_2 ring is non-planar. Although the four-membered Pd_2X_2 unit in binuclear allylpalladium complexes stabilized by a single-atom bridging ligand (*e.g.*, Cl) usually adopts a planar conformation,[15–19] bent structures are reported for $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}1,3\text{-}MeCHCH_2CHMe)_2]$[20] and $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2CH_2CHBu^t)_2]$.[21] The two palladium square planes in the present case are inclined to each other at 118.5°. The dihedral angle between the mean planes of C7, C8, Pd, S1, S1#1 and C7#1, C8#1, Pd#1, S1#1, S1 is 123.1°. The Pd–S distances are all equal and are within the expected range.[22]

Each palladium atom is symmetrically bonded to a 2-methylallyl group with a mean Pd–C distance of 2.51 Å which compares well with those found in other allylpalladium complexes.[15–18] The plane of the three allylic carbons forms a dihedral angle of 68.3° with the PdS_2 plane. The two 2-methylallyl ligands are mutually *syn*. The methyl group on the central carbon atom of the allyl ligand is 0.277 Å out of the plane of the three allyl carbons. The angle C(7)–Pd–C(8)

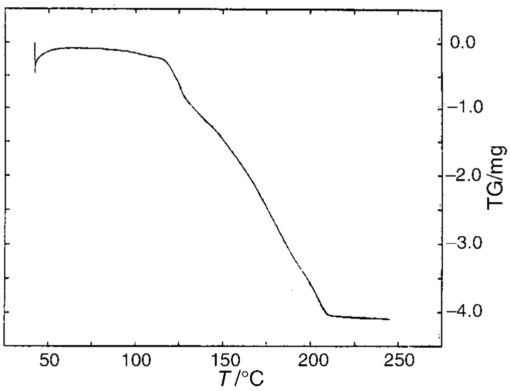

Fig. 2 TG curve for $[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$ (initial weight 6.4 mg).

Table 3 TGA data for $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}C_4H_7)_2]$ complexes[a]

Compound	Step I		Step II		Step III	
	T/°C	% wt. loss	T/°C	% wt. loss	T/°C	% wt. loss
$[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$	157	43[b]	—	—	197	10
$[Pd_2(\mu\text{-}SC_6F_5)_2(\eta^3\text{-}C_4H_7)_2]$	148	10.7	175	47.7	200	8.9
$[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_4H_7)_2]$	140	13.4	161	41.8[c]	—	—
$[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$	112	13.9	143	31.7	194	11.7

[a] The error observed in the mass loss is within ±2%. [b] Decomposes in two superimposable steps (I and II). [c] Decomposes in two superimposable steps (II and III).

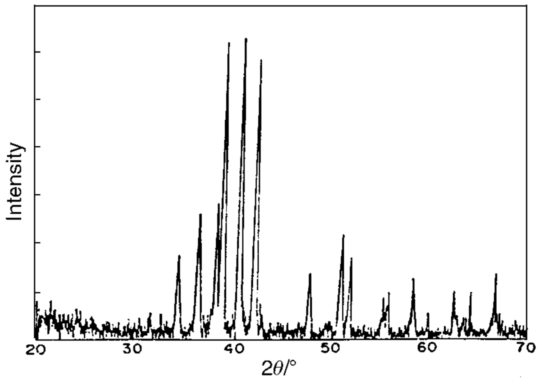

Fig. 3 XRD pattern for Pd_4Se obtained from $[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$ in refluxing xylene.

(66.6(2)°) agrees favourably with the corresponding angle observed in chloro-bridged allylpalladium dimers.[17,18] However, the S–Pd–S angle (78.09°) is reduced significantly from the corresponding X–Pd–X (~90°) reported in several bi-nuclear allyl palladium complexes.[16–19,23]

Thermal analysis of $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}C_4H_7)_2]$ complexes

The thermogravimetric analyses of $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}C_4H_7)_2]$ ($ER = SBu^t$, SC_6F_5, SPh, SePh) were carried out in a flowing argon atmosphere. The TG curves showed that these complexes decompose in three steps (Fig. 2; Table 3), finally leading to the formation of Pd_4E (E = S or Se). Because of the superimposing nature of decomposition steps, the mechanism of decomposition of these complexes could not be worked out with confidence. However, the total mass loss in all these complexes obtained from TG analysis agrees well within experimental error with the calculated mass loss for the formation of Pd_4E. As shown by the TG curves, the complexes $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-}C_4H_7)_2]$ decompose at 157, 148, 140 and 112 °C respectively for $ER = SBu^t$, SC_6F_5, SPh, and SePh. The decomposition of the phenyltellurato-bridged complex at room temperature coupled with the above observations indicates that the stabilities of these complexes vary in the following order: $SBu^t > SC_6F_5 > SPh > SePh \gg TePh$.

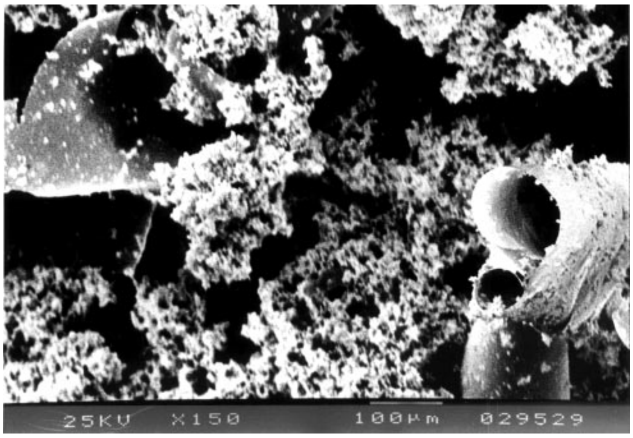

Fig. 4 SEM of Pd_4Se obtained from $[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$ in refluxing xylene.

To prepare large quantities of palladium chalcogenides, a large amount of the 2-methylallylpalladium precursor (100–500 mg) was heated in a furnace under a dry flowing argon atmosphere at a temperature where they start decomposing (as shown by TG curves) or refluxed in xylene for 30–60 min. Palladium chalcogenides obtained from all the three routes (*i.e.* TG, furnace decomposition, or by refluxing in xylene) show similar X-ray diffraction patterns indicating the formation of the same product in each case. Furthermore their X-ray powder diffraction patterns (Table 4; Fig. 3) compare well with the patterns reported for standard compounds.[24] The elemental

Table 4 X-Ray powder pattern data for palladium chalcogenides, obtained from allylpalladium complexes: observed *d*-values (Å) (intensity)

	$[Pd_2(\mu\text{-}SBu^t)(\eta^3\text{-}C_4H_7)_2]$ $\rightarrow Pd_4S$	$[Pd_2(\mu\text{-}SC_6F_5)_2(\eta^3\text{-}C_4H_7)_2]$ $\rightarrow Pd_4S$	$[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_4H_7)_2]$ $\rightarrow Pd_4S$	$[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$ $\rightarrow Pd_4Se$	$[Pd_2(\mu\text{-}TePh)_2(\eta^3\text{-}C_4H_7)_2]$ $\rightarrow Pd_3Te_2$
1	2.787 (11.6)	2.554 (55.0)	2.550 (83.2)	2.608 (25.0)	2.30 (100.0)
2	2.555 (69.4)	2.449 (48.1)	2.442 (33.5)	2.476 (44.4)	2.125 (15.2)
3	2.447 (28.4)	2.284 (93.6)	2.281 (100.0)	2.364 (37.7)	1.665 (10.8)
4	2.321 (20.2)	2.202 (100.0)	2.209 (96.5)	2.331 (100.0)	1.606 (10.8)
5	2.283 (79.5)	2.112 (57.4)	2.105 (49.2)	2.233 (87.9)	1.597 (10.8)
6	2.207 (100.0)	1.769 (28.3)	1.877 (25.9)	2.155 (82.1)	1.525 (10.0)
7	2.113 (60.0)	1.4559 (17.6)	1.762 (24.1)	1.915 (14.0)	
8	1.885 (10.0)	1.372 (16.3)	1.502 (20.8)	1.793 (21.1)	
9	1.806 (9.51)	1.355 (16.3)	1.450 (20.8)	1.765 (14.9)	
10	1.766 (15.3)		1.414 (19.2)	1.647 (7.91)	
11	1.748 (9.51)		1.371 (19.2)	1.582 (12.54)	
12	1.622 (5.06)			1.543 (7.34)	
13	1.553 (9.00)			1.480 (7.91)	
14	1.456 (8.51)			1.464 (6.78)	
15	1.417 (4.34)			1.401 (7.91)	
16	1.399 (4.34)				
17	1.374 (8.51)				

analyses revealed that there was considerable carbon contamination for the products obtained from SC_6F_5 or SBu^t bridged 2-methylallylpalladium complexes. The EPh bridged 2-methylallylpalladium complexes showed the least carbon contamination (~0.5%). The surface morphology of some of the palladium chalcogenides was studied by the SEM technique. The scanning electron micrographs (Fig. 4) taken at different resolutions of Pd_4S (from $[Pd_2(\mu\text{-}SBu^t)_2(\eta^3\text{-}C_4H_7)_2]$) and Pd_4Se (from $[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$) showed that these materials are polycrystalline in nature.

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