nyl)zirconium complex does not change in isomeric distribution after 4.5 h at reflux temperatures, the possibility that kineticaly favored isomers are produced in this work can be ruled out. Hence, it appears that calculations predicting electronic control of stereochemistry for organic reactions may not apply strictly to organomeallic compounds.

**Acknowledgment.** We wish to express our appreciation to the State of Ohio for funds from an Academic Challenge grant to acquire the 300-MHz NMR instrument used to perform these studies, and we wish to thank D. Ray and Dr. M. Tokles for obtaining some of the NMR spectra.

**Supplementary Material Available:** A complete set of $^1H$, $^{13}C$, COSY, and NOESY NMR spectra of the compounds prepared in this work (44 pages). Ordering information is given on any current masthead page.

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# Preparation of Sulfur Ylide Complexes of Palladium by Phase-Transfer Catalysis

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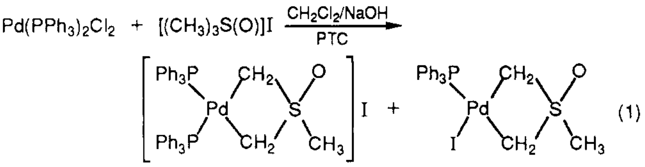
Sulfur ylide complexes of palladium were prepared under basic phase-transfer catalysis. Increasing the amount of phase-transfer catalyst enhanced the rates of formation of the complexes. The optimal range of base concentration was found to be 1.0–2.0 N. The proposed role of the phase-transfer catalyst is to carry $OH^-$ into the organic layer and to prevent the ylide from abstracting a proton from water present in the organic phase. The single-crystal structures of $\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ and $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ were determined. The former crystallized in the monoclinic space group $P2_1/n$, with $a = 11.337$ (2) Å, $b = 21.954$ (3) Å, $c = 15.406$ (2) Å, $\beta = 94.30$ (1)°, $V = 3823.6$ Å$^3$, $Z = 4$, and $R = 0.095$ for 4906 observed reflections. The latter crystallized in the orthorhombic space group $P2_12_12_1$, with $a = 9.691$ (3) Å, $b = 14.579$ (2) Å, $c = 15.642$ (3) Å, $V = 2209.9$ Å$^3$, $Z = 4$, and $R = 0.078$ for 2201 observed reflections. Both compounds have rather short ylidic S–C bonds (1.60–1.70 Å).

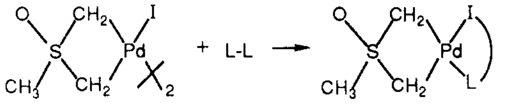
## Introduction

Phase-transfer catalysis (PTC) has been widely applied in organic chemistry.[1-4] In contrast, there have been relatively few examples in organometallic chemistry,[5-11] the first being reported in 1976.[10] The application of the PTC technique to organometallic synthesis is even rarer.[12-17] In a previous communication,[16] we have shown that palladium sulfur ylide complexes 1 and 2 were obtained in high yields by the reaction of trimethylsulfoxonium iodide with $Pd(PPh_3)_2Cl_2$ under basic PTC conditions (eq 1). This PTC reaction is unusual in view of the known instability of sulfur ylides in anhydrous solvents at room temperature.[18] In comparison, a reaction has been carried out in dry THF under $N_2$ and with NaH as the base, and we have shown that the $PTC/OH^-$ technique has the following advantages: anhydrous conditions are not required; relatively high yields of complexes are obtained; a cheap and easily used base, NaOH, can be used. In a subsequent paper,[19] it was shown that sulfur ylide complexes of palladium, zinc, and copper can be formed even in water. In another work[20] it was demonstrated that under PTC conditions both the reaction rates and yields (eq 2) of mixed-ligand complexes were enhanced. In this paper, we report our continued



(1)

1 2



(2)

L-L = 1,1-dithiolates, acetylacetonate

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[§] National Taiwan University.

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efforts to synthesize sulfur ylide complexes of palladium under PTC conditions and also the crystal structures of 1 and 2.

## Experimental Section

Infrared spectra were measured on a Beckman Acculab TM1 spectrometer in KBr pellets. UV-visible spectra were measured on a Shimadzu UV-200S spectrometer. $^1$H NMR spectra were recorded on a Varian EM-360 spectrometer operated at 60 MHz. Chemical shifts are downfield relative to the TMS standard. The $^1$H NMR spectrum shown in Figure 1 was recorded on a Varian Gemini 200 spectrometer operated at 200 MHz. Conductivities were measured with the WPA CMD 400 digital conductivity meter. Elemental analyses were done by the Taipei Instrumentation Center, Taipei, Taiwan.

All phosphines used in this work were purchased from Strem Chemicals. All phase-transfer catalysts were purchased from Aldrich. $[S(O)Me_3]I$ was purchased from Merck. $Pd(PPh_3)_2Cl_2$, $Pd(PMePh_2)_2Cl_2$, $Pd(PEt_3)_2Cl_2$, and $Pd(P(n\text{-}Bu)_3)_2Cl_2$ were prepared by known methods.[21-23] $Pd(P(p\text{-}C_6H_4CH_3)_3)_2Cl_2$ was prepared by the method used to prepare $Pd(PPh_3)_2Cl_2$. The compound was identified by elemental analysis. Anal. Calcd for $C_{42}H_{42}Cl_2P_2Pd$: C, 64.2; H, 5.4. Found: C, 64.0; H, 5.3. $^1$H NMR ($CDCl_3$): 7–8 (m, 24 H, $C_6H_4$), 2.5 (s, 18 H, $CH_3$) ppm.

**$\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ (1).** $Pd(PPh_3)_2Cl_2$ (350.9 mg, 0.5 mmol) and $PPh_3$ (524.6 mg, 2.0 mmol) in 10 mL of $CH_2Cl_2$ were mixed with trimethylsulfoxonium iodide (220.0 mg, 1.0 mmol) in 12 mL of 1.5 N NaOH, followed by the phase-transfer catalyst $n\text{-}Bu_4NI$ (18.5 mg, 0.05 mmol). The resultant solution was stirred at room temperature until it became very pale yellow. The organic layer was separated, and the solution was reduced to 3 mL by rotary evaporation. Precipitation occurred upon addition of a large amount of hexane. The powdery solid product was obtained by filtration and washed several times with water and ether. The yield was approximately 80%. Recrystallization from acetone gave a white crystalline material, mp 145–147 °C. Anal. Calcd for $C_{39}H_{37}IOP_2SPd$: C, 55.2; H, 4.4. Found: C, 54.8; H, 4.2. IR: $\nu$(SO) 1190 cm$^{-1}$. $^1$H NMR ($CDCl_3$): 7–8 (m, 30 H, $PC_6H_5$), 3.35 (t, 3 H, $^4J$(H,H) = 1.7 Hz, $SCH_3$), 1.95–2.78 (m, 4 H, $SCH_2$) ppm. $\Lambda_M$ ($10^{-4}$ M DMSO) = 36 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**$Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ (2).** This compound was obtained by following the preparation method of compound 1 except that no free $PPh_3$ was added: yield 70%; mp 182–184 °C. Anal. Calcd for $C_{21}H_{22}IOPSPd$: C, 43.0; H, 3.8. Found: C, 42.8; H, 3.8. IR: $\nu$(SO) 1180 cm$^{-1}$. $^1$H NMR ($CDCl_3$): 7–8 (m, 15 H, 15 H, $PC_6H_5$), 3.52 (m, 1 H, $SCH_2$), 3.29 (t, 3 H, $^4J$(H,H) = 1.7 Hz, $SCH_3$), 2.41 (m, 1 H, $SCH_2$), 2.19 (m, 1 H, $SCH_2$), 2.02 (m, 1 H, $SCH_2$) ppm.

The following compounds were prepared by using methods similar to that for the preparation of compound 2. Yields were approximately 50–80%.

**$Pd[P(p\text{-}C_6H_4CH_3)_3](I)[(CH_2)_2S(O)(CH_3)]$ (3).** Mp: 192–194 °C. Anal. Calcd for $C_{24}H_{28}IOPSPd$: C, 45.8; H, 4.5. Found: C, 45.2; H, 4.5. IR: $\nu$(SO) 1190 cm$^{-1}$. $^1$H NMR ($CDCl_3$): 7.1–7.6 (m, 12 H, $p\text{-}C_6H_4$), 3.3 (t, $^4J$(H,H) = 1.7 Hz, 3 H, $SCH_3$), 2.4 (s, 9 H, $PC_6H_5CH_3$), 3.6–1.9 (m, 4 H, $SCH_2$) ppm.

**$Pd(PEt_3)(I)[(CH_2)_2(SO)(CH_3)]$ (4).** Mp: 96–98 °C. Anal. Calcd for $C_9H_{22}IOPSPd$: C, 24.4; H, 5.0. Found: C, 24.2; H, 5.0. IR: $\nu$(SO) 1185 cm$^{-1}$. $^1$H NMR ($CDCl_3$): 3.32 (t, $^4J$(H,H) = 1.7 Hz, 3 H, $SCH_3$), 3.4–2.1 (m, 4 H, $SCH_2$), 1.82 (q of d, $^2J$(P,H) = 8.0 Hz, $^3J$(H,H) = 8.0 Hz, 6 H, $PCH_2$), 1.30 (t of d, $^3J$(P,H) = 16.0 Hz, $^3J$(H,H) = 8.0 Hz, 9 H, $PCH_2CH_3$) ppm.

**$Pd(P(n\text{-}Bu)_3)(I)[(CH_2)_2S(O)(CH_3)]$ (5).** Mp: 68–70 °C. Anal. Calcd for $C_{15}H_{34}IOPSPd$: C, 34.2; H, 6.5. Found: C, 33.8; H, 6.8. IR: $\nu$(SO) 1200 cm$^{-1}$. $^1$H NMR ($CDCl_3$): 3.30 (t, $^4J$(H,H) = 1.7 Hz, 3 H, $SCH_3$), 3.6–2.0 (m, 4 H, $SCH_2$), 1.79–1.44 (m, 18 H, $P(CH_2)_3$), 0.97 (t, 9 H, $P(CH_2)_3CH_3$) ppm.

**Table I. Crystal Data for $\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ (1) and $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ (2)**

| | compd 1 | compd 2 |
|---|---|---|
| formula | $\{Pd(PPh_3)_2[(CH_2)_2\text{-}S(O)(CH_3)]\}I$ | $Pd(PPh_3)(I)[(CH_2)_2\text{-}S(O)(CH_3)]$ |
| space group | $P2_1/n$ | $P2_12_12_1$ |
| $a$, Å | 11.337 (2) | 9.691 (3) |
| $b$, Å | 21.954 (3) | 14.579 (2) |
| $c$, Å | 15.406 (2) | 15.642 (3) |
| $\beta$, deg | 94.30 (1) | |
| $V$, Å | 3823.6 | 2209.9 |
| cell param detn | 25 rflns at 21 < $2\theta$ < 28° | 25 rflns at 25 < $2\theta$ < 28° |
| $Z$ | 4 | 4 |
| $D_m$, $D_c$, g cm$^{-3}$ | 1.50 (3), 1.53 | 1.87 (8), 1.76 |
| color | red | light yellow |
| cryst size, mm | 0.3 × 0.3 × 0.35 | 0.17 × 0.15 × 0.4 |
| $\lambda$, Å | 0.71069 | 0.71069 |
| $\mu$, cm$^{-1}$ | 14.40 | 23.81 |
| transmissn coeff | 0.83–1.00 | 0.615–0.680 |
| $\theta/2\theta$ scan range | $1.7 + 0.7 \tan\theta$ | $1.7 + 0.7 \tan\theta$ |
| $2\theta_{max}$, deg | 50 | 66 |
| no. of rflns (no. with $I \geq 2[\sigma(I)]$) | 6922 (4906) | 4642 (2201) |
| weights | $1/\sigma^2(F_o)$ | $1/\sigma^2(F_o)$ |
| $R(F)$, $R_w(F)$[a] | 0.095, 0.103 | 0.078, 0.056 |
| $hkl$ | $-13 < h < 13, 0 < k < 26, 0 < l < 18$ | $0 < h < 14, 0 < k < 22, 0 < l < 24$ |

[a] $R(F) = \sum_i(F_o - F_c)/\sum_i F_o$; $R_w(F) = [\sum_i w(F_o - F_c)^2/\sum_i wF_o^2]^{1/2}$.

**$\{Pd(PMePh_2)_2[(CH_2)_2S(O)(CH_3)]\}I$ (6).** Mp: 122–124 °C. Anal. Calcd for $C_{29}H_{33}IOP_2SPd$: C, 48.1; H, 4.6. Found: C, 48.2; H, 4.3. IR: $\nu$(SO) 1194 cm$^{-1}$. $^1$H NMR ($CDCl_3$): 7–8 (m, 20 H, $PC_6H_5$), 3.52 (t, $^4J$(H,H) = 1.7 Hz, 3 H, $SCH_3$), 2.7–2.1 (m, 4 H, $SCH_2$), 2.0 (d, $^3J$(P,H) = 9.0 Hz, 6 H, $PCH_3$) ppm. $\Lambda_M$ ($10^{-4}$ M acetone) = 103.6 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Structure Determination and Refinement.** Crystals of compounds 1 and 2 suitable for single-crystal X-ray work were recrystallized from acetone/hexane. X-ray diffraction data were collected on a CAD4 diffractometer at room temperature using monochromated Mo K$\alpha$ radiation. Three reflections were monitored every 2 h throughout the measurements; the variations of these reflections are within $3[\sigma(I)]$ and $2[\sigma(I)]$ for compounds 1 and 2, respectively. The other experimental details are given in Table I. The data were corrected for Lorentz and polarization effects. Absorption corrections were applied according to the experimental $\psi$ rotation for compound 1 and according to the measured dimension for compound 2. Both structures were solved by the heavy-atom method with the Pd and I atoms located in a Patterson map. All the non-hydrogen atoms were located in the subsequent Fourier synthesis maps. The scattering factors and anomalous dispersion corrections were applied according to ref 24. The usual least-squares process was used to refine the atomic and thermal parameters based on $F_o$. No extinction correction was applied. The agreement indices are also given in Table I. The final atomic coordinates and equivalent isotropic thermal parameters of compounds 1 and 2 from X-ray diffraction data are given in parts a and b, respectively, of Table II. The selected bond lengths and angles are listed in Table III. The $I^-$ ion in compound 1 is disordered. A model of four $I^-$ ions with various occupancies obtained from the least-squares refinement are indicated in Table IIa. Compound 2 belongs to a noncentrosymmetric space group; the other enantiomer was tried, but there was no significant difference between the two. The one presented here is only slightly better (0.001 in difference of $R_w$(F)). The final difference density map showed some residual density around Pd and I atoms with ±2.6 e Å$^{-3}$ for both structures; the rest of the maps are within their standard deviations.

## Results and Discussion

**Preparation and Characterization.** Various palladium sulfoxonium ylide complexes were prepared by simply mixing the metal complexes with trimethylsulfoxonium

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**Table II. Atomic Coordinates and Thermal Parameters**[a]

| | *x* | *y* | *z* | *B*(eq) | | *x* | *y* | *z* | *B*(eq) |
|---|---|---|---|---|---|---|---|---|---|
| a. $\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ (1)[b] | | | | | | | | | |
| Pd | 0.42424 (9) | 0.35365 (4) | 0.31450 (5) | 3.19 (4) | C42 | 0.2167 (11) | 0.4500 (6) | 0.1912 (8) | 3.7 (5) |
| S | 0.4666 (5) | 0.41481 (16) | 0.46710 (21) | 5.62 (21) | C43 | 0.1224 (12) | 0.4868 (7) | 0.1648 (10) | 4.9 (7) |
| P1 | 0.4388 (3) | 0.24903 (13) | 0.29446 (18) | 2.82 (12) | C44 | 0.1196 (13) | 0.5177 (6) | 0.0870 (10) | 5.2 (7) |
| P2 | 0.4393 (3) | 0.39830 (14) | 0.17775 (19) | 3.10 (13) | C45 | 0.2102 (14) | 0.5101 (7) | 0.0343 (10) | 5.3 (7) |
| O | 0.4419 (13) | 0.4450 (5) | 0.5478 (6) | 7.7 (7) | C46 | 0.3075 (12) | 0.4742 (6) | 0.0595 (8) | 4.2 (6) |
| C11 | 0.3069 (10) | 0.2111 (5) | 0.2465 (7) | 3.0 (5) | C51 | 0.4686 (11) | 0.3562 (6) | 0.0792 (7) | 3.7 (5) |
| C12 | 0.2089 (11) | 0.2444 (6) | 0.2208 (8) | 3.9 (6) | C52 | 0.4018 (12) | 0.3054 (7) | 0.0580 (8) | 4.4 (6) |
| C13 | 0.1067 (11) | 0.2157 (7) | 0.1900 (9) | 5.0 (7) | C53 | 0.4182 (16) | 0.2728 (7) | −0.0184 (9) | 6.0 (8) |
| C14 | 0.0995 (12) | 0.1535 (7) | 0.1886 (9) | 5.1 (7) | C54 | 0.4980 (15) | 0.2950 (8) | −0.0741 (9) | 6.0 (8) |
| C15 | 0.1975 (14) | 0.1200 (7) | 0.2134 (9) | 5.2 (7) | C55 | 0.5644 (14) | 0.3449 (8) | −0.0533 (9) | 5.8 (8) |
| C16 | 0.3017 (12) | 0.1477 (6) | 0.2433 (8) | 4.2 (6) | C56 | 0.5512 (12) | 0.3766 (7) | 0.0226 (8) | 4.6 (6) |
| C21 | 0.5656 (11) | 0.2285 (5) | 0.2346 (7) | 3.4 (5) | C61 | 0.5616 (11) | 0.4518 (6) | 0.1905 (7) | 3.6 (5) |
| C22 | 0.6718 (11) | 0.2562 (6) | 0.2603 (8) | 4.0 (6) | C62 | 0.5480 (12) | 0.5143 (7) | 0.1815 (9) | 4.8 (6) |
| C23 | 0.7733 (12) | 0.2428 (8) | 0.2206 (10) | 5.3 (8) | C63 | 0.6438 (16) | 0.5523 (8) | 0.1971 (12) | 6.6 (9) |
| C24 | 0.7669 (15) | 0.2011 (9) | 0.1525 (10) | 6.5 (9) | C64 | 0.7554 (16) | 0.5295 (9) | 0.2219 (12) | 7.3 (10) |
| C25 | 0.6604 (15) | 0.1752 (9) | 0.1238 (10) | 6.6 (9) | C65 | 0.7697 (14) | 0.4678 (8) | 0.2284 (11) | 6.2 (8) |
| C26 | 0.5591 (12) | 0.1879 (7) | 0.1654 (9) | 4.8 (7) | C66 | 0.6740 (13) | 0.4296 (7) | 0.2141 (10) | 5.1 (7) |
| C31 | 0.4614 (10) | 0.2063 (5) | 0.3976 (7) | 3.1 (5) | C7 | 0.4197 (17) | 0.3411 (6) | 0.4500 (8) | 5.8 (9) |
| C32 | 0.5695 (12) | 0.1808 (6) | 0.4269 (9) | 4.4 (6) | C8 | 0.4104 (16) | 0.4419 (6) | 0.3684 (8) | 5.4 (8) |
| C33 | 0.5798 (13) | 0.1520 (7) | 0.5087 (9) | 5.2 (7) | C9 | 0.6217 (19) | 0.4126 (8) | 0.4614 (11) | 7.3 (10) |
| C34 | 0.4837 (14) | 0.1490 (7) | 0.5581 (9) | 5.1 (7) | I1 | 0.0463 (5) | 0.3747 (3) | 0.3638 (4) | 17.15 (17) |
| C35 | 0.3782 (13) | 0.1726 (6) | 0.5283 (8) | 4.5 (6) | I2 | 0.0317 (3) | 0.35974 (18) | 0.34056 (24) | 4.77 (7) |
| C36 | 0.3647 (12) | 0.2019 (6) | 0.4480 (8) | 3.9 (6) | I3 | 0.124 (3) | 0.4827 (15) | 0.5425 (21) | 18.0 (10) |
| C41 | 0.3120 (10) | 0.4445 (5) | 0.1402 (8) | 3.2 (5) | I4 | 0.075 (3) | 0.5398 (14) | 0.4147 (19) | 16.1 (8) |
| b. $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ (2) | | | | | | | | | |
| Pd | 0.75525 (17) | 0.18861 (9) | 0.01643 (8) | 3.90 (6) | C16 | 0.5612 (18) | −0.0411 (14) | −0.1641 (13) | 5.6 (12) |
| I | 0.70217 (15) | 0.30573 (10) | −0.10763 (8) | 5.33 (7) | C21 | 0.8412 (19) | 0.0648 (11) | −0.1719 (10) | 3.5 (8) |
| P | 0.7636 (5) | 0.0568 (3) | −0.0662 (3) | 2.81 (17) | C22 | 0.9757 (19) | 0.0335 (12) | −0.1864 (13) | 4.7 (10) |
| S | 0.7336 (6) | 0.2223 (3) | 0.1867 (3) | 4.35 (23) | C23 | 1.0279 (23) | 0.0471 (17) | −0.2621 (17) | 7.4 (14) |
| O | 0.7695 (20) | 0.2393 (9) | 0.2732 (8) | 8.5 (10) | C24 | 0.9751 (23) | 0.0863 (14) | −0.3276 (12) | 6.3 (12) |
| C1 | 0.7852 (16) | 0.1272 (12) | 0.1321 (10) | 4.1 (9) | C25 | 0.843 (3) | 0.1217 (12) | −0.3150 (12) | 8.1 (16) |
| C2 | 0.7545 (19) | 0.2881 (12) | 0.1055 (11) | 5.0 (10) | C26 | 0.7744 (23) | 0.1090 (12) | −0.2371 (10) | 5.8 (11) |
| C3 | 0.567 (3) | 0.2104 (16) | 0.1955 (15) | 10.8 (20) | C31 | 0.8539 (15) | −0.0410 (10) | −0.0187 (11) | 3.2 (8) |
| C11 | 0.5877 (14) | 0.0115 (10) | −0.0873 (11) | 3.2 (8) | C32 | 0.9657 (19) | −0.0275 (13) | 0.0318 (15) | 5.8 (12) |
| C12 | 0.4937 (19) | 0.0284 (12) | −0.0279 (13) | 4.8 (10) | C33 | 1.0267 (21) | −0.0996 (15) | 0.0718 (16) | 7.2 (14) |
| C13 | 0.3677 (20) | −0.0147 (13) | −0.0422 (13) | 5.1 (10) | C34 | 0.9906 (18) | −0.1845 (14) | 0.0536 (17) | 7.5 (14) |
| C14 | 0.3393 (15) | −0.0654 (13) | −0.1120 (14) | 5.7 (11) | C35 | 0.8901 (21) | −0.2016 (13) | −0.0013 (16) | 7.2 (13) |
| C15 | 0.4318 (20) | −0.0795 (15) | −0.1707 (13) | 6.5 (12) | C36 | 0.8205 (19) | −0.1297 (11) | −0.0381 (12) | 4.8 (10) |

[a] $B(eq) = (8\pi^2/3)\sum_{i,j}U_{ij}a_ia_ja_i^*a_j^*$. [b] Occupancies: I1, 0.55; I2, 0.25; I3, 0.1; I4, 0.1.

**Table III. Selected Bond Lengths (Å) and Angles (deg) for $\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ (1) and $Pd(PPh_3)(I)[(CH_2)S(O)(CH_3)]$ (2)**

| compd 1 | | compd 2 | |
|---|---|---|---|
| Pd-P1 | 2.321 (2) | Pd-P | 2.317 (4) |
| Pd-P2 | 2.352 (2) | Pd-I | 2.635 (1) |
| Pd-C7 | 2.128 (8) | Pd-C1 | 2.04 (1) |
| Pd-C8 | 2.12 (1) | Pd-C2 | 2.01 (1) |
| S-C7 | 1.696 (9) | S-C1 | 1.70 (1) |
| S-C8 | 1.689 (9) | S-C2 | 1.60 (1) |
| S-C9 | 1.78 (1) | S-C3 | 1.63 (3) |
| S-O | 1.457 (7) | S-O | 1.42 (1) |
| P1-C11 | 1.808 (9) | P-C11 | 1.86 (1) |
| P1-C21 | 1.800 (9) | P-C21 | 1.82 (1) |
| P1-C31 | 1.838 (9) | P-C31 | 1.83 (1) |
| P2-C41 | 1.819 (9) | | |
| P2-C51 | 1.846 (9) | | |
| P2-C61 | 1.83 (1) | | |
| P1-Pd-P2 | 106.44 (9) | P-Pd-I | 97.7 (1) |
| P1-Pd-C7 | 90.6 (2) | P-Pd-C1 | 97.2 (4) |
| P2-Pd-C8 | 89.2 (2) | I-Pd-C2 | 92.4 (5) |
| C7-Pd-C8 | 73.6 (3) | C1-Pd-C2 | 72.7 (6) |
| O-S-C7 | 119.1 (4) | O-S-C1 | 123.3 (8) |
| O-S-C8 | 121.4 (5) | O-S-C2 | 128.3 (9) |
| O-S-C9 | 109.3 (5) | O-S-C3 | 100.0 (1) |
| C7-S-C8 | 97.7 (4) | C1-S-C2 | 93.0 (8) |
| S-C7-Pd | 89.8 (3) | S-C1-Pd | 92.7 (8) |
| S-C8-Pd | 90.1 (4) | S-C2-Pd | 96.8 (8) |

iodide in NaOH under PTC conditions. Metal complexes of the general formula $Pd(PR_3)_2X_2$, (R = alkyl, aryl; X = Cl, Br, I) all work equally well. With $Pd(PPh_3)_2Cl_2$, when the reactants were mixed, the initially yellow solution turned orange-red and then colorless. The orange-red color is likely due to the substitution of chloride in $Pd(PPh_3)_2Cl_2$ by iodide. The same color change was observed by mixing $Pd(PPh_3)_2Cl_2$ with $n$-$Bu_4NI$ in $CHCl_3$. Substitution of the chloride in the metal complex by iodide is important for the reaction. Under basic conditions, $Pd(PPh_3)_2Cl_2$ was decomposed when sulfoxonium chloride was used instead of sulfoxonium iodide. In solution, compound **1** was slowly converted to **2** through phosphine dissociation; thus, during the preparation of **1**, excess phosphine was always added. The exchange between **1** and **2** through the dissociation or association of phosphine was also evidenced by the broad $^1H$ NMR signals for a mixture of **1** and **2** in $CDCl_3$ at room temperature. If the spectrum was taken at 0 °C, sharp signals assignable to **1** and **2** were observed. For the preparation of ionic compound **6**, no additional phosphine was required, probably due to the less steric crowding and more $\sigma$-donating ability of the $PMePh_2$ ligand compared with that of $PPh_3$. However, phosphine dissociation was also observed after prolonged standing of a solution of compound **6** in air.

In all compounds, the $^1H$ NMR signals of the methyl group on the sulfur ylides are triplets due to the long-range coupling with the axial protons of the methylene groups.[25] The methylene proton signals are complicated. We have examined the $^1H$ NMR spectrum of compound **2** in detail

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[25] Bravo, P.; Fronza, G.; Ticozzi, C. *J. Organomet. Chem.* **1976**, *118*, C78.

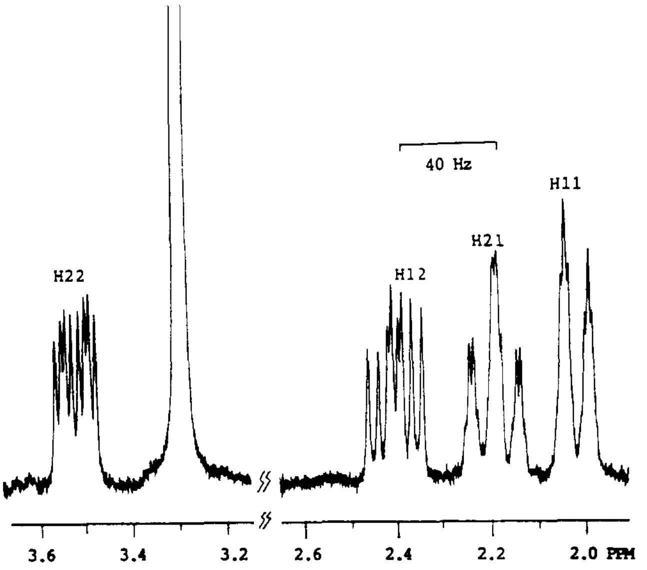
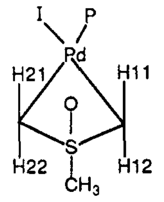


**Figure 1.** $^1H$ NMR spectrum of $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ in $CDCl_3$. Only part of the spectrum is shown.

**Chart I**



$^2J$(H11,H12) = 10.3 Hz

$^2J$(H21,H22) = 10.0 Hz

$^4J$(H12,H22) = 4.5 Hz

$^4J$(H11,H21) ≈ 0 Hz

$^4J$($CH_3$,H11) = $J$($CH_3$,H21) = 1.7 Hz

$^3J$(P,H21) = 9.8 Hz

$^3J$(P,H22) = 3.0 Hz

$^3J$(P,H11) = 1.5 Hz

$^3J$(P,H12) = 8.5 Hz

(see Figure 1). The four methylene protons are nonequivalent and are centered at δ 2.02 (H11), 2.19 (H21), 2.41 (H12), and 3.52 ppm (H22). The triplet for the methyl proton is located at 3.27 ppm. The chemical shifts of the four methylene protons are assigned by their coupling constants and by the comparison of various $Pd(PR_3)(I)[(CH_2)_2S(O)(CH_3)]$ type compounds[20] with $[Pd(\mu\text{-}I)((CH_2)_2S(O)(CH_3))]_2$.[25] Coupling constants were obtained from the 2D NMR spectrum and successive double-resonance experiments. The tentative assignment with coupling constants is given in Chart I.

The crystal structure of **2**, as determined by X-ray diffraction, indicates that the four membered ring Pd–C–S–C is folded and the methyl group is in the axial position (see Figure 2). The two methylene protons H11 and H21, which are trans to the methyl group, are also in axial positions; the H12 and H22 protons are in equatorial positions. The long-range coupling constant between the methyl protons and the H11, H21 protons (1.7 Hz) is close to the value found in the dimeric $\{Pd(\mu\text{-}I)[(CH_2)_2S(O)(CH_3)]\}_2$ (1.8 Hz).[25] The H11, H12 and H21, H22 geminal protons have large coupling constants (10.2 and 10.0 Hz, respectively) as expected. The W-shaped coupling[26] of the two equatorial protons ($^4J$(H12,H22) = 4.5 Hz) is larger than that of the two H11 and H21 axial protons ($J$ = 0). The large coupling constant suggests that the four-membered ring is substantially strained.[26]

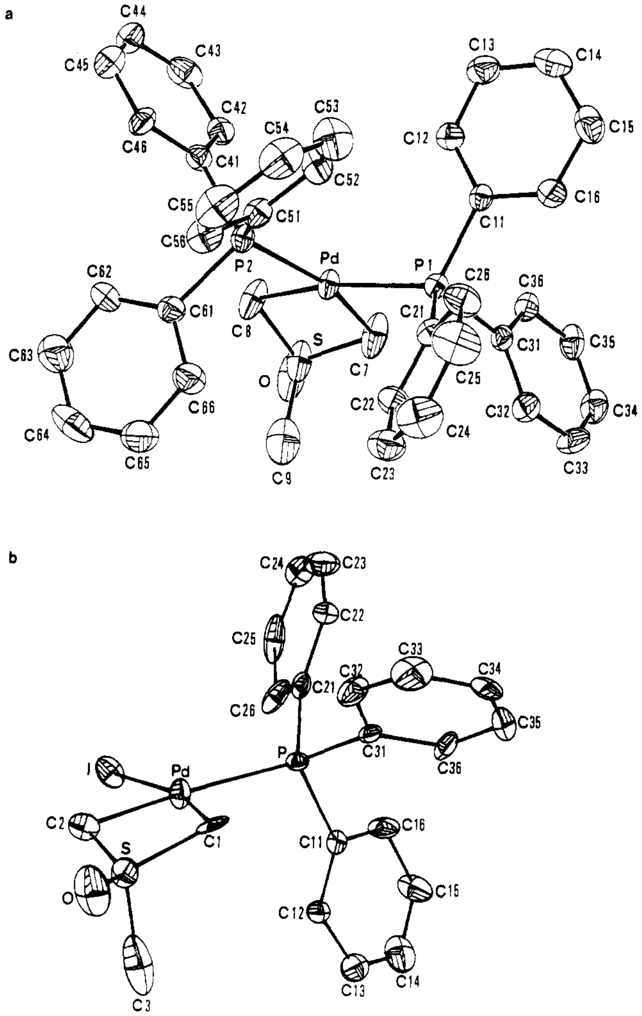


**Figure 2.** ORTEP drawings and atomic labelings for (a) the cation of $\{Pd(PPh_3)_2[(CH_2)S(O)(CH_3)]\}I$ (**1**) and (b) $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ (**2**).

We have examined the individual effects of the stirring rate, and the concentrations of NaOH and phase-transfer (PT) catalyst, on the reaction rates. No appreciable rate change was observed when the stirring rate was increased above 400 rpm. The effect of NaOH concentration was monitored spectroscopically by the disappearance of the orange-red color ($\lambda_{max}$ = 332 nm in $CH_2Cl_2$). When the base concentration was below 0.08 N, hardly any ylide complexes were formed. However, with an increase in the base concentration, i.e. beyond 0.08 N, the reaction rate was enhanced. The relationship, however, is not simple pseudo first or second order. At a base concentration greater than 2.5 N, some unidentified compounds were obtained, and sometimes extensive decomposition of the metal complexes occurred. The optimal range of base concentration for our PTC reactions is between 1.0 and 2.0 N.

We have also studied the effect of PT catalyst concentration on the reaction rate for eq 1. When the molar ratios of PT catalyst/$Pd(PPh_3)_2Cl_2$ were greater than 0.05, there was a linear relationship between the concentration of PT catalyst and the reaction rate (first order with respect to the PT catalyst). Below this ratio, or with no catalyst present, results were varied. Under the best condition, a 40% yield of compound **1** was formed. Use of a crown ether instead of $n\text{-}Bu_4NI$ enhanced the reaction rate, but the product yield remained the same. In the presence of PEG 400, the reaction rate also increased, but the product

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[26] Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr. *Introduction to Spectroscopy*; Saunders: Philadelphia, PA, 1979; p 160.

yield was lower, probably due to the difficulty in product separation. When $NaBPh_4$ was employed instead of other PT catalysts, no ylide complexes were obtained.

The cyclopropanation reaction of trimethylsulfoxonium iodide with $\alpha,\beta$-unsaturated ketones under basic PTC conditions was reported by Merz and Markl.[27] A PT catalyst was essential for these reactions. A similar ylide type reaction, i.e. a Wittig reaction, has also been carried out by Merz and Markl[28] under biphasic conditions. In this reaction, the addition of a PT catalyst had only a marginal effect on the reaction rate and yield.[29] It has been argued that, in the Wittig reaction, the phosphonium ion itself is a PT catalyst.[4] This is not the case for trimethylsulfoxonium iodide, which showed no catalytic activity due to its small alkyl groups.[27] Thus, experimentally, the yields of these ylide type reactions are indeed enhanced by the PT catalyst, be it from an ylide precursor or from external addition.

The role of the PT catalyst in our system needs to be commented upon further. It was believed[4] that deprotonation of the onium ions occurred at the phase boundary. The neutral ylide formed can then diffuse into the organic layer. This argues against the need for a PT catalyst and appears to contradict our results as well as those of others.[28] In our previous publication,[19] the formation of sulfur ylide complexes in an aqueous solvent was reported. This is only possible if the sulfoxonium ion is in equilibrium with the deprotonated neutral ylide in water (H–D exchange between $D_2O$ and $[(CH_3)_3S]I$ has been observed[30]). Although the ylide formation from $[(CH_3)_3S(O)]I$ is not thermodynamically favorable in water, the ylide reacts readily with the metal ion once formed. In other words, the metal ion stabilizes the ylide formed in the water layer. If the reactants are not water soluble (e.g. $Pd(PPh_3)_2Cl_2$ or $\alpha,\beta$-unsaturated ketones), and there is no PT catalyst present, only the ylide formed at the boundary can react. Although the neutral ylide can then diffuse further into the organic layer, it quickly reacts with the water dissolved in the organic phase. We have observed that, in the absence of a PT catalyst, the metal ylide complex is obtained, albeit with a lower yield. In the presence of a PT catalyst, $OH^-$ will be carried to the organic layer, and the ylide in the organic layer is stabilized by $OH^-$. Thus, suitable PT catalysts are those that can carry $OH^-$ into the organic layer (e.g. crown ether, $n$-$Bu_4NX$). Therefore, the presence of $NaBPh_4$ will not enhance the reaction rate, as we have observed.

**Molecular Structures of $\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ (1) and $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ (2).** The molecular structures with the atomic labeling of both complexes are depicted in Figure 2. The coordination around the Pd is square planar for both complexes. A puckered four-membered ring is formed when the bidentate ligand $[(CH_2)_2S(O)(CH_3)]^-$ is bonded to Pd. The C–Pd–C angles are quite small (73.6 and 72.7°, respectively). When the two complexes are compared, it is obvious that steric effects play an important role in the coordination geometry. The two bulky $PPh_3$ ligands in compound **1** cause a much larger P–Pd–P angle (106.4°) than the corresponding I–Pd–P angle (97.7°) in compound **2**. The Pd–P2 bond length of compound **1** is slightly larger than that in compound **2**. This probably explains the ease of conversion of **1** to **2** in $CHCl_3$. The dihedral angles between the C–S–C and C–Pd–C planes for compounds **1** and **2** are 32.3 (9) and 22.6 (9)°, respectively. The sulfur atom is 0.624 (9) Å above the $PdL_4$ square plane in compound **1** and is 0.507 (8) Å above the plane in compound **2**. The former value is slightly larger than those found in $Pd[(CH_2)_2S(O)(CH_3)]_2$ (0.53 Å)[20] and $PdI[(CH_2)S(O)(CH_3)_2][(CH_2)_2S(O)(CH_3)]$ (0.55 Å).[19] In all cases, the $CH_3$ groups are in the axial positions. The $I^-$ ion in compound **1** is disordered, and it has no close contact (<4 Å) with any atoms in the cation.

The ylidic S–C bond lengths (1.60–1.70 Å) found in compounds **1** and **2** are substantially shorter than the ordinary S–C single-bond lengths in the organic sulfonium salt (1.78–1.84 Å);[31] however, they are comparable to those reported for nickel and palladium sulfur ylide complexes.[19,20,32] Thus, again, this structural result suggests that the ylidic character is partially retained in these two compounds.

**Acknowledgment.** We express our appreciation to the National Science Council of the Republic of China for the support of this work.

**Supplementary Material Available:** Tables of all atomic coordinates, bond distances, bond angles, and anisotropic thermal parameters for $\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ and $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ (10 pages); tables of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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