Mixed Sulphur and Phosphorus Ylide Complexes of Palladium formed by Phase-transfer Catalysis. *X*-Ray Crystal Structure of $[Pd\{(CH_2)_2S(O)Me\}\{Ph_2PCH_2PPh_2CHC(O)Ph\}]I\cdot CH_2Cl_2\cdot H_2O$†

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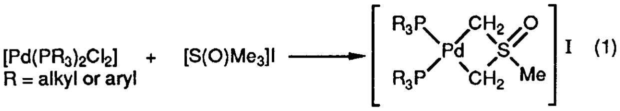
Phosphorus ylide complexes $[PdBr_2\{Ph_2P(CH_2)_nPPh_2CHC(O)R\}]$ (n = 1 or 2; R = Me, Ph, or OEt), and mixed sulphur and phosphorus ylide complexes $[Pd\{(CH_2)_2S(O)Me\}\{Ph_2P(CH_2)_n$-$PPh_2CHC(O)R\}]I$, have been synthesized by the phase-transfer technique. The presence of the phase-transfer catalyst has only a marginal effect in the preparation of phosphorus ylide-containing complexes. The mixed ylide compounds have both a chelated double sulphur ylide and a C,P-chelated phosphorus ylide. A mixed-ylide complex $[Pd\{(CH_2)_2S(O)Me\}\{Ph_2PCH_2$-$PPh_2CHC(O)Ph\}]I\cdot CH_2Cl_2\cdot H_2O$ has been investigated by means of *X*-ray crystallography. The Pd–C bond length of 2.183 5) Å for the phosphorus ylide co-ordination is longer than that for the sulphur ylide co-ordination [2.094(3) Å (average)].

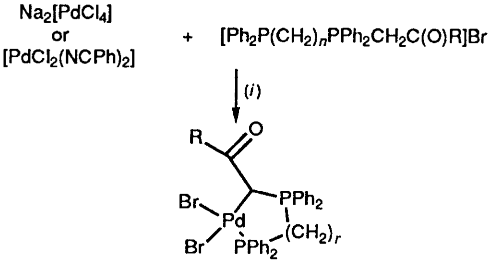
Phase-transfer catalysis (p.t.c.) is one of the most useful techniques in recent organic synthesis. Numerous reports have appeared in the literature,[1–4] however the application of this technique to organometallic synthesis is rare.[5–14] In our previous work, we have successfully demonstrated that sulphoxonium ylide (S-ylide) complexes of palladium can easily be prepared by the p.t.c. technique [equation (1)].[12,13]



This technique has many advantages: (*a*) the avoidance of anhydrous conditions; (*b*) relatively higher yields of pure products; (*c*) the use of the easily handled base NaOH; (*d*) easier work-up. We have been interested in applying this technique to other systems, such as phosphorus ylides (P-ylide). The first few attempted p.t.c. reactions were of $[Pd(PR_3)_2Cl_2]$ with ylide precursors such as $[PPh_2Me_2]I$, $[PPh_3Me]I$, and $[PPh_3\{CH_2$-$C(O)Ph\}]I$ under basic conditions. These reactions were unsuccessful. Our next candidate was the keto-stabilized P-ylide, $Ph_2P(CH_2)_nPPh_2[CHC(O)R]$ (n = 1 or 2; R = Me, Ph, or OEt). The keto-stabilized C,P-bonded P-ylide complexes of palladium were previously synthesized from the preformed neutral ylide and organic soluble $[PdCl_2(NCPh)_2]$ *via* a tedious scheme.[15–17] In this paper we report the synthesis of C,P-bonded P-ylide complexes of palladium by the p.t.c. technique, and the crystal structure of $[Pd\{(CH_2)_2S(O)Me\}$-$\{Ph_2PCH_2PPh_2CHC(O)Ph\}]I$ which contains a chelated S-ylide and a chelated P-ylide.

Results and Discussion

With the p.t.c. technique the ylide complexes can be prepared in a one-flask reaction using readily accessible starting materials (Scheme 1). In other words, $[PdCl_2(NCPh)_2]$ or $Na_2[PdCl_4]$ can be used as a source of palladium(II), and the phosphonium salt can be used directly as the ylide precursor. When $[PdCl_2(NCPh)_2]$ is used both reactants are soluble in CH_2Cl_2. Therefore the formation of the neutral compound $[PdX_3$-$\{Ph_2P(CH_2)_nPPh_2CH_2C(O)R\}]$ (X = Cl and/or Br) is facile.



	R	n
(**1a**)	Ph	1
(**1b**)	Me	1
(**1c**)	OEt	1
(**1d**)	Ph	2
(**1e**)	Me	2

Scheme 1. (*i*) (*a*) OH^-, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), (*b*) NaBr

Deprotonating the methylene proton next to the carbonyl group by OH^- (transfer from the aqueous layer to the organic layer *via* a p.t. catalyst) yields the C,P-chelated P-ylide complex. The water-soluble $Na_2[PdCl_4]$ can be transported to the organic layer by a p.t. catalyst. Reaction of the keto-stabilized phosphonium salt with $[PdCl_4]^{2-}$ in the organic phase produces the same neutral compound, which after deprotonation yields the C,P-chelated P-ylide complex. The preparation employing the p.t.c. technique is more versatile and much simpler than that reported by Oosawa *et al.*[15–17]

The preparation of mixed S- and P-ylide compounds can also be achieved by this simple p.t.c. technique. The starting material $[\{PdI[(CH_2)_2S(O)Me]\}_2]$ is only slightly soluble in CH_2Cl_2.

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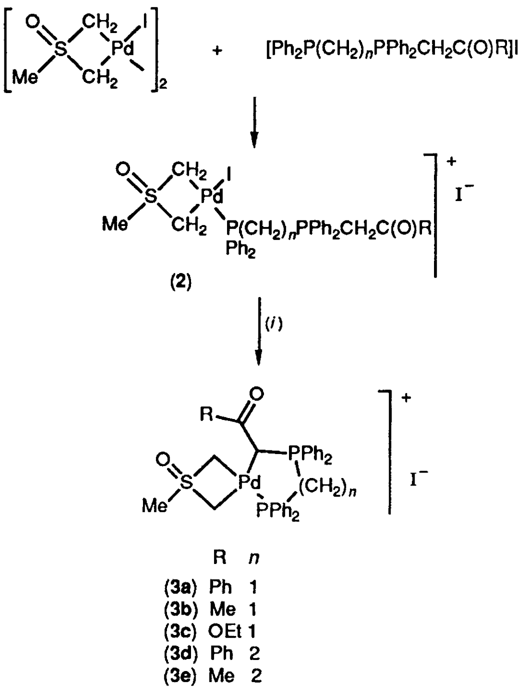
† {Benzoyl[diphenyl(diphenylphosphino-κ*P*-methyl)phosphonio]-methanide-κ*C*}(3-methyl-3-oxo-3λ^5-thioniapropane-1,2-diyl)palladium(II) iodide–dichloromethane–water (1/1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: $lbf\ in^{-2} \approx 6\,895$ Pa.

The addition of a phosphonium salt which is soluble in dichloromethane results in reaction with the suspended palladium dimer to form a dichloromethane-soluble compound (**2**) which is converted into (**3**) in the presence of base (Scheme 2). Among the intermediates (**2**), only [Pd{$(CH_2)_2S(O)Me$}I-{$Ph_2P(CH_2)_2PPh_2CH_2C(O)Ph$}]I has been isolated and characterized.



Scheme 2. (*i*) p.t.c., OH^-

Interestingly, Scheme 2 can proceed even without a p.t. catalyst and base when $n = 1$. That is, the palladium(II) ion can activate the methylene CH bond next to the carbonyl group. However, when $n = 2$ the reaction stops at (**2**) in the absence of OH^-. Also in Scheme 1, OH^- is always required to produce the C,P-chelated P-ylide compounds. The exact reason for the above observation is not yet clear, but we speculate that the special stability of the five-membered C,P-chelate ring and the stability of the ligand *trans* to this might be important.

In our previous work we have reported that the presence of a p.t. catalyst enhances the reaction rate and the yield of equation (1). In this work, however, the presence of a p.t. catalyst has only a marginal effect in the preparation of C,P-chelated P-ylide complexes. For example, in the presence of 18-crown-6, compound (**1a**) was obtained in 70% yield, while in the absence of the p.t. catalyst, a 60% yield was obtained. The different effects of the p.t. catalyst in these two reactions is not surprising. The trimethylsulphoxonium salt is soluble in water but not in organic solvents. Phosphonium salts, however, are very soluble in polar organic solvents and slightly soluble in water. They are at the same time good p.t. catalysts and reactants. The addition of a small amount of a second p.t. catalyst, therefore, has only a marginal effect on the p.t.c. reactions reported in this work.

The ^{31}P-{H} n.m.r. spectrum of compound (**3a**) displays two doublets centred at δ 41.45 and 23.86 p.p.m. The former is assigned to the keto-stabilized ylidic phosphorus and the latter to the phosphinic phosphorus. The two-bond ^{31}P–^{31}P coupling constant is 70 Hz. The ^{31}P-{H} n.m.r. spectra of (**3d**) and (**3e**) also show two doublets with smaller ^{31}P–^{31}P coupling constants (both 55 Hz). For compounds (**3b**) and (**3c**), however, there are two sets (with unequal intensities) of two doublets. Since there are two chiral centres in a mixed ylide compound (one at the ylidic carbon and another one at the sulphur atom), four different isomers are possible: (*R*,*R*), (*R*,*S*), (*S*,*R*), and (*S*,*S*). Taking enantiomer pairs into consideration, only two different sets of n.m.r. signals are expected. The observation of two sets of signals for (**3b**) and (**3c**) thus indicates that there are two pairs of enantiomers in these products.

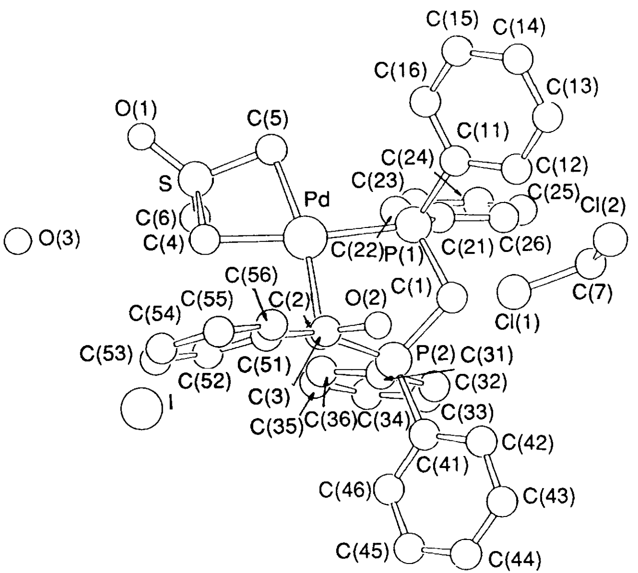


Figure. SCHAKAL drawing of complex (**3a**). The hydrogen atoms are omitted for clarity. The atomic numbering sequence is attached

Co-ordination unsaturation is a key factor for a transition-metal complex to act as a homogeneous catalyst. The keto-stabilized C,P-bonded complexes studied in this work contain a phosphine ligand and a weak ylidic Pd–C bond; the latter will potentially generate a vacant site around the palladium co-ordination sphere under hydrogen pressure. Therefore, it is worthwhile to investigate their possible use as hydrogenation catalysts. The hydrogenations were carried out in a Parr autoclave, under 120 lbf in^{-2} hydrogen pressure at 70 °C. The results are listed in Table 1. In general, the hydrogenation activities of these compounds are sensitive to the ligands present in the complexes. Compounds (**1a**) and (**1d**) prepared in this work are active hydrogenation catalysts toward simple olefins. Compound (**3a**) is not effective for alkene hydrogenation under the reaction conditions, but it is very selective toward the hydrogenation of phenylacetylene to styrene. The induction time is longer than 5 h, suggesting that the S-ylide anion is strongly bonded to the palladium metal. With the more sterically hindered diphenylacetylene, (**1d**) is a better catalyst. Under the same reaction conditions, the conversion is 47% after 24 h, and the *cis*:*trans* stilbene ratio is *ca.* 4:1. When compound (**3a**) was pretreated with $AgBF_4$, tetradecene was quantitatively hydrogenated to tetradecane and phenylacetylene was completely converted into ethylbenzene. Apparently the iodide anion deactivates the hydrogenation ability of (**3a**). Presumably, once the vacant site is produced during the reaction, the iodide anion will attach itself to the palladium metal. The reaction conditions have not been optimized for the hydrogenation reaction although better results can be expected.

To establish the mode of co-ordination in complex (**3a**), where both the P- and S-ylide fragments are present in the cation, it has been fully characterized by a single-crystal *X*-ray diffraction study. The final atomic parameters and selected bond distances and angles are presented in Tables 2 and 3, respectively. A SCHAKAL[18] drawing of the molecule, together with the atomic numbering sequence, is shown in the Figure. The centrosymmetric unit cell contains both enantiomeric forms. The chiral carbon atom C(2) is bonded to the Pd^{II}.

Table 1. Hydrogenation reactions

Substrate	Catalyst	Reaction time/h	Substrate/catalyst ratio	Product/%
1-Octene	**(1a)**	15	50:1	Octane, 100
	(1d)	15	50:1	Octane, 100
1-Tetradecene	**(1a)**	18	50:1	Tetradecane, 100
	(1d)	18	50:1	Tetradecane, 100
	(3a)	18	50:1	
	(3a) + $AgBF_4$[a]	18	100:1	Tetradecane, 100
PhC≡CH	**(3a)**	18(5)[b]	35:1	$PhCHCH_2$, 100(0)[b]
	(3a) + $AgBF_4$[a]	18	35:1	$PhCH_2CH_3$, 100
	(1d)	8	35:1	$PhCHCH_2$, 80 $PhCH_2CH_3$, 20
PhC≡CPh	**(1d)**	24	35:1	*cis*-PhCH=CHPh, 38 *trans*-PhCH=CHPh, 9

[a] The catalyst was prepared by adding one molar equivalent of $AgBF_4$ to compound (3) in CH_2Cl_2, and the precipitate was removed by filtration.
[b] Reaction time 5 h.

Table 2. Final atomic co-ordinates for the non-hydrogen atoms of complex **(3a)**

Atom	*X/a*	*Y/b*	*Z/c*
Pd	0.667 25(4)	0.170 08(2)	0.380 87(2)
I	0.734 23(5)	0.428 52(2)	0.302 50(2)
C(11)	0.147 26(21)	0.045 15(11)	0.375 37(11)
C(12)	−0.015 61(31)	−0.067 94(13)	0.421 24(13)
S	0.884 22(15)	0.222 42(8)	0.438 50(7)
P(1)	0.605 04(13)	0.060 65(6)	0.334 87(6)
P(2)	0.472 98(13)	0.174 37(7)	0.262 84(6)
O(1)	0.968 0(4)	0.242 4(2)	0.491 5(2)
O(2)	0.320 8(4)	0.183 7(2)	0.376 3(2)
O(3)	0.944 2(6)	0.431 7(3)	0.489 7(3)
C(1)	0.461 2(5)	0.079 9(2)	0.286 9(2)
C(2)	0.510 6(5)	0.227 6(2)	0.332 8(2)
C(3)	0.403 6(5)	0.231 2(2)	0.376 7(2)
C(4)	0.739 9(6)	0.263 6(3)	0.428 1(3)
C(5)	0.825 6(5)	0.134 6(3)	0.434 0(3)
C(6)	0.963 3(7)	0.238 5(3)	0.364 8(3)
C(7)	0.095 2(9)	−0.044 1(4)	0.364 9(4)
C(11)	0.562 5(5)	−0.015 5(2)	0.386 9(2)
C(12)	0.464 2(6)	−0.062 2(3)	0.370 5(3)
C(13)	0.437 7(6)	−0.122 5(3)	0.411 5(3)
C(14)	0.509 2(6)	−0.134 3(3)	0.466 4(3)
C(15)	0.606 8(6)	−0.088 3(3)	0.482 5(3)
C(16)	0.633 4(6)	−0.028 3(3)	0.443 3(3)
C(21)	0.711 2(5)	0.020 4(3)	0.276 9(2)
C(22)	0.829 7(6)	0.048 5(3)	0.268 7(3)
C(23)	0.913 1(6)	0.017 1(3)	0.226 5(3)
C(24)	0.880 2(7)	−0.043 7(4)	0.191 2(3)
C(25)	0.762 3(7)	−0.071 1(4)	0.197 8(4)
C(26)	0.677 7(7)	−0.040 4(4)	0.239 9(3)
C(31)	0.598 3(5)	0.182 8(3)	0.206 0(2)
C(32)	0.594 9(6)	0.137 5(4)	0.151 3(3)
C(33)	0.692 0(7)	0.142 5(5)	0.106 3(3)
C(34)	0.789 4(6)	0.190 8(4)	0.115 4(3)
C(35)	0.789 1(6)	0.235 3(3)	0.168 6(3)
C(36)	0.696 3(5)	0.231 0(3)	0.214 4(3)
C(41)	0.333 0(5)	0.201 6(3)	0.219 6(2)
C(42)	0.228 7(6)	0.159 1(3)	0.210 9(3)
C(43)	0.126 3(7)	0.185 1(4)	0.174 8(4)
C(44)	0.128 2(6)	0.252 5(4)	0.146 9(3)
C(45)	0.230 7(7)	0.295 2(4)	0.155 3(4)
C(46)	0.334 4(6)	0.270 0(3)	0.190 2(4)
C(51)	0.392 0(5)	0.294 0(3)	0.423 9(2)
C(52)	0.467 4(6)	0.355 4(3)	0.420 2(3)
C(53)	0.446 6(8)	0.413 3(3)	0.463 7(4)
C(54)	0.356 0(8)	0.409 4(4)	0.509 1(4)
C(55)	0.282 4(9)	0.349 0(4)	0.512 1(4)
C(56)	0.299 9(7)	0.290 8(3)	0.469 5(3)

Complexes of Pd^{II} with P-ylides have been the subject of detailed studies.[19] This is particularly true for P-ylides bearing an additional donor function, so that chelate formation is possible. For **(3a)**, the bidentate P-ylide is C,P-bonded to Pd^{II}. The other two sites around Pd^{II} accommodate the S-ylide anion, $[(CH_2)_2S(O)Me]^-$. The Pd^{II} is therefore co-ordinated by two chelate ligands. The co-ordination sphere around the Pd^{II} deviates slightly from square planar: the angle C(4)–Pd–C(5) is only 74.2(2)°, though the five atoms [Pd, P(1), C(2), C(4), C(5)] are coplanar within 0.008 Å. Among the ylide C atoms, C(2) is nearly sp^3 hybridized, whereas C(4) and C(5) are distorted sp^3 due to the four-membered chelate ring in which the inner angles of C(4) and C(5) are 91.1(2) and 91.4(2)°, respectively. The phosphine P(1) is co-ordinated to Pd^{II} with a length of 2.301(1) Å, and a five-membered chelate ring is formed in the chair form: the atom P(2) is 0.762(5) Å out of the Pd, P, C(1), C(2) base plane.

Out of a handful of reported *X*-ray structures of palladium(II) complexes of P- and S-ylides, **(3a)** is believed to be the first containing both σ-bonded chelates. Hence, a direct comparison of their bonding and structure in relation to the Pd–C bonds is possible. The Pd–C lengths, formed by the P-ylide, have been reported to be 2.097(5) Å in $[Pd(1,5\text{-}C_8H_{12})\{CH(PPhMe_2)(SiMe_3)\}Cl]PF_6$,[20] 2.193(3) Å in $[PdCl(CH_2CMeCH_2)\{CH[C(O)Me](PPh_3)\}]$,[21] and 2.115(15) Å in the dichloride analogue of **(1d)**.[22] The corresponding length in complex **(3a)** is seen to be 2.183(5) Å, a relatively long bond. On the other hand, the Pd–C lengths for S-ylides have been reported[14] to be 2.120(15) Å. For the S-ylide anions the Pd–C lengths are 2.07(2) and 2.08(2) Å in $[Pd\{(CH_2)S(O)Me_2\}I\{(CH_2)_2S(O)Me\}]$[14] and 2.093(1) and 2.099(1) Å in $[Pd\{(CH_2)_2S(O)Me\}_2]$.[23] In complex **(3a)** the lengths for the S-ylide anion are 2.087(5) and 2.103(5) Å, in good agreement with previously reported values.

In complex **(3a)** both Pd–C σ bonds derived from the S-ylide are significantly shorter than the Pd–C σ bond derived from the P-ylide, leading to the conclusion that the former bonds are stronger than the latter. It is certainly expected because both ylides are regarded as P- or S-stabilized carbenes. The P-ylide is further stabilized by the ketone group, hence its donor ability is less than that of the S-ylide. Among the two Pd–C bonds derived from the S-ylide, the one [Pd–C(5)] *trans* to the P-ylide C(2) atom is somewhat shorter than the one [Pd–C(4)] *trans* to the phosphine P(1) atom, an indication that the *trans* influence of the P-ylide C(2) atom is comparable with but smaller than

Table 3. Bond lengths (Å) and angles (°) involving non-hydrogen atoms of complex (**3a**)

Pd–P(1)	2.301(1)	P(1)–C(21)	1.810(5)	C(15)–C(16)	1.392(7)	C(41)–C(42)	1.360(8)
Pd–C(2)	2.183(5)	P(2)–C(1)	1.799(5)	C(21)–C(22)	1.371(8)	C(41)–C(46)	1.388(7)
Pd–C(4)	2.103(5)	P(2)–C(2)	1.773(5)	C(21)–C(26)	1.387(8)	C(42)–C(43)	1.386(9)
Pd–C(5)	2.087(5)	P(2)–C(31)	1.792(5)	C(22)–C(23)	1.374(9)	C(43)–C(44)	1.357(9)
Cl(1) • • • Cl(2)	2.864(3)	P(2)–C(41)	1.784(5)	C(23)–C(24)	1.367(9)	C(44)–C(45)	1.346(10)
Cl(1)–C(7)	1.732(8)	O(2)–C(3)	1.235(6)	C(24)–C(25)	1.357(10)	C(45)–C(46)	1.380(9)
Cl(2)–C(7)	1.720(9)	C(2)–C(3)	1.465(7)	C(25)–C(26)	1.376(9)	C(51)–C(52)	1.380(8)
S–O(1)	1.437(4)	C(3)–C(51)	1.508(7)	C(31)–C(32)	1.393(8)	C(51)–C(56)	1.366(8)
S–C(4)	1.714(6)	C(11)–C(12)	1.384(8)	C(31)–C(36)	1.371(8)	C(52)–C(53)	1.404(8)
S–C(5)	1.723(5)	C(11)–C(16)	1.388(7)	C(32)–C(33)	1.401(9)	C(53)–C(54)	1.354(10)
S–C(6)	1.767(7)	C(12)–C(13)	1.419(8)	C(33)–C(34)	1.368(10)	C(54)–C(55)	1.353(10)
P(1)–C(1)	1.833(5)	C(13)–C(14)	1.361(9)	C(34)–C(35)	1.362(10)	C(55)–C(56)	1.392(9)
P(1)–C(11)	1.815(5)	C(14)–C(15)	1.368(9)	C(35)–C(36)	1.375(8)		
P(1)–Pd–C(2)	91.4(1)	C(11)–P(1)–C(21)	103.9(2)	C(12)–C(11)–C(16)	119.5(4)	C(33)–C(34)–C(35)	118.7(6)
P(1)–Pd–C(4)	173.7(2)	C(1)–P(2)–C(2)	108.7(2)	C(11)–C(12)–C(13)	119.5(5)	C(34)–C(35)–C(36)	121.8(6)
P(1)–Pd–C(5)	99.5(1)	C(1)–P(2)–C(31)	108.5(2)	C(12)–C(13)–C(14)	120.0(5)	C(31)–C(36)–C(35)	120.1(5)
C(2)–Pd–C(4)	94.9(2)	C(1)–P(2)–C(41)	110.0(2)	C(13)–C(14)–C(15)	120.6(5)	P(2)–C(41)–C(42)	125.0(4)
C(2)–Pd–C(5)	169.1(2)	C(2)–P(2)–C(31)	108.8(2)	C(14)–C(15)–C(16)	120.3(5)	P(2)–C(41)–C(46)	116.8(4)
C(4)–Pd–C(5)	74.2(2)	C(2)–P(2)–C(41)	114.9(2)	C(11)–C(16)–C(15)	120.1(5)	C(42)–C(41)–C(46)	118.1(5)
Cl(2)–Cl(1)–C(7)	33.8(3)	C(31)–P(2)–C(41)	105.9(2)	P(1)–C(21)–C(22)	120.8(4)	C(41)–C(42)–C(43)	120.1(5)
Cl(1)–Cl(2)–C(7)	34.1(3)	P(1)–C(1)–P(2)	105.6(3)	P(1)–C(21)–C(26)	121.9(5)	C(42)–C(43)–C(44)	121.2(6)
O(1)–S–C(4)	121.3(3)	Pd–C(2)–P(2)	105.0(2)	C(22)–C(21)–C(26)	117.3(5)	C(43)–C(44)–C(45)	119.4(6)
O(1)–S–C(5)	119.6(3)	Pd–C(2)–C(3)	109.7(3)	C(21)–C(22)–C(23)	121.6(5)	C(44)–C(45)–C(46)	120.4(6)
O(1)–S–C(6)	107.9(3)	P(2)–C(2)–C(3)	110.9(4)	C(22)–C(23)–C(24)	120.7(6)	C(41)–C(46)–C(45)	120.7(6)
C(4)–S–C(5)	94.7(3)	O(2)–C(3)–C(2)	121.6(4)	C(23)–C(24)–C(25)	118.2(6)	C(3)–C(51)–C(52)	121.8(5)
C(4)–S–C(6)	105.0(3)	O(2)–C(3)–C(51)	118.2(5)	C(24)–C(25)–C(26)	121.7(6)	C(3)–C(51)–C(56)	118.3(5)
C(5)–S–C(6)	106.6(3)	C(2)–C(3)–C(51)	120.2(4)	C(21)–C(26)–C(25)	120.4(6)	C(52)–C(51)–C(56)	119.8(5)
Pd–P(1)–C(1)	106.4(2)	Pd–C(4)–S	91.1(2)	P(2)–C(31)–C(32)	117.7(4)	C(51)–C(52)–C(53)	118.5(6)
Pd–P(1)–C(11)	119.8(2)	Pd–C(5)–S	91.4(2)	P(2)–C(31)–C(36)	122.9(4)	C(52)–C(53)–C(54)	121.4(6)
Pd–P(1)–C(21)	116.4(2)	Cl(1)–C(7)–Cl(2)	112.1(4)	C(32)–C(31)–C(36)	119.3(5)	C(53)–C(54)–C(55)	119.5(6)
C(1)–P(1)–C(11)	104.4(2)	P(1)–C(11)–C(12)	121.6(4)	C(31)–C(32)–C(33)	119.0(6)	C(54)–C(55)–C(56)	120.7(7)
C(1)–P(1)–C(21)	104.3(2)	P(1)–C(11)–C(16)	118.9(4)	C(32)–C(33)–C(34)	121.0(6)	C(51)–C(56)–C(55)	120.1(6)

that of the phosphine P(1) atom. A similar *trans* influence has been reported for the dichloride analogue of (**1d**).[22]

Both the ylidic S–C and P–C bond lengths (average 1.727 and 1.772 Å, respectively) found in compound (**3**) are shorter than the ordinary S–C and P–C single-bond lengths found in organic sulphonium salts (1.78—1.84 Å)[24] and phosphonium salts (1.79—1.81).[25] Thus the ylidic properties for both the S- and P-ylides are partially retained. Shorter ylidic S–C and P–C bond lengths have been noted in other S- and P-ylide complexes.[13,19,23]

The crystal structure has CH_2Cl_2 and H_2O molecules packed in voids formed by the complex (**3a**). The H_2O molecules are dimeric because of hydrogen bonding. The molecular interaction between CH_2Cl_2 and compound (**3**) is normal judging from the closest intermolecular contacts at *ca.* 3 Å.

Experimental

Infrared spectra were recorded as KBr disks on a Analect RFX-600 spectrometer, ^1H n.m.r. spectra on a Varian EM-360 at 60 MHz or on a Bruker AM-300WM spectrometer at 300 MHz. Chemical shifts are downfield relative to $SiMe_4$. The $^{31}P-\{H\}$ n.m.r. spectra were recorded on a Bruker AM-300WB spectrometer at 120 MHz with 85% H_3PO_4 as external reference. Elemental analyses were by the Taipei Instrumentation Center, Taipei, Taiwan.

The compounds $[PdCl_2(NCPh)_2]$,[26] $[\{Pd(\mu-I)[(CH_2)_2S(O)Me]\}_2]$,[14] and $[Ph_2P(CH_2)_nPPh_2CH_2C(O)R]Br$,[16] where n = 1 or 2, R = Me, Ph, or OEt, were prepared as described in the literature.

Complex (**1a**).—*Method* (*a*). The compound $[PdCl_2(NCPh)_2]$ (0.078 g, 0.20 mmol) in CH_2Cl_2 (8 cm^3) was added to a CH_2Cl_2 solution (5 cm^3) of $[Ph_2PCH_2PPh_2CH_2C(O)Ph]Br$ (0.12 g, 0.206 mmol), followed by aqueous KOH (0.1 N, 3 cm^3) and 18-crown-6 (0.01 g, 0.038 mmol). The initially brown solution turned orange and then yellow. It was stirred for 30 min, then NaBr (0.021 g, 0.205 mmol in 2 cm^3 MeOH) was added. Reaction continued for 30 min, then CH_2Cl_2 (5 cm^3) and water (15 cm^3) were added to the two-phase solution to facilitate separation. The organic layer was separated, washed three times with water (15 cm^3 each), dried (with $MgSO_4$), filtered, and finally evaporated to dryness on a vacuum rotary evaporator. The residue was washed with copious amounts of diethyl ether. The crude yellow product was obtained in 70% yield. It can be recrystallized from CH_3Cl–n-hexane in 65% yield.

Method (*b*). The salt $Na_2[PdCl_4]$ (0.06 g, 0.204 mmol) in water (3 cm^3), was added to a solution of $[Ph_2PCH_2PPh_2C(O)Ph]Br$ (0.12 g, 0.206 mmol) in CH_2Cl_2 (5 cm^3). To this two-phase solution, 18-crown-6 (0.01 g, 0.038 mmol) and a KOH solution (0.1 N, 3 cm^3) were added. The rest of the reaction procedure and work-up were similar to that in (*a*). A 60% yield of product was obtained.

Method (*c*): *reaction without a p.t. catalyst.* The same procedure was followed as in (*a*) except that no p.t. catalyst was added. The product was obtained in 60% yield, m.p. 279—281 °C (Found: C, 50.6; H, 3.7. Calc. for $C_{33}H_{28}Br_2OP_2Pd$: C, 51.6; H, 3.7%). I.r.: ν(CO) 1 614 cm^{-1}. ^1H N.m.r. $[(CD_3)_2SO]$: δ 8.3—7.2 (m, 25 H, C_6H_5), 6.18 (m, 1 H, CH), and 4.9—4.5 (m, 2 H, CH_2).

Compounds (**1b**)—(**1d**) which have been reported can also be prepared by method (*a*).

Complex (**2**).—The compound $[\{Pd(\mu-I)[(CH_2)_2S(O)Me]\}_2]$ (0.1 mg, 0.154 mmol) was stirred in CH_2Cl_2 (10 cm^3) for 10 min, then the salt $[Ph_2P(CH_2)_2PPh_2C(O)Ph]Br$ (0.142 g, 0.308

mmol) was added. After the yellow cloudy solution became clear yellow, a methanol solution (2 cm^3) of NaI (0.046 g, 0.308 mmol) was added and stirred for 1 h. The reaction mixture was washed with water three times, then dried with $MgSO_4$, filtered, and reduced in volume. Addition of hexane afforded the product in 60% yield (Found: C, 47.1; H, 4.2. Calc. for $C_{37}H_{38}I_2P_2PdS$: C, 47.4; H, 4.1%). I.r.: ν(SO) 1 196, ν(CO) 1 672 cm^{-1}. N.m.r. [$(CD_3)_2SO$]: ^{1}H, δ 8.2—7.3 (m, 25 H, C_6H_5), 6.2 (m, 2 H, PCH_2), 3.5 [t, 3 H, ^4J(HH) 1.7 Hz, SCH_3], 3.0—2.5 (m, 4 H, SCH_2), and 2.0 (m, 4 H, PCH_2); ^{31}P-{H}, δ 26.78 [d, 1 P, ^3J(PP) 50, phosphine P] and 19.54 p.p.m. [d, 1 P, ^3J(PP) 50 Hz, phosphonium P].

Complex (**3a**).—*Method* (*a*): *preparation under p.t.c. conditions*. A sample of [{Pd(μ-I)[$(CH_2)_2S(O)Me$]}$_2$] (100 mg, 0.154 mmol) was suspended in CH_2Cl_2 (8 cm^3) and after stirring for 10 min was added to [$Ph_2PCH_2PPh_2C(O)Ph$]Br (179 mg, 0.308 mmol). The suspension gradually became clear yellow. To it were added KOH (0.1 N, 2.5 cm^3), 18-crown-6 (10 mg, 0.038 mmol), and NaI (46 mg, 0.306 mmol). After stirring for 30 min, CH_2Cl_2 (5 cm^3) and water (15 cm^3) were added. After the usual procedures for phase separation, washing, and drying, the organic layer was evaporated under vacuum. An 80% yield of the product was obtained after washing with ether and n-hexane. Recrystallization from CH_2Cl_2 gave two different types of crystal, one rectangular and the other needle shaped. Both showed identical cell parameters (by *X*-ray diffraction) and identical ^{31}P n.m.r. signals.

Method (*b*): *preparation without a p.t. catalyst and* OH^-. A similar procedure was followed as in (*a*), except that KOH and 18-crown-6 were not added. The yield after recrystallization was 56%, m.p. 170—172 °C (Found: C, 47.2; H, 4.0. Calc. for $C_{36}H_{35}IO_2P_2PdS$: C, 47.3; H, 4.0%). I.r.: ν(SO) 1 198, ν(CO) 1 604 cm^{-1}. N.m.r. [$(CD_3)_2SO$]: ^{1}H, δ 8.1—7.3 (m, 25 H, C_6H_5), 5.64 [d, 1 H, ^2J(PH) 15, CH], 5.0—4.5 (m, 2 H, PCH_2), 3.5 [t, 3 H, ^4J(HH) 1.8 Hz, SCH_3], and 3.2—2.1 (m, 4 H, SCH_2); ^{31}P-{H}, δ 41.45 [d, 1 P, ^2J(PP) 70, ylide P] and 23.86 p.p.m. [d, 1 P, ^2J(PP) 70 Hz, phosphine P].

Complex (**3b**).—The compound was prepared by the methods described for (**3a**). A 63% yield was obtained by method (*a*) and a 50% yield by (*b*), m.p. 154—156 °C (Found: C, 49.0; H, 4.3. Calc. for $C_{31}H_{33}IO_2P_2PdS$: C, 48.7; H, 4.3%). I.r.: ν(SO) 1 194, ν(CO) 1 626 cm^{-1}. N.m.r. [$(CD_3)_2SO$]: ^{1}H, first set, δ 8.0—7.3 (m, 20 H, C_6H_5), 4.90 (m, 1 H, CH), 4.5—4.3 (m, 2 H, PCH_2), 3.50 [t, 3 H, ^4J(HH) 1.7, SCH_3], 4.1—2.4 (m, 4 H, SCH_2), and 2.20 (s, 3 H, CCH_3); second set 8.0—7.3 (m, 20 H, C_6H_5), 4.80 (m, 1 H, CH), 3.45 [t, 3 H, ^4J(HH) 1.7 Hz, SCH_3], 3.7—2.7 (m, 4 H, SCH_2), and 2.16 (s, 3 H, CH_3); ^{31}P-{H}, first set, δ 39.43 [d, 1 P, ^2J(PP) 78, ylide P] and 23.50 [d, 1 P, ^2J(PP) 78, phosphine P]; second set, 38.81 [d, 1 P, ^2J(PP) 68, phosphine P] and 22.28 p.p.m. [d, 1 P, ^2J(PP) 68 Hz, ylide P].

Complex (**3c**).—This compound was also prepared by the methods described for (**3a**). The yield was *ca.* 70%, m.p. 165 °C (Found: C, 47.6; H, 4.3. Calc. for $C_{32}H_{35}IO_3P_2PdS$: C, 48.4; H, 4.4%). I.r.: ν(SO) 1 194, ν(CO) 1 664 cm^{-1}. N.m.r. [$(CD_3)_2SO$]: ^{1}H, first set, δ 7.9—7.3 (m, 20 H, C_6H_5), 4.78 (m, 1 H, PCH), 4.5—4.3 (m, 2 H, PCH_2), 3.95 [q, 2 H, ^3J(HH) 7.3, OCH_2], 3.62 [t, 3 H, ^4J(HH) 1.7, SCH_3], 3.5—3.2 (m, 4 H, SCH_2), and 0.9 [t, 3 H, ^3J(HH) 7.3, CH_3]; second set, *ca.* 7.9—7.3 (m, 20 H, C_6H_5), 5.24 (m, 1 H, CH), 3.89 [q, 2 H, ^3J(HH) 7.1, OCH_2], 3.70 [t, 3 H, ^4J(HH) 1.7, SCH_3], and 1.41 [t, 3 H, ^3J(HH) 7.1 Hz, CH_3]; ^{31}P-{H}, first set, δ 42.97 [d, 1 P, ^2J(PP) 66, ylide P] and 22.52 [d, 1 P, ^2J(PP) 66, phosphine P]; second set, 40.66 [d, 1 P, ^2J(PP) 66, ylide P] and 21.45 p.p.m. [d, 1 P, ^2J(PP) 6 Hz, phosphine P].

Complex (**3d**).—The compound was prepared by method (*a*) described for (**3a**) (60% yield), but not method (*b*). If the reaction was carried out under similar conditions except without the p.t. catalyst, the product yield was 55%, m.p. 135—139 °C (Found: C, 51.8; H, 4.4. Calc. for $C_{37}H_{37}IO_2P_2PdS$: C, 50.1; H, 4.4%). I.r.: ν(SO) 1 194, ν(CO) 1 616 cm^{-1}. N.m.r. [$(CD_3)_2SO$]: ^{1}H, δ 8.0—7.5 (m, 25 H, C_6H_5), 5.6 (m, 1 H, PCH), 3.5 [t, 3 H, ^4J(HH) 1.7 Hz, SCH_3], 3.0—2.6 (m, 4 H, SCH), and 2.4—2.0 (m, 4 H, PCH_2); ^{31}P-{H}, δ 30.16 [d, 1 P, ^3J(PP) 55, ylide P] and 24.13 p.p.m. [d, 1 P, ^3J(PP) 55 Hz, phosphine P].

Complex (**3e**).—This compound was prepared using the same procedures as for (**3a**), m.p. 138—142 °C (Found: C, 49.6; H, 4.5. Calc. for $C_{32}H_{35}IO_2P_2PdS$: C, 49.4; H, 4.5%). I.r.: ν(SO) 1 186, ν(CO) 1 683 cm^{-1}. N.m.r. [$(CD_3)_2SO$]: ^{1}H, δ 8.0—7.4 (m, 20 H, C_6H_5), 5.15 [d, 1 H, ^2J(PH) 12.3, PCH], 3.6 [t, 3 H, ^4J(HH) 1.7 Hz, SCH_3], 3.2—2.8 (m, 4 H, SCH_2), 2.1 (s, 3 H, CH_3), and 2.4—1.8 (m, 4 H, CH_2 on S-ylide); ^{31}P-{H}, δ 35.21 [d, 1 P, ^3J(PP) 55, ylide P] and 24.12 p.p.m. [d, 1 P, ^3J(PP) 55 Hz, phosphine P].

Typical Hydrogenation Reaction.—In a Parr autoclave (45 cm^3) were placed phenylacetylene (0.94 mmol), complex (**1d**) (0.026 mmol), and CH_2Cl_2 (3 cm^3). Nitrogen gas was bubbled through this solution for 3 min, followed by hydrogen gas for 1 min. The autoclave was then sealed and charged with 120 lbf in^{-2} of hydrogen gas. The reactor was heated in an oil-bath at 65 °C for 8 h. It was then cooled to room temperature and the unreacted H_2 was vented. The product was analysed by ^{1}H n.m.r. spectroscopy and g.c. with an EP-200 column.

X-*Ray Structure Analysis of Complex* (**3a**).—*Crystal data*. $C_{36}H_{35}IO_2P_2PdS\cdot CH_2Cl_2\cdot H_2O$, $M = 929.61$, monoclinic, space group $P2_1/c$, $a = 10.606(1)$, $b = 18.265(6)$, $c = 20.507(2)$ Å, $\beta = 91.15(1)°$, $U = 3\,972(1)$ Å^3 (25 reflections with 2θ between 9.4 and 11.9°), $Z = 4$, $F(000) = 1\,815.87$, $D_c = 1.56$ g cm^{-3}, Mo-K_α radiation, μ(Mo-K_α) = 1.52 mm^{-1}, $T = 298$ K, crystal size 0.10 × 0.25 × 0.50 mm; crystallization from CH_2Cl_2.

Nonius CAD-4 diffractometer; ω—2θ scan; 2θ up to 50°; three standards (−4, 4, −3), (−1, −5, −8), (−1, 5, −8) remeasured after every 3 600 s. Intensities corrected for Lorentz, polarization, and absorption (empirical ψ rotation,[27] minimum and maximum transmission 0.82 and 1.00); 6 990 reflections measured, 4 812 observed [$I_0 \geq 2.5\sigma(I)$]. Structure solved by the heavy-atom method; non-hydrogen atoms located; least-squares routine minimizing $\Sigma w||F_o| - |F_c||^2$ (*w* based on counting statistics and a modifier of 0.02 on F_o). Hydrogen atoms idealized at anisotropic convergence; final *R* 0.040 and *R′* 0.070; goodness of fit 2.17; maximum Δ/σ 0.005; maximum and minimum residual in final electron-density map 1.31 and −0.72 e Å^{-3}, largest peak 1.3 Å from I.

The scattering factors and anomalous dispersion corrections were applied according to ref. 28. All calculations were carried out on a VAX 11/780 computer using the NRCC structure analysis package.[29]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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