

THE SYNTHESIS OF SULFUR YLIDE COMPLEXES OF PALLADIUM, ZINC AND COPPER IN WATER

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(Received March 24th, 1986; in revised form May 20th, 1986)

Summary

Various sulfur ylide complexes have been prepared by a simple technique, using simple starting materials, in water. Thus in aqueous solution, the sulfur ylide complexes $[\text{Pd}(\mu\text{-I})((\text{CH}_2)_2(\text{SO})(\text{CH}_3))]_2$ and $\text{PdI}[(\text{CH}_2)(\text{SO})(\text{CH}_3)_2][(\text{CH}_2)_2(\text{SO})(\text{CH}_3)]$ were obtained by the reaction of $(\text{NH}_4)_2\text{PdCl}_4$ with $[(\text{CH}_3)_3(\text{SO})\text{I}]$ in the presence of NaOH in water. Further reactions of the first product with $[(\text{CH}_3)_3(\text{SO})\text{I}]$ in basic solution gave $\text{Pd}[(\text{CH}_2)_2(\text{SO})(\text{CH}_3)]_2$ and $[\text{Pd}((\text{CH}_2)(\text{SO})(\text{CH}_3)_2)(\text{CH}_2)_2(\text{SO})(\text{CH}_3)]\text{I}$ under various conditions. Reactions of ZnCl_2 and CuCl with $[(\text{CH}_3)_3(\text{SO})\text{I}]$ in NaOH solution afforded compounds containing nonstoichiometric amounts of sulfur ylide. One of the palladium compounds, $\text{PdI}[(\text{CH}_2)(\text{SO})(\text{CH}_3)_2][(\text{CH}_2)(\text{SO})(\text{CH}_3)]$, was subjected to X-ray, single crystal structure, analysis. The compound crystallizes in the space group $P2_1/c$ with a 11.033(4), b 11.981(5), and c 9.407(3) Å, β 103.23(1)°, $Z = 4$. Final R was 0.064 for 1870 observed reflections. The compound contained a monodentate sulfoxonium ylide and a bidentate sulfoxonium double-ylide.

Introduction

For the last twenty years, ylides have been known to be versatile ligands for transition metals [1]. The phosphorus ylide is the best known, and the most extensively studied. The relatively unknown chemistry of sulfur ylide complexes has been reviewed by Weber [2].

Normally ylide complexes are prepared in non-protonic solvents. Only when ylides are stabilized by functional groups such as $\text{C}(\text{O})\text{Ph}$ can the ylide complexes be prepared in protonic solvents [3]. In our previous work [4], we observed the formation of nonstabilized sulfur ylide complexes using the "Phase Transfer Cataly-

sis Technique.” In that method sulfur ylide complexes of palladium were prepared by the reaction of palladium starting materials in an organic solvent with the sulfur ylide precursor, trimethylsulfoxonium iodide in an aqueous NaOH solution in the presence of a phase transfer catalyst. The next logical question was: if we begin with a water soluble, metal starting compound, would it not be possible to prepare sulfur ylide complexes in an aqueous solvent simply by mixing the metal compounds, sulfur ylide precursor-sulfoxonium salt, and NaOH in water? Such a formation of sulfur ylide complexes in water may be relevant to Cohen’s proposal [5] that the biosynthesis of presqualene pyrophosphate is possible through a metabolic pathway involving sulfur ylide complexes of copper formed under physiological conditions. One of the physiological conditions is that the reaction medium must be water.

In this article we wish to report for the first time the synthesis in water of some sulfur ylide complexes of palladium. We also report our attempts to synthesize the sulfur ylide complexes of zinc and copper in water.

Experimental section

Infrared spectra were measured on a Beckman Acculab TM1 spectrometer in KBr pellets. NMR spectra were recorded on a Varian EM-360 spectrometer. Conductivities were measured using the WPA CMD 400 digital conductivity meter. Trimethylsulfoxonium iodide was prepared by the reaction of dimethylsulfoxide and methyl iodide [6]. All other chemicals were purchased and were used without further purification. Elemental analyses were done by the Chung Shung Research Center, Taiwan.

$[Pd(\mu-I)((CH_2)_2(SO)(CH_3))]_2$ (1)

Trimethylsulfoxonium iodide (1.54 g, 7.0 mmol) in 60 ml 0.3 *N* (14.0 mmol) NaOH was stirred for 10 min and was then added to 20 ml of aqueous $(NH_4)_2PdCl_4$ solution (0.8 g, 2.8 mmol). The solution turned from brown to orange and then became colorless in 3 h. After stirring for 1 d, insoluble material was filtered out and the solution was set aside. A yellow solid, formed after standing for 2 d, was collected with 93% (0.85 g) yield. Anal. Found: C, 11.4; H, 2.2; C_3H_7IOPdS calcd.: C, 11.1; H, 2.2%.

$PdI[(CH_2)(SO)(CH_3)_2][(CH_2)_2(SO)(CH_3)]$ (2)

This compound was prepared by a method similar to 1 except that the molar ratio of trimethylsulfoxonium iodide to $(NH_4)_2PdCl_4$, was increased to 3.5. The pale yellow crystalline compound formed had an ~ 81% (0.236 g) yield. Anal. Found: C, 17.3; H, 3.6; $C_6H_{15}IO_2PdS_2$ calcd.: C, 17.3; H, 3.6%. IR $\nu(SO)$ 1192, 1150 cm^{-1} . 1H NMR (DMSO- d_6) δ 3.55 (s, 6H, monodentate CH_3), 3.45 (t, 3H, $^4J(H, H)$ 1.8 Hz, bidentate CH_3), 2.56 (s, 2H, monodentate CH_2), 1.69–2.18 (m, 4H, bidentate CH_2) ppm.

$Pd[(CH_2)_2(SO)(CH_3)]_2$ (3)

Compound 1 (0.1 g, 0.15 mmol) and trimethylsulfoxonium iodide (0.075 g, 0.34 mmol) were dissolved in 2 ml DMSO. To this yellow solution, aqueous NaOH (0.83 *N* \times 0.9 ml, 0.75 mmol) was added dropwise within 5 min. During this period the yellow colored solution turned colorless and a white solid precipitated out. After

stirring for 2 h, the white solid was filtered and collected. Recrystallization from CHCl_3 gave white needle-like crystals with a 40% (0.035 g) yield. The solid decomposes in air in about a week. Anal. Found: C, 25.0; H, 4.8; $\text{C}_6\text{H}_{14}\text{O}_2\text{PdS}_2$ calcd.: C, 25.0; H, 4.9%. IR (KBr) $\nu(\text{SO})$ 1150 cm^{-1} . $^1\text{H NMR}$ (CDCl_3) δ 3.25 (t, $^4J(\text{H}, \text{H})$ 1.8 Hz, 3H, CH_3), 1.88–2.78 (2 sets of m, 4H, CH_2) ppm.

[Pd((CH₂)(SO)(CH₃)₂)₂((CH₂)₂(SO)(CH₃))]I (4)

Compound 1 (0.1 g, 0.15 mmol) and trimethylsulfoxonium iodide (0.15 g, 0.68 mmol) in 2 ml DMSO were mixed with aqueous NaOH (0.6 N \times 1.4 ml, 0.84 mmol) and stirred for 2 h. The white precipitate was filtered and washed three times with 5 ml CHCl_3 . The yield of the white powder was 86 mg (55%). The product was soluble in DMSO. Anal. Found: C, 21.0; H, 4.6; I, 24.7. $\text{C}_9\text{H}_{23}\text{IO}_3\text{PdS}_3$ calcd.: C, 21.2; H, 4.6; I, 24.9%. IR (KBr) $\nu(\text{SO})$ $1215, 1170\text{ cm}^{-1}$. $^1\text{H NMR}$ ($\text{DMSO}-d_6$) δ 3.38 (t, $^4J(\text{H}, \text{H})$ 1.8 Hz, 3H, bidentate CH_3), 3.43 (s, 12H, monodentate CH_3), 1.75–2.82 (2 sets of m, 4H, bidentate CH_2), 2.5 (s, 4H, monodentate CH_2) ppm. Molar conductivity (DMSO, $8.8 \times 10^{-4}\text{ M}$) $42.8\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$.

Reaction of CuCl with [(CH₃)₃(SO)]I in NaOH solution

CuCl (0.5 g, 5.0 mmol) and $[(\text{CH}_3)_3(\text{SO})]\text{I}$ (2.2 g, 10.0 mmol) were dissolved in 20 ml H_2O under N_2 gas. NaOH (0.8 N, 12 ml) was added to the solution within 10 min. After stirring for another 5 min, the grass-green solid was filtered, washed with H_2O and ethanol and was dried under vacuum. The yield was $\sim 50\%$. The product was found to be insoluble in almost all solvents. $\nu(\text{SO})$ 1200 cm^{-1} . Anal. Found: C, 2.6; H, 1.3%.

TABLE 1

CRYSTAL DATA FOR $\text{PdI}[(\text{CH}_2)(\text{SO})(\text{CH}_3)_2][(\text{CH}_2)_2(\text{SO})(\text{CH}_3)]$

Formula	$\text{PdIS}_2\text{O}_2\text{C}_6\text{H}_{15}$
Space group	$P2_1/c$
a (Å)	11.033(4)
b (Å)	11.981(5)
c (Å)	9.407(3)
β (°)	103.23(1)
V (Å ³)	1210.47
Cell parameter determination	$12.26 < \theta < 14.76^\circ$ (24 refl)
Z	4
D_m, D_c (g cm^{-3})	2.20 (5), 2.29
Color	pale-yellow
Crystal size (mm)	$0.25 \times 0.4 \times 0.5$
μ (cm^{-1})	43.78
Normalized transmission coeff.	0.775, 1.0
λ (radiation)	Mo-K_α
$\theta/2\theta$ scan range	$1.4 + 0.7 \tan \theta$
$2\theta_{\text{max}}$	50°
No. of reflexions ($I \geq 3\sigma(I)$)	2351, 1870
Weighting	$1/\sigma^2 (F)$
R, R_w	0.064, 0.073
h, k, l	0–13, 0–14, –11–11

TABLE 2

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR PdI[(CH₂)₂(SO)(CH₃)₂][(CH₂)₂(SO)(CH₃)]

Atom	x	y	z	B _{eq}
I	0.6948(1)	-0.59805(9)	0.2858(1)	3.99(2)
Pd	0.8237(1)	-0.5016(1)	0.5298(1)	3.03(2)
S(1)	0.9387(4)	-0.5805(4)	0.7944(4)	3.83(9)
S(2)	0.6471(4)	-0.2969(4)	0.5228(4)	3.55(8)
O(1)	1.045(1)	-0.616(1)	0.905(1)	6.2(3)
O(2)	0.654(1)	-0.325(1)	0.672(1)	5.4(3)
C(1)	0.942(1)	-0.449(1)	0.722(2)	4.1(4)
C(2)	0.902(2)	-0.647(1)	0.630(2)	5.1(4)
C(3)	0.805(2)	-0.584(2)	0.862(2)	4.7(4)
C(4)	0.514(2)	-0.353(1)	0.402(2)	4.6(4)
C(5)	0.629(2)	-0.152(2)	0.503(2)	4.7(4)
C(6)	0.778(2)	-0.334(1)	0.468(2)	3.9(4)

Reaction of ZnCl₂ with [(CH₃)₃(SO)]Cl in NaOH solution

ZnCl₂ (0.405 g, 3.0 mmol), [(CH₃)₃(SO)]Cl (0.8 g, 6.0 mmol), and NaOH (0.8 N, 32 ml) were mixed together. The white precipitate originally formed, slowly dissolved in 10 min. After stirring for 1 d a white solid again precipitated out. The solid was filtered and washed with water. The yield was about 30%. The product was found to be insoluble in almost all solvents. $\nu(\text{SO})$ 1178 cm⁻¹. Anal. Found: C, 7.0; H, 1.24%.

Structure determination and refinement of PdI[(CH₂)₂(SO)(CH₃)][(CH₂)₂(SO)(CH₃)₂]

The diffraction data were collected on a CAD-4 diffractometer at room temperature, the experimental details are given in Table 1 *. The structure was solved by the

TABLE 3

SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°) FOR PdI[(CH₂)₂(SO)(CH₃)₂][(CH₂)₂(SO)(CH₃)]^a

I-Pd	2.671(1)	S(1)-C(1)	1.72(2)
S(2)-C(6)	1.71(2)	S(1)-C(2)	1.70(2)
Pd-C(1)	2.07(2)	S(1)-C(3)	1.74(2)
Pd-C(2)	2.08(2)	S(2)-O(2)	1.427(12)
Pd-C(6)	2.120(15)	S(2)-C(4)	1.77(2)
S(1)-O(1)	1.442(13)	S(2)-C(5)	1.76(2)
I-Pd-C(1)	170.8(5)	O(1)-S(1)-C(2)	120.3(9)
I-Pd-C(2)	96.4(5)	O(1)-S(1)-C(3)	110.2(8)
I-Pd-C(6)	97.3(4)	C(1)-S(1)-C(2)	95.4(9)
C(1)-Pd-C(2)	75.2(7)	O(2)-S(2)-C(5)	108.5(8)
C(1)-Pd-C(6)	90.8(6)	O(2)-S(2)-C(6)	112.2(8)
C(2)-Pd-C(6)	165.7(6)	C(4)-S(2)-C(5)	104.4(8)
C(1)-S(1)-C(3)	105.2(9)	Pd-C(2)-S(1)	90.3(8)
C(2)-S(1)-C(3)	106.1(9)	O(2)-S(2)-C(4)	112.9(9)
C(4)-S(2)-C(6)	110.3(8)	O(1)-S(1)-C(1)	117.8(8)
C(5)-S(2)-C(6)	108.2(9)	Pd-C(6)-S(2)	109.0(9)
Pd-C(1)-S(1)	90.1(7)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

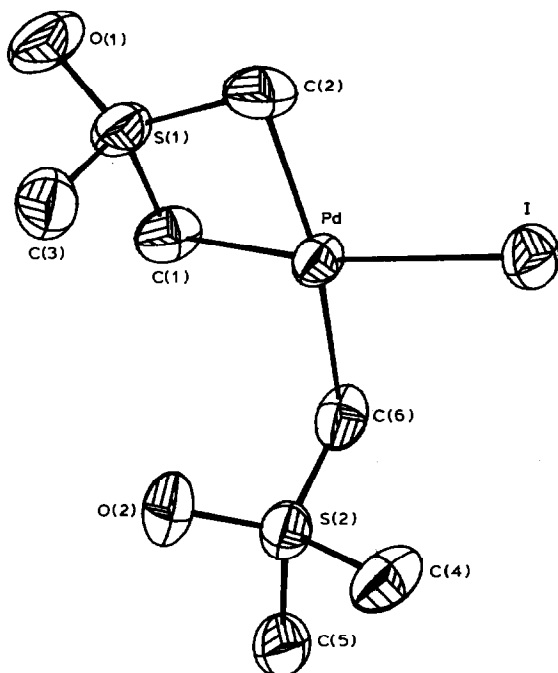


Fig. 1. Molecular structure of $\text{PdI}[(\text{CH}_2)(\text{SO})(\text{CH}_3)_2][(\text{CH}_2)_2(\text{SO})(\text{CH}_3)]$.

heavy atom method with the Pd and I atoms located by a Patterson map. All the non-hydrogen atoms were located in the subsequent Fourier syntheses. The usual least-squares process was used to refine the atomic and thermal parameters based on F_0 . The agreement indices are given in Table 1. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. The final residual map is featureless. Procedures and computing programs used are presented elsewhere [7]. The selected bond lengths and angles are listed in Table 3. The scattering factors and anomalous dispersion corrections were applied according to the International Tables for Crystallography Vol. IV. The molecular structure with labelled atoms of the complex is depicted in Fig. 1.

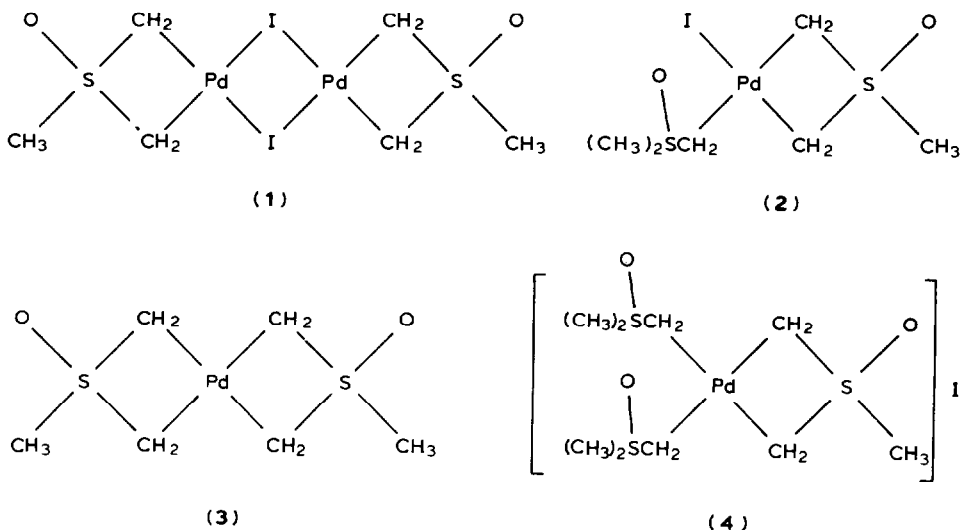
Results and discussion

Preparation and characterization of complexes

Complex $[\text{Pd}(\mu\text{-I})(\text{CH}_2)_2(\text{SO})(\text{CH}_3)]_2$ (**1**) as reported by Bravo et al. [8], was prepared by mixing $(\text{CH}_2)(\text{SO})(\text{CH}_3)_2$ with $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CH}=\text{CH}_2)_2$ in DMSO. The sulfur ylide $(\text{CH}_2)(\text{SO})(\text{CH}_3)_2$ had to be preformed by treating $[(\text{CH}_3)_3(\text{SO})\text{I}]$ with NaH in a dry non aqueous solvent [9]. In our laboratory the same compound can be obtained in high yield from readily accessible starting materials in water. Compound **2** occasionally precipitates out along with compound **1**, in which case,

* All the data are processed by Enraf-Nonius SDP.

recrystallization from warm DMSO is adequate to separate 1 from 2. The molar ratio of $[(\text{CH}_3)_3(\text{SO})]^+ \text{I}^-$ to Pd^{II} affects the yields of 1 and 2. A higher molar ratio (up to 3.5) favors 2 while a lower molar ratio (2.5) favors 1. NaOH also affects the yields of 1 and 2. A NaOH/ Pd^{II} ratio in the range of 5.0–8.0 is usually preferred. At a higher molar ratio (> 12), black metallic palladium was formed. The molar ratio of sulfoxonium iodide to Pd is also an important factor controlling the relative amounts of 3 and 4 formed. A 1/1 molar ratio favors 3, a high molar ratio favors 4.



The ^1H NMR spectrum of 1 was discussed by Bravo et al. [8]. The bidentate sulfur double-ylide has a triplet signal for the methyl protons and two sets of complicated multiplets for the methylene protons. The monodentate sulfur ylide complexes discussed in this work, however, always gave a singlet methyl and a singlet methylene signal. Therefore ^1H NMR spectroscopy has proved to be a good tool to distinguish between monodentate and bidentate ylides of the type considered in this study. For example, ^1H NMR of 2 shows a singlet and a triplet methyl signal, thus indicating both a monodentate and a bidentate sulfur ylide. Originally, it was assumed that compound 2 was a dimeric species with a bridging double-ylide owing to its solubility in DMSO but not in CHCl_3 . However, the structural determination which is discussed below, has proved that this conclusion is incorrect. The ^1H NMR spectrum of 3 shows a triplet CH_3 signal and two multiplets for the CH_2 protons. The spectral pattern is similar to 1. Thus the ^1H NMR spectrum, elemental analysis, and the high solubility in organic solvents are all consistent with two double-ylides bonded to a palladium atom. Compound 4 is a 1:1 electrolyte. The ^1H NMR of 4 shows a singlet and a triplet CH_3 signal. These results, together with the elemental analysis suggest that this compound is ionic and has one bidentate double-ylide and two monodentate ylide ligands.

The $\nu(\text{SO})$ of compounds 1 to 4 deserves some comment. The free trimethylsulfoxonium iodide has $\nu(\text{SO})$ at 1220 cm^{-1} [10]. Compounds 1 and 3 contain only bidentate sulfur ylides and show only one $\nu(\text{SO})$ (1175 , 1150 cm^{-1} , respectively). Compounds 2 and 4 both contain monodentate and bidentate sulfur ylides and there are two $\nu(\text{SO})$ s for each compound (1150 , 1192 and 1170 , 1215 cm^{-1} for 2 and

4). The lower frequency is assigned to the bidentate ylide and the higher frequency one to the monodentate ligand. Thus, $\nu(\text{SO})$ may be a useful way to distinguish a simple-ylide ($< 1180 \text{ cm}^{-1}$) from a double-ylide ($\sim 1190 \text{ cm}^{-1}$).

Reactions of trimethylsulfoxonium iodide in NaOH solution with ZnCl_2 and CuCl afforded non-reproducible results. Different reaction batches gave different C, H content. One of the problems with the reactions involving Zn and Cu is their instant precipitation with OH^- . Thus unlike the polymeric $[\text{M}((\text{CH}_2)_2(\text{SO})(\text{CH}_3))_2]_n$ ($\text{M} = \text{Zn}, \text{Cd}$) [11], our compounds may have various degrees of hydroxy and sulfur double-ylide bridges or monodentate ylide. The $\nu(\text{SO})$ of 1200 cm^{-1} for the copper compound suggests that the sulfur ylide has a monodentate ylide. The $\nu(\text{SO})$ value of 1178 cm^{-1} for the zinc compound is closer to the double-ylide described for the palladium compounds. Although the isolated sulfur ylide complexes of zinc and copper are non-stoichiometric, we have demonstrated that sulfur ylide complexes of copper can be formed in water. This provides indirect evidence for Cohen's proposal that the biosynthesis of presqualene pyrophosphate involving sulfur ylide complexes of copper, is possible.

In this work we have prepared various sulfur ylide complexes by a simple technique, using simple starting materials, in water. The sulfur ylide itself is unstable in water. However, because the sulfur ylide is in equilibrium with the sulfoxonium salt in the basic, aqueous solution, the equilibrium amount of ylide reacts readily with the metal. The reaction thus shifts from the sulfoxonium salt towards the deprotonated ylide. The stability of the metal salts in NaOH solution is another key factor in preparing the complexes in water. For example, if sulfoxonium chloride is used instead of iodide, $(\text{NH}_4)_2\text{PdCl}_4$ turned black within several minutes. Nonetheless, suitable conditions can be found to prepare ylide metal complexes in water.

Crystal and molecular structures

The structural study of $\text{PdI}[(\text{CH}_2)(\text{SO})(\text{CH}_3)_2][(\text{CH}_2)_2(\text{SO})(\text{CH}_3)]$ presents the first example of a metal complex containing both a monodentate sulfoxonium ylide and a chelated sulfoxonium double-ylide. The geometry about the palladium is distorted square planar. The four membered ring formed by the chelated double-ylide is puckered. The dihedral angle between the $\text{Cl-Pd-C}(2)$ plane and the $\text{C}(1)\text{-S}(1)\text{-C}(2)$ plane is 31.7° . The $\text{S}(1)$ sulfur atom is 0.55 \AA out of the

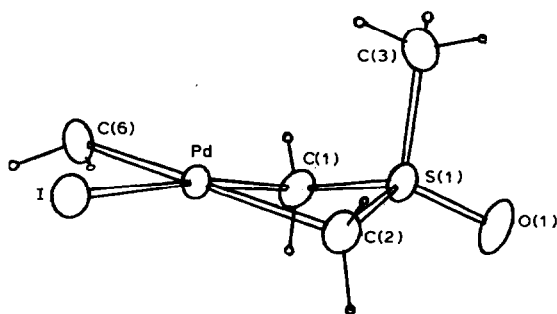


Fig. 2. Different view of $\text{PdI}[(\text{CH}_2)(\text{SO})(\text{CH}_3)_2][(\text{CH}_2)_2(\text{SO})(\text{CH}_3)]$, only part of the atoms are shown.

I-Pd-C(1)-C(2)-C(6) plane and the chelated ylide CH_3 group is in the axial position (Fig. 2). This is as previously suggested by Bravo et al. based on ^1H NMR data [8].

The Pd-Cl and Pd-C(2) distances, which are *trans* to the I and C(6), respectively, are within the range of one standard deviation and essentially equal. The Pd-C(6) bond is longer than the Pd-C(1) and Pd-C(2) bonds but the differences are within the 3σ range. The S-C (methyl) distances are consistently longer than the S-C (methylene) distances but, once again, within the 3σ range. Nonetheless the S-C (methylene) distances are shorter than the normal S- CH_3 distance in $\text{S}(\text{CH}_3)_2$ (1.81 Å) [12]. Similar observations were made for the other two sulfur ylide compounds [13]. Thus upon complexation the ylidic character is partly retained. The lower $\nu(\text{SO})$ values for the chelated double ylides, compared with the monodentate simple ylides, suggest that the double ylides have longer S-O distances than the simple ylides. However, due to the high standard deviations in the S-O distances, the above argument cannot be justified.

Acknowledgement

We would like to thank the NSC (ROC Taiwan) for its financial support.

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