Synthesis and reactions of some sulfur ylide complexes of palladium

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Abstract

The iodo-bridged sulfur ylide complex $[Pd(\mu\text{-}I)((CH_2)_2(SO)(CH_3))]_2$ (**1**) when treated with dithiolates, acetylacetone and various Lewis bases gave $[Pd((CH_2)_2\text{-}(SO)(CH_3))(S \sim S)]$ $(S \sim S = S_2CN(C_2H_5)_2,\ S_2COC_2H_5$ and $S_2P(OC_2H_5)_2),$ $[Pd((CH_2)_2(SO)(CH_3))(acac)]$ (acac = acetylacetonate) and $[PdI((CH_2)_2(SO)\text{-}(CH_3))(base)]$ (base = PPh_3, $P(OMe)_3$, $P(OPh)_3$ and C_5H_5N). In the presence of a phase transfer catalyst (PTC), the reaction rates and yields were greatly increased. Reaction of several related sulfur ylide complexes with I_2, HI or aqueous NaOH gave **1**. The single crystal structure of $[Pd((CH_2)_2(SO)(CH_3))_2]$ was determined (orthorhombic, *Pbcn*, *a* 13.379(2), *b* 8.081(1), *c* 9.048(2) Å, *V* 978.2 Å³, *Z* = 4). The compound has a rather long Pd–CH₂ bond (2.096(1) Å, mean).

Introduction

Metal sulfur ylide complexes were normally prepared in aprotic solvents [1]. In a previous report [2] we described the synthesis of sulfur ylide complexes by the phase transfer technique, a rarely used method [3]. Subsequently we found that some interesting metal complexes of sulfoxonium ylide could be prepared in aqueous solution [4]. Our continuing interest in metal ylide complexes, especially with the application of the phase transfer technique in their synthesis, has led us to study the reactions of these complexes, as made in our laboratory. One of the compounds studied in detail has been the iodo-bridged palladium dimer, $[Pd(\mu\text{-}I)((CH_2)_2(SO)(CH_3))]_2$ (**1**), which was obtained in almost quantitative yield by a simple technique developed in our laboratory. In this paper we also describe an X-ray diffraction study of $[Pd((CH_2)_2(SO)(CH_3))_2]$ which contains two bidentate sulfoxonium ylides.

Experimental

Infrared spectra were recorded on a Beckman Acculab TM1 spectrometer in KBr pellets. The ^{1}H NMR spectra were recorded on a Varian EM360 spectrometer. Chemical shifts are downfield relative to TMS standard. Melting points were measured on a Fisher–Johns Melting Point Apparatus. Elemental analyses were carried out by Taipei Instrumentation Center, Taiwan. The compounds 1, $[PdI((CH_2)(SO)(CH_3)_2))((CH_2)_2(SO)(CH_3))]$ (2), and $[Pd((CH_2)_2(SO)(CH_3))-((CH_2)(SO)(CH_3)_2)_2]I$ (3) were prepared by the methods developed in our laboratory [4]. $[Pd((CH_2)_2(SO)(CH_3))_2]$ (4) was prepared according to our previous work [4] but was modified slightly so that a better yield was obtained. Compound 1 (1.0 g, 1.5 mmol) and $((CH_3)_3(SO))I$ (0.75 g, 3.4 mmol) were dissolved in 4 ml DMSO. To this yellow solution was added dropwise 5 N aqueous NaOH until the solution became colorless, this was then stirred overnight and 50 ml of water was added. The yield was 53%.

[Pd((CH$_2$)$_2$(SO)(CH$_3$))(S$_2$P(OC$_2$H$_5$)$_2$)] (5)
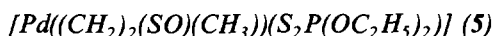
To compound 1 (0.5 g, 7.7×10^{-5} mol) suspended in 20 ml CH_2Cl_2 was added $NH_4S_2P(OC_2H_5)_2$ (0.034 g, 1.67×10^{-4} mol). After stirring the mixture for 10 min, the yellow suspension went into solution and some white solid was precipitated. The solution was stirred for a further hour, and then washed three times with water. The solvent was removed and the residue was recrystallized from n-hexane/CH_2Cl_2. White needle-like crystals were obtained (0.037 g, 63% yield). When n-Bu$_4$NI (0.01 g, 2.7×10^{-5} mol) was added to the above reaction mixture, the yellow suspension dissolved within 5 min. The final yield was 85% (0.05 g); m.p. 88°C. Anal. Found: C, 22.1; H, 4.4. $C_7H_{17}O_3S_3Pd$ calc: C, 22.0; H, 4.5%. IR ν(SO) 1187 cm^{-1}. ^{1}H NMR 4.12(q of d, 4H, ^2J(H, H) 7 Hz, ^3J(P, H) 10 Hz, OCH$_2$), 3.45(t, 3H, ^4J(H, H) 1.8 Hz, SCH$_3$), 1.8–3.3(2 sets of m, 4H, SCH$_2$), 1.32(t, 6H, ^2J(H, H) 7 Hz, CH$_3$) ppm.

[Pd((CH$_2$)$_2$(SO)(CH$_3$))(S$_2$COC$_2$H$_5$)] (6)
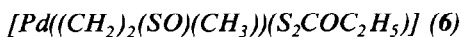
This compound was prepared in a way similar to that for 5. When no phase transfer catalyst (PTC) was added, the yellow solid 1 dissolved within 15 min and 0.039 g (79% yield) of 6 was isolated. In the presence of n-Bu$_4$NI, the solution went clear after 6 min and 0.044 g of 6 (90% yield) was obtained. After recrystallization, light yellow needle-like crystals were obtained; m.p. 136°C. Anal. Found: C, 22.8; H, 3.8. $C_6H_{12}O_2S_3Pd$ calc: C, 22.6; H, 3.8%. IR ν(SO) 1168 cm^{-1}. ^{1}H NMR (CDCl$_3$) 4.60(q, 2H, ^2J(H, H) 7 Hz, CH$_2$), 3.43(t, 3H, ^4J(H, H) 1.8 Hz, SCH$_3$), 1.87–3.24(2 sets m, 4H, SCH$_2$), 1.42(t, 3H, ^2J(H, H) 7 Hz, CH$_3$) ppm.

[Pd((CH$_2$)$_2$(SO)(CH$_3$))(S$_2$CN(C$_2$H$_5$)$_2$)] (7)
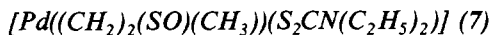
This compound was prepared in a way similar that for 5. Without PTC, a 56% yield (0.030 g) was obtained. In the presence of n-Bu$_4$NI, 83% yield (0.044 g) was obtained. The compound forms golden needles after recrystallization; m.p. 115°C. Anal. Found: C, 27.7; H, 4.9; N, 4.0. $C_8H_{17}NOS_3Pd$ calc: C, 27.8; H, 4.9; N, 4.1%. IR ν(SO) 1175 cm^{-1}. ^{1}H NMR (CDCl$_3$) 3.73(q, 4H, ^2J(H, H) 7 Hz, CH$_2$), 3.46(t, 3H, ^4J(H, H) 1.8 Hz, SCH$_3$) 1.87–3.13 (2 sets m, 4H, SCH$_2$), 1.23(t, 6H, ^2J(H, H) 7 Hz, CH$_3$) ppm.

[Pd((CH₂)₂(SO)(CH₃))(acac)] (8)

[Pd((CH$_2$)$_2$(SO)(CH$_3$))(acac)] (8)

To compound **1** (0.05 g, 7.7×10^{-5} mol) and 0.02 ml Hacac (1.93×10^{-4} mol) in 20 ml CH_2Cl_2 was added 0.05 N NaOH solution (20 ml). The two-phase solution was stirred for 50 min before it went clear. After stirring for another 1 h, the organic layer was separated and washed four times with water. The organic solution was then dried under vacuum. The pale yellow residue was washed with ether and recrystallized from n-hexane/CH_2Cl_2 yielding 0.033 g (72% yield) of **8**. When 0.01 g (2.71×10^{-5} mol) of n-Bu$_4$NI was added to the solution, it became clear within 10 min. Addition of 18-crown-6 ether with KOH gave a similar result. The yields for the latter two reactions were 90% (0.04 g); m.p. 128°C (decomposed). Anal. Found: C, 32.7; H, 4.9. $C_8H_{14}O_3SPd$ calc: C, 32.4; H, 4.7%. IR ν(SO) 1177 cm^{-1}. ^{1}H NMR (CDCl$_3$) 5.3(s, 1H, CH), 3.5(t, 3H, ^4J(H, H) 1.8 Hz, SCH$_3$), 1.8–3.0(2 sets m, 4H, SCH$_2$), 1.91(s, 6H, CCH$_3$) ppm.

[PdI((CH$_2$)$_2$(SO)(CH$_3$))(PPh$_3$)] (9)

To compound **1** (0.1 g, 1.54×10^{-4} mol) in 20 ml CH_2Cl_2 was added PPh$_3$ (0.08 g, 3.08×10^{-4} mol). The resultant solution was stirred for 1 h. The solvent was then removed in vacuum. The yellow residue was washed three times with ether. Recrystallization from n-hexane/CH_2Cl_2 gave yellow crystals (0.64 g (91% yield)), which were identified as compound **9** by comparison of its IR and ^{1}H NMR spectra, m.p. and elemental analysis with the authentic compound.

[PdI((CH$_2$)$_2$(SO)(CH$_3$))(P(OMe)$_3$)] (10)

This compound was prepared by the method analogous to that for **9**, but was recrystallized from ethanol, yielding yellow needle-like crystals. Yield, 85% (0.117 g); m.p. 132°C (decomposed). Anal. Found: C, 16.1; H, 3.6. $C_6H_{16}IO_4PSPd$ calc: C, 16.1; H, 3.6%. IR ν(SO) 1202 cm^{-1}. ^{1}H NMR (CDCl$_3$) 3.75(d, 9H, ^3J(P, H) 12 Hz, OCH$_3$), 3.32(t, 3H, ^4J(H, H) 1.8 Hz, SCH$_3$), 1.95–3.47(m, 4H,SCH$_2$) ppm.

The following two compounds were prepared by the method similar to that described for **10**.

[PdI((CH$_2$)$_2$(SO)(CH$_3$))(P(OPh)$_3$)] (11)

Color, yellow. Yield 80%; m.p. 139°C (decomposed). Anal. Found: C, 39.9; H, 3.3. $C_{21}H_{22}IO_4PSPd$ calc: C, 39.7; H, 3.5%. IR ν(SO) 1205 cm^{-1}. ^{1}H NMR (CDCl$_3$) 7.0–7.6(m, 30H, C$_6$H$_5$), 2.5(t, 3H, ^4J(H, H) 1.8 Hz, SCH$_3$), 1.1–3.47(m, 4H, SCH$_2$) ppm.

[PdI((CH$_2$)$_2$(SO)(CH$_3$))(C$_5$H$_5$N)] (12)

Color, yellow. Yield 86%; m.p. 165°C (decomposed). Anal. Found: C, 23.9; H, 3.0; N, 3.6. $C_8H_{12}INOSPd$ calc: C, 23.8; H, 3.0; N, 3.5%. IR ν(SO) 1187 cm^{-1}. ^{1}H NMR (CDCl$_3$) 7.3–8.9(m, 5H, C$_5$H$_5$N), 3.59(t, 3H, ^4J(H, H) 1.8 Hz, SCH$_3$), 1.9–3.5(m, 4H, SCH$_2$) ppm.

Reaction of [Pd((CH$_2$)$_2$(SO)(CH$_3$))$_2$] with HI

To compound **4** (0.2 g, 6.9×10^{-4} mol) in 20 ml CHCl$_3$ was added dropwise to aqueous HI (0.09 ml, 7.6 M), and immediately a yellow precipitation formed. After 1 h the solid was filtered and washed with water, alcohol, and then ether. The solid was identified as compound **1** by comparison of its IR, ^{1}H NMR spectra and m.p., with the authentic compound.

Reaction of [PdI((CH₂)(SO)(CH₃)₂)((CH₂)₂(SO)(CH₃))] and [Pd((CH₂)₂-(SO)(CH₃))((CH₂)(SO)(CH₃)₂)₂]I with HI

These two reactions were carried out under the same conditions as the previous experiment, except that the solvent used in this case was DMSO. The products isolated were identified as **1**.

[Pd(μ-Cl)((CH₂)₂(SO)(CH₃))]₂ (13)

Compound **4** (0.1 g, 3.5×10^{-4} mol) in 20 ml CHCl₃ was treated with HCl (12 M, 0.064 ml), after stirring for 20 min, some yellow solid was separated. Stirring was continued for a further 24 h. The solid was then filtered and washed with H₂O. Recrystallization from DMSO/H₂O gave needle-like crystals. Yield 50%. Anal. Found: C, 15.6; H, 3.1. $C_6H_{14}O_2S_2Cl_2Pd_2$ calc: C, 15.5; H, 3.9%. IR ν(CO) 1192 cm^{-1}. ^{1}H NMR (DMSO-d_6) 3.53(t, 3H, ^4J(H, H) 1.8 Hz, SCH₃) 1.83–3.23(m, 4H, SCH₂) ppm.

Reaction of [Pd((CH₂)₂(SO)(CH₃))]₂ with I₂

To a solution of compound **4** (0.29 g, 6.9×10^{-4} mol) in 30 ml CHCl₃, was added I₂ (0.359 g, 1.4×10^{-3} mol) in 15 ml CCl₄. After 5 min the solution turned to golden yellow and a yellow solid precipitated. Stirring was continued for 30 min. The solid was filtered and washed with CHCl₃. The yellow solid was formulated to be Pd((CH₂)₂(SO)(CH₃))₂I₂ (Found: C, 13.8; H, 2.6. $C_6H_{14}O_2I_2S_2Pd$ calc: C, 13.3; H, 2.6%) It decomposed in air within 2 h. It decomposed immediately in DMSO solution. The compounds isolated from both the filtrate and the decomposed product were found to be compound **1**.

Reaction of [PdI((CH₂)(SO)(CH₃)₂)((CH₂)₂(SO)(CH₃))] with NaOH

To compound **2** (0.2 g, 4.8×10^{-4} mol) in 3 ml DMSO was added dropwise 5 N NaOH 0.05 ml. The resultant solution was set aside for 2 d. The solid thus obtained was found to be compound **1**.

Crystal data for [Pd((CH₂)₂(SO)(CH₃))₂]

[Pd((CH₂)₂(SO)(CH₃))₂], mol. wt. 288.4, orthorhombic, *Pbcn*, *a* 13.379(2), *b* 8.081(1), *c* 9.048(2) Å, *V* 978.2 Å³, *Z* = 4, D_c 1.96 g/cm³, D_m 1.92 g/cm³, λ(Mo-K_α) = 0.7093 Å, μ 22.38 cm^{-1}. $F(000)$ = 576.

Collection and reduction of X-ray data

A black crystal of dimensions $0.2 \times 0.4 \times 0.7$ mm was used for data collection. Diffraction data were collected on a CAD4 diffractometer using graphite-mono-chromated Mo-K_α radiation. Unit cell dimensions were determined from a least squares refinement of 24 carefully centered reflections ($27.98 < 2\theta < 40.88°$). Intensity data within $2\theta < 70°$ were collected at scan speeds between 20/3 to 20/23 deg/min by use of ω–2θ scan techniques, and a scan range calculated from the expression $\Delta\theta = 2(0.7 + 0.35 \tan \theta)°$. Stationary background measurements were taken before and after each scan for a time equal to quarter of the scan time. Variation of three standard reflections monitored every two hours < 3%. After correction for background, the intensities were reduced to F and $\sigma(F)$ from counting statistics, and weights were assigned as $w = 1/\sigma^2(F)$. Of 2469 total reflections, 1294 having $I > 2.5\sigma(I)$ were considered observed. Intensity data were

Table 1

Positional and thermal parameters ^{a} of $[Pd((CH_2)_2SO(CH_3))_2]$

Atom	x	y	z	B_{iso}
Pd	0.00000	0.00000	0.00000	2.02(1)
S	0.11172(2)	0.27266(3)	0.05860(3)	2.31(1)
O	0.1448(1)	0.4126(1)	0.1469(1)	3.37(5)
C(1)	−0.0114(1)	0.2590(1)	0.0048(2)	2.69(5)
C(2)	−0.1221(1)	−0.0764(1)	−0.1274(2)	2.46(6)
C(3)	0.1813(2)	0.2716(2)	−0.1079(2)	4.03(9)
H(11)	−0.0490(7)	0.2974(14)	0.0804(10)	2.9(3)
H(12)	−0.0273(8)	0.3358(13)	−0.0707(10)	4.2(3)
H(21)	−0.0974(8)	−0.0663(10)	−0.2120(9)	1.5(2)
H(22)	−0.1825(7)	−0.0388(11)	−0.1232(11)	2.0(2)
H(31)	0.1727(11)	0.3552(17)	0.8523(16)	5.2(5)
H(32)	0.2430(11)	0.2597(19)	−0.0793(15)	7.7(5)
H(33)	0.1741(14)	0.1766(25)	−0.1838(19)	13.8(7)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	2.52(1)	2.21(1)	2.96(1)	−0.16(1)	−0.14(1)	0.14(1)
S	2.86(2)	2.56(1)	3.34(2)	−0.34(1)	0.06(1)	−0.24(1)
O	4.39(5)	3.11(4)	5.28(6)	−0.71(4)	−0.54(5)	−1.11(4)
C(1)	3.07(7)	2.72(5)	4.45(6)	0.20(6)	−0.14(8)	0.24(8)
C(2)	2.72(7)	3.21(6)	3.41(8)	0.26(6)	−0.23(7)	0.12(6)
C(3)	5.50(11)	4.95(10)	4.86(11)	−0.90(9)	2.10(9)	0.42(9)

^{a} Temperature factors $= -2\pi^2(U_{11}hha^{\star}a^{\star} + \ldots + 2U_{12}hka^{\star}b^{\star} + \ldots)$, the U_{ij} values are $\times 100$.

TABLE 2

Bond distances (Å) and angles ($^\circ$) of $[Pd((CH_2)_2SO(CH_3))_2]$

Pd–S	2.7148(3)	Pd–C(1)	2.099(1)	Pd–C(2)	2.093(1)
Pd–C(2)	2.093(1)	S–O	1.453(1)	S–C(1)	1.722(1)
S–C(2)	1.709(1)	S–C(3)	1.771(1)	C(1)–H(11)	0.904(9)
C(1)–H(12)	0.947(9)	C(2)–H(21)	0.838(8)	C(2)–H(22)	0.864(9)
C(3)–H(31)	0.77(1)	C(3)–H(32)	0.87(1)	C(3)–H(33)	1.03(2)
C(1)–Pd–C(1)	180.00(0)	C(1)–Pd–C(2)	104.40(4)		
C(1)–Pd–C(2)	75.60(4)	C(1)–Pd–C(2)	75.60(4)		
C(1)–Pd–C(2)	104.40(4)	C(2)–Pd–C(2)	180.00(0)		
O–S–C(1)	119.79(5)	O–S–C(2)	119.78(5)		
O–S–C(3)	108.13(7)	C(1)–S–C(2)	96.97(5)		
C(1)–S–C(3)	105.21(8)	C(2)–S–C(3)	105.22(8)		
Pd–C(1)–S	90.01(5)	Pd–C(1)–H(11)	113.5(6)		
Pd–C(1)–H(12)	130.9(6)	S–C(1)–H(11)	107.2(6)		
S–C(1)–H(12)	112.1(6)	H(11)–C(1)–H(12)	101.3(9)		
Pd–C(2)–S	90.54(5)	Pd–C(2)–H(21)	99.6(6)		
Pd–C(2)–H(22)	127.0(6)	S–C(2)–H(21)	113.0(5)		
S–C(2)–H(22)	112.7(5)	H(21)–C(2)–H(22)	112.0(9)		
S–C(3)–H(31)	108(1)	S–C(3)–H(32)	104.3(8)		
S–C(3)–H(33)	121(1)	H(31)–C(3)–H(32)	112(1)		
H(31)–C(3)–H(33)	109(1)	H(32)–C(3)–H(33)	102(1)		

corrected for Lorentz-polarization effects and absorption by experimental ψ rotation [11].
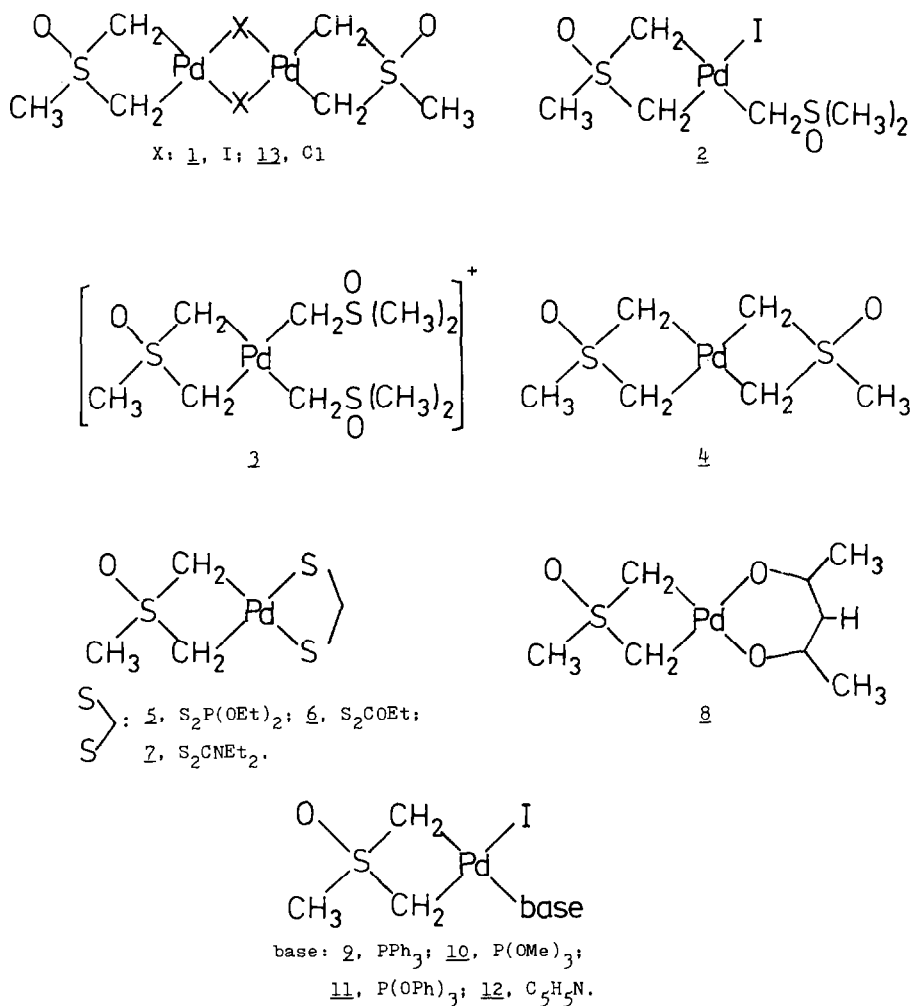
Solution and refinement of structure

All calculations were carried out with the NRCC SDP PDP-11 package [5], and ORTEP from Enraf–Nonius structure determination package [6] on a PDP-11/23 computer. The palladium atom was located from Patterson map, and subsequent heavy-atom Fourier synthesis revealed the position of the non-hydrogen atoms of the complex. The H atoms were located from difference Fourier map. The final least-squares cycle with anisotropic thermal parameters for all non-hydrogen atoms and isotropic parameters for hydrogen atoms gave R and R_w factors of 5.6% and 2.2% respectively. The positional and thermal parameters of all the atoms are given in Table 1. The bond distances and angles are listed in Table 2. Tables of structure factors may be obtained from the authors.

Results and discussion

Reaction of **1** with soft chelating ligands such as sodium 1,1-dithiolates gave stable mixed-ligand compounds (5–7) which contain a bidentate sulfoxonium ylide and a bidentate 1,1-dithiolate ligand. All reactions proceeded very smoothly in chloroform solution. The reaction of **1** with NaS_2COEt ($Et = C_2H_5$) was followed by ^1H NMR spectroscopy. Without PTC, the ratio of complexed to free NaS_2COEt was 8.3 after 2 h. In the presence of n-Bu_4NI (10% molar ratio of NaS_2COEt), the ratio of complexed to uncomplexed NaS_2COEt was 12.6 (after 2 h). Prolonged reaction did not increase the yield. An analogous compound, $[Ni((CH_2)_2(SO)(CH_3))(SacSac)]$, reported by Dudis et al. was prepared through a different route [7]. The reaction of **1** with diketone under basic conditions gave **8**. Although PTC is not required for the above reaction, addition of PTC increased the reaction rate drastically. To our surprise, **1** did not react with oxalate anion, not even in the presence of PTC in various solvent systems. When **1** was treated with bases such as phosphine or pyridine, compounds formulated as $[PdI((CH_2)_2(SO)(CH_3))(base)]$ (9–12) were obtained. One compound, $[PdI((CH_2)_2(SO)(CH_3))(PPh_3)]$, which has been reported previously by us [2], was prepared by phase transfer catalyzed reaction of $[PdCl_2(PPh_3)_2)]$ with $((CH_3)_3(SO))I$ and NaOH (Scheme 1).

Fackler et al. [8] suggested that a chelating ylide might have the ability to stabilize the high oxidation state of metals. Thus we attempted the oxidation of **4** with CH_3I and I_2. Compound **4** was found to be unreactive toward CH_3I but reactive toward I_2. After reaction of **4** with I_2, we isolated an unstable yellow compound and the pale yellow compound **1**. The former slowly turned to brown in air. The final decomposed product was found to be **1**.

We have also carried out the reaction of HI and HCl with various sulfur ylide compounds such as **2**, **3**, and **4**. All the reactions with HI gave **1**, however, reaction of **4** with HCl gave a new compound $[Pd(\mu\text{-}Cl)((CH_2)_2(SO)(CH_3))]_2$ (**13**), which is the chloro-analog of **1**. Attempts to prepare **13** directly by treating $(NH_4)_2PdCl_4$ with $((CH_3)_3(SO))Cl$ and NaOH under various conditions were unsuccessful. In all cases black metallic powder was formed. In one case a small amount of **13** was obtained.

Scheme 1

$$X: \underline{1}, I; \underline{13}, Cl$$

(2)

(3)

(4)

$$\underline{5}, S_2P(OEt)_2; \underline{6}, S_2COEt; \underline{7}, S_2CNEt_2.$$

(8)

base: $\underline{9}$, PPh_3; $\underline{10}$, $P(OMe)_3$; $\underline{11}$, $P(OPh)_3$; $\underline{12}$, C_5H_5N.

It occurred to us that **2** is both a bidentate and a monodentate sulfoxonium ylide, thus removal of a methyl proton from the monodentate ylide should convert **2** to **4**. In our hands the reaction of NaOH with **2**, however, gave **1** instead of **4**.

Thus treating HX and NaOH with various sulfoxonium ylide compounds suggest that the monodentate sulfoxonium ylide is unstable toward both acids and bases.

Crystal and molecular structure

The structural study of $[Pd((CH_2)_2(SO)(CH_3))_2]$ presents the first example of a homoleptic complex containing two chelated sulfoxonium double-ylides (Fig. 1). The geometry about the palladium atom is distorted square-planar. The molecule has a center of inversion about the palladium atom. The four-membered ring formed by the chelated double ylide is puckered (Fig. 2). The dihedral angle between the C(1)-Pd-C(2) plane and the C(1)-S(1)-C(2) plane is 22.19°. The sulfur

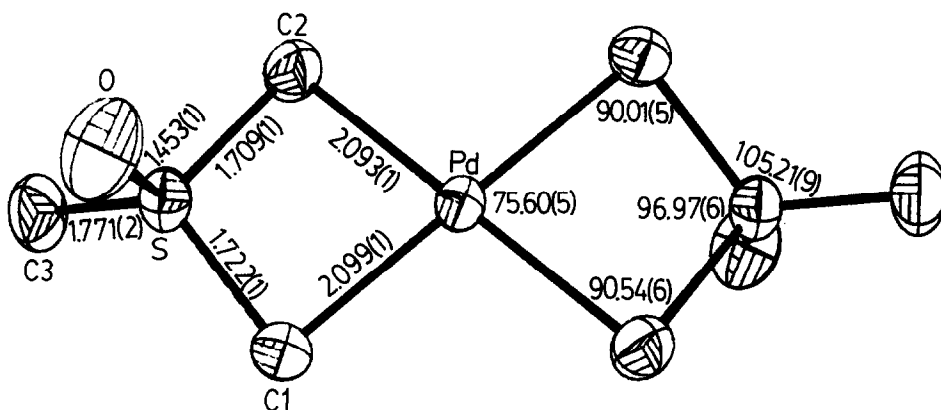Fig. 1. ORTEP drawing of [Pd((CH$_2$)$_2$(SO)(CH$_3$))$_2$] with labelling scheme and selected bond parameters.

atom is 0.53 Å above the C(1)-Pd-C(2) plane. This value is very close to the 0.55 Å found in [Pd((CH$_2$)$_2$(SO)(CH$_3$))((CH$_2$)(SO)(CH$_3$)$_2$)$_2$]I [4]. The two CH$_3$ groups are in the axial positions, such that the compound adopts the chair conformation.

Two geometric isomers are possible for this compound. One isomer with two oxygen atoms in the *cis* position and the other with two oxygen atoms in a *trans* position. The structure we arrived at is a *trans* isomer which is required for centrosymmetric geometry. When this compound was freshly precipitated from DMSO only one set of ^{1}H NMR signals was observed in CDCl$_3$. The IR spectrum of the freshly precipitated solid and that of the solid obtained after recrystallization were identical. Thus the *trans* isomer was obtained directly from the reaction
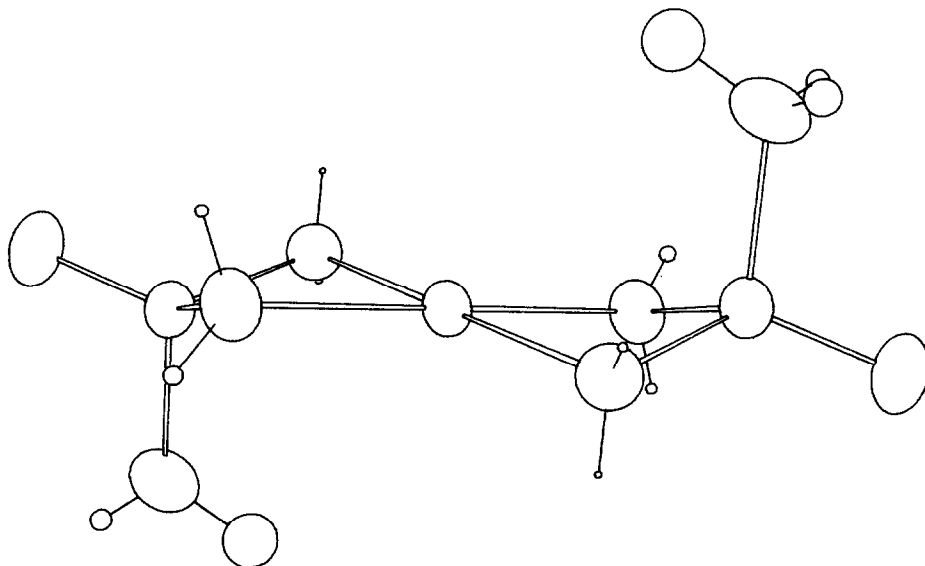

Fig. 2. Different view of [Pd((CH$_2$)$_2$(SO)(CH$_3$))$_2$] illustrating the puckered conformation.

solution and not from the isomerization of *cis* isomer. In spite of the data we were unable to justify the reason for the *trans* configuration, since the *trans* isomer seems the more sterically favored.

In this compound the S–C(3) distance (1.771(2) Å) is longer than the ylide type S–CH_2 distances (1.721(1), 1.709(1) Å), but is slightly shorter than ordinary S–C bond lengths found in organic sulfonium salts (1.78–1.84 Å) [9]. The averaged Pd–CH_2 distance (2.096(1) Å) is longer than that found in [Pd(CH_2C(=NNMe_2)C(CH_3)$_3$)(acac)]$^+$ (1.991 Å) [10]. Thus the structural results of our compound suggest that the ylidic character is partly retained upon complexation and that the metal–ylide bond might be weaker than normal metal–carbon bonds.

Acknowledgement

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