Preparation and Properties of Ethylpalladium Thiolate Complexes. Reaction with Organic Halides leading to C–S Bond Formation; Crystal Structure of *trans*-[PdEt(Br)(PMe_3)$_2$]‡

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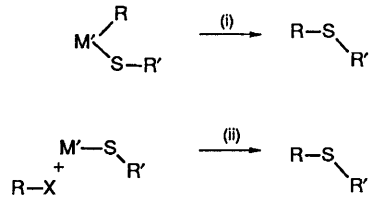
The complexes *trans*-[PdEt(SR)(PMe_3)$_2$] (R = Ph, **1**; or C_6H_4Me-*p*, **2**) and *trans*-[PdMe(SPh)(PMe_3)$_2$] **3** have been prepared by reactions of *trans*-[$PdEt_2$(PMe_3)$_2$] or *trans*-[$PdMe_2$(PMe_3)$_2$] with allyl aryl sulphides. Complex **1** reacts with various organic halides such as allyl chloride, benzyl bromide and methyl iodide to give allyl phenyl sulphide, benzyl phenyl sulphide and methyl phenyl sulphide, respectively; *trans*-[PdEt(X)(PMe_3)$_2$] (X = Cl, **4**; Br, **5**; or I, **6**) were isolated from the reaction mixtures. The complex *trans*-[PdEt(OPh)(PMe_3)$_2$(HOPh)] also reacts with allyl chloride to give allyl phenyl ether together with complex **4**. The structure of complex **5** has been determined by X-ray crystallography: orthorhombic, space group *Pbca* with a = 12.306(3), b = 20.078(5), c = 11.753(2) Å, Z = 8, R = 0.036 and R' = 0.042. It has a square-planar co-ordination around the palladium centre. The reaction of allyl chloride with complex **1** in toluene obeys first-order kinetics in the concentrations of both allyl chloride and **1**.

Organometallic complexes of late transition metals having alkoxide, amide and thiolate ligands have recently attracted increased attention.[1] One of the interesting properties of these compounds is their reactivity with electrophilic reagents such as organic halides leading to C–O, C–N and C–S bond formation; such reactions are considered to be involved as crucial steps in several transition-metal-catalysed reactions. A platinum phenoxide complex was reported to react with phenyl chloroformate to give diphenyl carbonate.[2] Platinum methoxide and 1-phenylethylamido complexes react with methyl iodide to give the corresponding ether and tertiary amine, respectively.[3] We have also observed the reaction of carboxylic esters with methylpalladium fluoroalkoxide complexes which results in transesterification.[4] These reactions can be considered to proceed through electrophilic attack of the organic halides or carboxylic esters on the alkoxide or amide ligand. On the other hand, reaction of alkyl or acyl halides with alkoxide complexes of Rh^I and Ir^I resulting in C–O bond formation was supposed to proceed through initial oxidative addition of the substrates followed by reductive elimination of ethers or esters.[5] In the former reactions C–O bond formation proceeds through intermolecular reaction of organic halides with the alkoxide ligand, while reductive elimination[6] is essential to the C–O bond formation in the latter reactions.

Previously Murahashi and Kosugi, and their respective co-workers[7,8] reported palladium-catalysed cross-coupling of organic halides with lithium and sodium thiolate to give sulphides. Nickel complexes were also reported to promote similar cross-coupling reactions.[9] Two pathways are possible for the reactions depending on the mode of formation of the C–S bond in the product. One involves reductive elimination of sulphides from organo-palladium or -nickel thiolate intermediate complexes, the other electrophilic attack of organic halides on the thiolate ligands.



Scheme 1 M′ = NiL_n or PdL_n, L = PPh_3

Although C–S bond formation by reductive elimination of aryl(thiolato)nickel complexes as in path (i) of Scheme 1 has been reported,[10] there has been no report on the reaction of nickel and palladium thiolate complexes with organic halides to cause C–S bond formation in a manner similar to path (ii). The paucity of such studies may be due to the scarcity of isolated and well characterized nickel and palladium thiolate complexes. We have found that dialkylpalladium complexes having basic tertiary phosphine ligands are reactive and suitable for the preparation of alkylpalladium thiolate complexes. Here we report the preparation of alkylpalladium thiolate complexes that proved to be suitable for an examination of their reactivities toward organic halides.

Results and Discussion

(*a*) *Preparation of Complexes* **1**–**3**.—Reaction of *trans*-[$PdEt_2$(PMe_3)$_2$] with equimolar allyl phenyl sulphide at room temperature gives *trans*-[PdEt(SPh)(PMe_3)$_2$] **1**, as in equation (1). Complex **1** can also be obtained by reaction of [$PdEt_2$-(PMe_3)$_2$] with thiophenol [equation (2)]. Reaction of allyl *p*-tolyl sulphide with **1** gives *trans*-[PdEt(SC_6H_4Me-*p*)(PMe_3)$_2$] **2** similarly. Reaction of allyl phenyl sulphide with *trans*-[$PdMe_2$(PMe_3)$_2$] gives *trans*-[PdMe(SPh)(PMe_3)$_2$] **3**. The latter reaction is slower than that with *trans*-[$PdEt_2$(PMe_3)$_2$]

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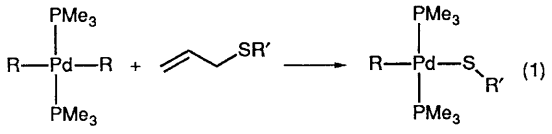
‡ *trans*-Bromo(ethyl)bis(trimethylphosphine)palladium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

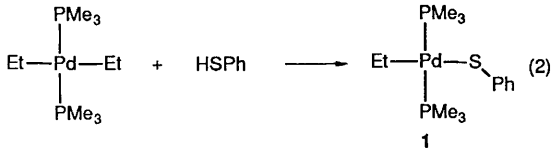
Table 1 NMR data for complexes **1**, **2** and **4**–**6**

	^1H[a]			^{13}C[b]			^{31}P-$\{^1H\}$[c]
Complex	$P(CH_3)_3$[d]	CH_2	CH_3	$P(CH_3)_3$[d]	CH_2	CH_3	
1[e]	1.29	1.35–1.15(m)[f]		13.2 (130)	9.4 (131)	16.1 (124)	−15.3
2	1.30	1.35–1.15(m)[f]					−14.9
4	1.35	1.58(m)	1.00(tt) $J(PH) = 4$ $J(HH) = 8$	12.9 (131)	8.6 (134)	16.5 (125)	−15.4
5	1.40	1.57(m)	1.09(tt) $J(PH) = 5$ $J(HH) = 8$				−16.7
6	1.47	1.57(tq) $J(PH) = 9$ $J(HH) = 8$	1.02(tt) $J(PH) = 5$ $J(HH) = 8$	15.2 (130)	15.5 (133)	16.5 (125)	−17.8

[a] 500 MHz at −40 °C in CD_2Cl_2. [b] 125 MHz at −40 °C in CD_2Cl_2, J(CH)/Hz in parentheses. [c] 40 MHz at −40 °C in CD_2Cl_2 except for complex **6** (at −20 °C). [d] Apparent triplet due to virtual coupling. Observed splittings are 3 (^1H) and 14–15 Hz (^{13}C). [e] Other signals: ^1H, δ 7.34, (*o*), 6.98 (*m*) and 6.72 (*p*); ^{13}C, 151.1 (*ipso*), 131.8 (*m*), 127.2 (*o*) and 120.0 (*p*). [f] Coupling pattern and coupling constants were not obtained due to overlapping of the signals (see text).



1 R = Et, R′ = Ph
2 R = Et, R′ = C_6H_4Me-*p*
3 R = Me, R′ = Ph



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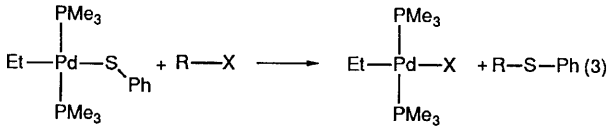
under similar conditions, and the yield of **3** in reaction (2) is 24% even after 96 h. Allyl phenyl sulphide does not react with *cis*-$[PtMe_2(PMe_3)_2]$ under similar conditions.

Complexes **1** and **2** were characterized by IR and NMR spectroscopy as well as by elemental analysis. NMR data are shown in Table 1. The spectroscopic data for complex **3** agree well with those of *trans*-$[PdMe(SPh)(PMe_3)_2]$.[4] The ^1H NMR spectrum of **1** shows a signal at δ 1.29 due to the PMe_3 ligands as an apparent triplet by virtual coupling.[11] Signals due to the CH_2 and CH_3 hydrogens appear as a multiplet at δ 1.35–1.15. They show complicated splitting due to the close proximity of the individual peaks. Values of J(HP) and J(HH) could not be obtained due to this splitting and to the partial overlapping of the signals with those of the PMe_3 hydrogens. The signals due to phenyl hydrogens of the thiolate ligand appear at δ 7.34, 6.98 and 6.72, which are assigned to the *o*-, *m*- and *p*-hydrogens, respectively, based on a comparison with the peak positions of complex **3**.[4] The ^{13}C-$\{^1H\}$ NMR spectrum of **1** shows signals due to the CH_3 and CH_2 carbons of the ethyl ligand at δ 16.1 and 9.4, respectively. The signals are assigned on the basis of the spectrum obtained under ^1H-gated-decoupled conditions. The J(CH) value of the CH_2 signal (131 Hz) is somewhat larger than that of common sp^3 carbon atoms as is generally observed for carbon atoms σ-bonded to a metal centre. The signal of the PMe_3 ligand appears as an apparent triplet due to virtual coupling. Four signals due to the carbon atoms of the phenyl ring are observed at δ 151.1, 131.8, 127.2 and 120.0, which are assigned to *ipso*-, *m*-, *o*- and *p*-carbons respectively. The above spectroscopic results are consistent with a square-planar *trans* structure for **1**. X-Ray crystallography of **1** also support the *trans* co-ordination.[12]

Although C–S bond cleavage of allyl phenyl sulphide by palladium(0) complexes has been reported to proceed smoothly,[13] there have been no reports on C–S bond cleavage promoted by palladium(II) complexes. Reaction of allyl phenyl sulphide with *trans*-$[PdEt_2(PMe_3)_2]$ is accompanied by evolution of a mixture of hydrocarbons such as ethylene, ethane pent-2-ene and hexa-1,5-diene, while the corresponding reaction with *trans*-$[PdMe_2(PMe_3)_2]$ gives but-1-ene exclusively as the hydrocarbon product at the initial stage of the reaction. Previously, the reaction of thiophenol with a platinum dialkyl complex to give $[PtMe(SPh)(PR_3)_2]$ was reported to proceed through a radical intermediate.[14] The formation of but-1-ene in the reaction of *trans*-$[PdMe_2(PMe_3)_2]$ with allyl phenyl sulphide is not inconsistent with a similar radical mechanism. However, the formation of various hydrocarbons in the reaction of *trans*-$[PdEt_2(PMe_3)_2]$ suggests that the reaction involves several complicated processes.

(*b*) *Reaction of Complexes* **1**–**3** *with Organic Halides.*—Reactions of complex **1** with allyl chloride, benzyl bromide and methyl iodide proceed smoothly at room temperature to give the corresponding phenyl sulphides in high yields [equation (3)]. The results are summarized in Table 2. Complexes *trans*-



R—X = CH_2=$CHCH_2Cl$ or MeCOCl — **4** X = Cl
$PhCH_2Br$ — **5** X = Br
MeI — **6** X = I

$[PdEt(X)(PMe_3)_2]$ **4**–**6** (X = Cl, Br or I) were isolated from the reaction mixtures and characterized by means of NMR (^1H, ^{31}P-$\{^1H\}$ and ^{13}C-$\{^1H\}$) spectroscopy. Complex **5** was characterized also by X-ray crystallography. The ^1H NMR spectrum of **4** shows signals at δ 1.58 and 1.00 due to CH_2 and CH_3 hydrogens of the ethyl ligand, respectively. The signal due to the PMe_3 hydrogens appears at δ 1.35 as an apparent triplet due to virtual coupling. The ^{13}C NMR spectrum of **4** shows signals due to CH_2 and CH_3 carbon atoms at reasonable peak

Table 2 Reaction of organic halides with complex **1**

Run	RX	RX:Pd	Solvent	Time	Product and yield (%) Complex[a]	Sulphide[b]
1	CH_2=$CHCH_2Cl$	1.1	Me_2CO	30 h	**4** (100)	CH_2=$CHCH_2SPh$ (100)
2	CH_2=$CHCH_2Cl$	1.0	C_6H_6	33 h	**4** (61)	CH_2=$CHCH_2SPh$ (79)
3[c]	MeCOCl	1.0	CD_2Cl_2	6 h	**4**[d]	MeCOSPh (64)
4	$PhCH_2Cl$	1.1	Me_2CO	47 h	*e*	$PhCH_2SPh$ (trace)
5[c]	$PhCH_2Br$	1.0	CD_2Cl_2	4 h	**5**[d]	$PhCH_2SPh$ (76)
6	$PhCH_2Br$	1.0	CH_2Cl_2	6 h	**5** (86)	$PhCH_2SPh$ (74)
7[c]	MeI	1.1	CD_2Cl_2	30 min	**6**[d]	MeSPh (100)
8	MeI	1.0	Me_2CO	45 min	**6** (82)	MeSPh (64)
9	MeI	2.0	C_6H_5Me	11 h	**6** (62)	MeSPh (74)

[a] Isolated yields. [b] Yields by GC or ^1H NMR spectroscopy. [c] Reactions were carried out in NMR sample tubes. [d] Formation of the compound was confirmed by NMR spectroscopy, but the yields were not determined. [e] Formation of a small amount of *trans*-$[Pd(SPh)_2(PEt_3)_2]$ was observed in the ^1H and ^{31}P-$\{^1H\}$ NMR spectra of the reaction mixture. Unreacted complex **1** (> 80%) was also observed.

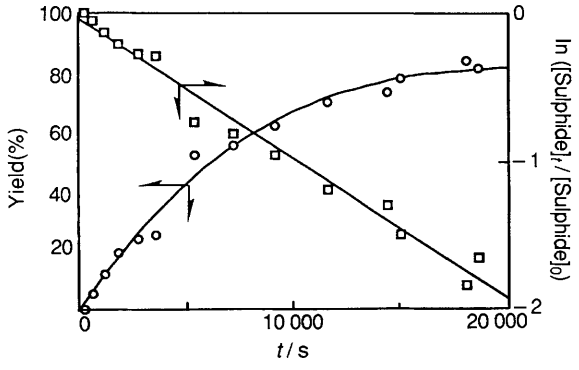


Fig. 1 Time *vs.* conversion curve and first-order plot of the reaction of allyl chloride with complex **1** in [$^2H_8$]toluene at 32.9 °C; $[1]_0$ = 0.104, $[CH_2$=$CHCH_2Cl]_0$ = 2.04 mol dm^{-3}

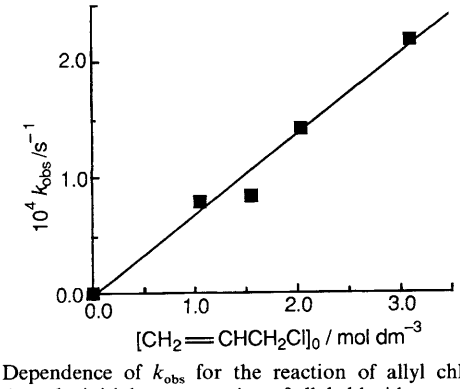


Fig. 2 Dependence of k_{obs} for the reaction of allyl chloride with complex **1** on the initial concentration of allyl chloride

positions and with reasonable *J*(CH) values. Complexes **5** and **6** also give NMR spectra in accord with a *trans* configuration.

The differences in the chemical shifts between the CH_2 and CH_3 hydrogens, $\Delta[\delta(CH_2) - \delta(CH_3)]$, of complexes **4**–**6** are similar (0.49–0.58 ppm) and are considerably larger than that of **1** (*ca.* 0.15 ppm). Previously we have reported a comparison of the peak positions of the CH_2 and CH_3 hydrogen signals in ethyl nickel complexes: $\Delta[\delta(CH_2) - \delta(CH_3)]$ increases in the order $NiEt_2$(bipy), NiEt(acac)(bipy), NiEt(Cl)(bipy) (bipy = 2,2′-bipyridine, acac = acetylacetonate), indicating that the electron-donating ability of the ligand increases in the order Cl, acac, Et.[15] The present results seem to indicate that the electron-donating ability of the thiolate ligand is larger than those of Cl, Br and I.

The formation of allyl phenyl sulphide in the reaction of complex **1** with an excess of allyl chloride in toluene has been followed by ^1H NMR spectroscopy. The reaction obeys first-order kinetics in the complex. Fig. 1 shows a typical time *vs.* conversion curve and a first-order plot of the reaction in the presence of an excess of allyl chloride. Fig. 2 shows the dependence of k_{obs} on the initial concentration of allyl chloride, indicating that the reaction is first order also in the concentration of allyl chloride.

The results of the kinetic study support a mechanism involving electrophilic attack of the allyl chloride on the thiolate ligand in complex **1**. It may be argued, however, that a reaction mechanism involving oxidative addition of allyl chloride to **1** to give an allylethylpalladium(IV) complex* having chloride and thiolate ligands followed by rapid reductive elimination of allyl phenyl sulphide is also compatible with the kinetic results. However, this pathway seems less likely than the former because of the following observation of the reaction products in reaction (3).

In the reaction of allyl chloride with complex **1** the formation of pentene by coupling of the allyl group with the ethyl ligand is not observed. If this reaction involves formation of an intermediate palladium(IV) complex having ethyl and allyl ligands one would expect formation of cross- and self-coupling products of the two groups. Formation of other complexes such as an allylpalladium complex and $[PdX(SPh)(PMe_3)_2]$ (X = Cl, Br or I) is not observed either.† These results seem to indicate that the reaction proceeds through a pathway involving electrophilic attack of the organic halide on the thiolate ligand rather than oxidative addition of the organic halides to **1** giving a palladium(IV) intermediate.

Reaction of benzyl chloride with complex **1** is much slower than that of allyl chloride. The rate of the reaction of MeI with **1** is influenced by the solvent used: with equimolar MeI it proceeds smoothly in acetone and in CD_2Cl_2 and is completed within 45 min, whereas in toluene it takes 11 h for completion even when 2 equivalents of MeI are used.

Reaction of allyl chloride with the corresponding phenoxide palladium complexes was also examined. The complex *trans*-$[PdEt(OPh)(PMe_3)_2(HOPh)]$[4] reacts with allyl chloride at room temperature to give allyl phenyl ether (64%) and **4** [equation (4)]. Since complex **7** was reported to be in equilibrium with the phenoxide complex $[PdMe(OPh)(PMe_3)_2]$ without associated phenol in the solution, the active

* Recently the properties of organopalladium(IV) complexes having diamine auxiliary ligands have been investigated in detail.[16]

† Prolonged reactions of benzyl bromide and methyl iodide with complex **1** in acetone or CH_2Cl_2 give *trans*-$[PdBr_2(PMe_3)_2]$ and *trans*-$[PdI_2(PMe_3)_2]$ in 10–40% yields. Since complexes **5** and **6** undergo intermolecular disproportionation to give the dibromo or diiodo complex gradually in these solvents, formation of these dihalogeno complexes in the reaction mixture is probably due to disproportionation of **5** and **6**. Equimolar reactions of the organic halides with **1** in toluene do not give such by-products.

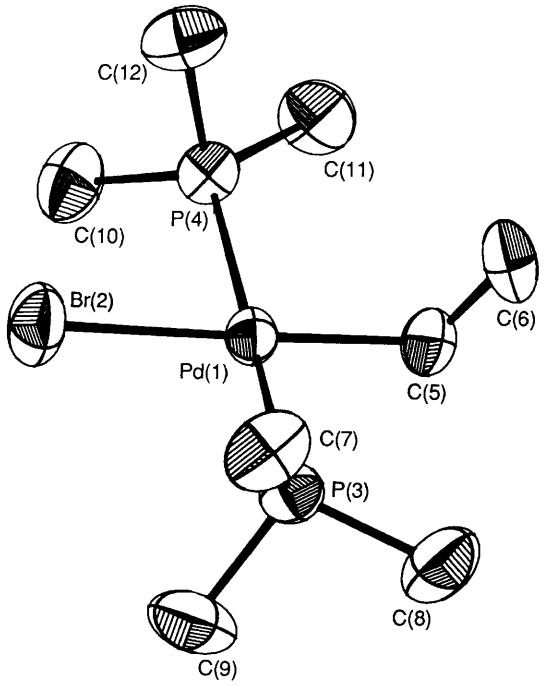
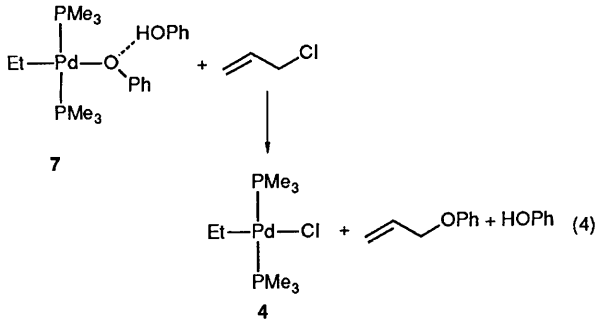


Fig. 3 ORTEP drawing of *trans*-[PdEt(Br)(PMe_3)$_2$] **5** showing thermal ellipsoids at 50% probability



species in reaction (4) may be the unassociated phenoxide complex.

Although ethylpalladium complexes had been considered unstable, the ethylpalladium complexes having thiolate and halide ligands reported here proved to be quite stable. Although the diethylpalladium complexes are reactive toward electrophilic attack, the ethyl ligand in the ethylpalladium thiolate and halide complexes was inert to such attack. The main role of the ethyl ligand in the present complexes seems to enhance the electron density of the ligand at the position *trans* to the ethyl group.

(*c*) *Crystal Structure of Complex* **5**.—Fig. 3 shows the molecular structure of complex **5** determined by X-ray crystallography and Table 3 summarizes the bond distances and angles. The complex has a square-planar co-ordination around the palladium centre. Angles C(5)–Pd(1)–P(3) [90.1(2)°], C(5)–Pd(1)–P(4) [91.6(2)°], P(3)–Pd(1)–P(4) [176.67(5)°], C(5)–Pd(1)–Br(2) [176.9(2)°], Br(2)–Pd(1)–P(3) [89.04(5)°] and Br(2)–Pd(1)–P(4) [89.13(4)°] indicate nearly ideal square-planar geometry with a slight bending up of the four ligands from the co-ordination plane. The molecule has a pseudo-mirror plane which includes Pd, Br and the carbon atoms in the ethyl ligand. Two Pd–P bond distances [2.311(2) and 2.314(2) Å] are quite similar and are somewhat longer than those of methylpalladium phenoxide and fluoroalkoxide complexes (2.298–2.304 Å).[4] The Pd–C bond distance [2.063(5) Å] is shorter than that in *trans*-[PdEt(SPh)(PMe_3)$_2$][2.098(9) Å].[12]

Table 3 Bond distances (Å) and angles (°) of complex **5**

Pd(1)–Br(2)	2.554(1)	Pd(1)–P(3)	2.311(2)
Pd(1)–P(4)	2.314(2)	Pd(1)–C(5)	2.063(5)
C(5)–C(6)	1.52(1)	P(3)–C(7)	1.809(7)
P(3)–C(8)	1.821(8)	P(3)–C(9)	1.800(8)
P(4)–C(10)	1.806(7)	P(4)–C(11)	1.816(8)
P(4)–C(12)	1.803(7)		
Br(2)–Pd(1)–P(3)	89.04(5)	Br(2)–Pd(1)–P(4)	89.13(4)
Br(2)–Pd(1)–C(5)	176.9(2)	P(3)–Pd(1)–P(4)	176.67(5)
P(3)–Pd(1)–C(5)	90.1(2)	P(4)–Pd(1)–C(5)	91.6(2)
Pd(1)–C(5)–C(6)	110.5(5)	Pd(1)–P(3)–C(7)	112.7(3)
Pd(1)–P(3)–C(8)	121.7(3)	Pd(1)–P(3)–C(9)	112.6(3)
C(7)–P(3)–C(8)	101.5(4)	C(8)–P(3)–C(9)	102.3(4)
C(7)–P(3)–C(9)	104.0(4)	Pd(1)–P(4)–C(10)	116.7(3)
Pd(1)–P(4)–C(11)	121.4(3)	Pd(1)–P(4)–C(12)	110.6(2)
C(10)–P(4)–C(11)	102.0(3)	C(11)–P(4)–C(12)	101.1(4)
C(10)–P(4)–C(12)	102.5(4)		

This fact suggests a larger trans influence of the thiolate group than that of the bromo ligand, and is in accord with the difference in electron-donating ability observed as $\Delta[\delta(CH_2) - \delta(CH_3)]$ of the ^{1}H NMR spectra.

Conclusion

Ethylpalladium thiolate complexes prepared by reaction of allyl phenyl sulphide with diethylpalladium complexes react selectively with organic halides to give various phenyl sulphides as cross-coupling products. The reaction involves direct attack of the organic halides on the thiolate ligand rather than oxidative addition of organic halides to give a palladium(IV) intermediate complex. The reactions may have a potential use in developing new transition-metal-catalysed synthetic organic reactions involving C–S bond formation as a crucial step.

Experimental

All manipulations were carried out under nitrogen or argon using Schlenk-type flasks. Solvents were dried, purified in the usual manner, and stored under nitrogen. Elemental analyses were carried out by Dr. M. Tanaka using an Yanagimoto CHN autocorder and Yazawa halogen analyser. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer, NMR spectra by Dr. Y. Nakamura and Ms. A. Kajiwara of our laboratory on JEOL-FX-100 and -GX-500 spectrometers. Gas chromatographic analyses were performed on Shimadzu GC-3BF, GC-7A and GC-8A gas chromatographs packed with Porapak-Q, VZ-7 (for analysis of hydrocarbons), and SE-30 (for analysis of sulphides).

The complexes *trans*-[$PdMe_2(PMe_3)_2$], *trans*-[$PdEt_2(PMe_3)_2$] and *cis*-[$PtMe_2(PMe_3)_2$] were prepared as reported,[4,17,18] as were allyl aryl sulphides.[19]

Preparations.—Complexes **1** *and* **2**. To an acetone (10 cm^3) solution of *trans*-[$PdEt_2(PMe_3)_2$] (420 mg, 1.33 mmol) was added allyl phenyl sulphide (200 mg 1.33 mmol) with cooling of the reaction flask by liquid N_2. After evacuation of the system the reaction mixture was stirred at room temperature. The yellow solution gradually turned yellow-brown. After reaction for 6 h, GC analysis of the gaseous products showed the formation of ethylene (45%), ethane (41%), pent-2-ene (28%) and hexa-1,5-diene (31%). Evaporation of the solvent gave a yellow solid, which was washed with Et_2O (3 cm^3) and then with pentane (2 cm^3). Recrystallization from acetone at −20 °C gave complex **1** as yellow crystals (350 mg, 66%) (Found: C, 41.7; H, 7.3; S, 8.0. $C_{14}H_{28}P_2PdS$ requires C, 42.4; H, 7.1; S, 8.1%).

Complex **2** was prepared analogously (38% yield) (Found: C, 44.1; H, 7.3. $C_{15}H_{30}P_2PdS$ requires C, 43.9; H, 7.3%).

Table 4 Fractional atomic coordinates for complex **5** with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Pd(1)	0.253 54(2)	0.360 88(2)	0.256 61(2)
Br(2)	0.061 22(6)	0.367 09(3)	0.106 20(6)
P(3)	0.290 34(14)	0.275 09(7)	0.150 53(11)
P(4)	0.214 03(13)	0.450 56(7)	−0.090 43(10)
C(5)	0.411 8(5)	0.358 2(3)	−0.031 5(5)
C(6)	0.483 8(6)	0.402 7(4)	0.041 6(7)
C(7)	0.268 7(7)	0.298 4(4)	0.297 4(6)
C(8)	0.423 8(7)	0.236 5(4)	0.157 5(8)
C(9)	0.202 4(8)	0.204 4(3)	0.130 1(7)
C(10)	0.091 3(6)	0.444 9(4)	−0.173 8(6)
C(11)	0.311 2(7)	0.481 1(4)	−0.194 3(6)
C(12)	0.191 2(7)	0.524 5(4)	−0.006 8(5)

Complex **3**. To an acetone (10 cm^3) solution of *trans*-$[PdMe_2(PMe_3)_2]$ (270 mg, 0.94 mmol) was added allyl phenyl sulphide (140 mg, 0.93 mmol) with cooling of the reaction flask by liquid N_2. After evacuation of the system the reaction mixture was stirred for 6 h at room temperature. GC analysis of the gaseous products showed the formation of but-1-ene (*ca.* 11%). After further reaction for 90 h the solvent was removed by evaporation. Addition of pentane to the resulting yellow-brown oily product gave complex **3** as a yellow solid which was recrystallised from acetone (85 mg, 24%). The IR and NMR data of the product agreed with those of an authentic sample.

Reaction of Complex **1**.—*With allyl chloride.* To an acetone (4 cm^3) solution of complex **1** (230 mg, 0.58 mmol) was added allyl chloride (49 mg, 0.64 mmol) at room temperature. The pale yellow solution gradually turned yellow. After stirring for 30 h at room temperature, GC analysis using mesitylene as an internal standard showed the formation of allyl phenyl sulphide in 100% yield. The resulting yellow solution was evaporated to dryness to give an oily material which was washed several times with pentane to give complex **4** as a yellow solid (180 mg, 96%). Recrystallization from Et_2O (10 cm^3) gave yellow crystals (Found: C, 30.5; H, 7.0. $C_8H_{23}ClP_2Pd$ requires C, 29.7; H, 7.2%).

With benzyl bromide. To a CH_2Cl_2 (4 cm^3) solution of complex **1** (250 mg, 0.63 mmol) was added benzyl bromide (110 mg, 0.64 mmol) at room temperature. After stirring for 6 h GC analysis showed the formation of benzyl phenyl sulphide (93 mg, 74%). The reaction mixture was filtered to remove a small amount of insoluble material. The resulting yellow solution was condensed under reduced pressure to give yellow oily material which was washed several times with pentane to give complex **5** as a yellow solid (200 mg, 86%). The product was recrystallized from a CH_2Cl_2–Et_2O mixture at −80 °C.

With methyl iodide. To an acetone (4 cm^3) solution of complex **1** (250 mg, 0.63 mmol) was added methyl iodide (88 mg, 0.62 mmol) at room temperature. After stirring for 45 min GC analysis showed the formation of methyl phenyl sulphide (50 mg, 64%). The reaction mixture was evaporated to dryness, and the resulting oily material washed three times with pentane to give complex **6** as an orange solid (210 mg, 80%). The product was recrystallized from a CH_2Cl_2–Et_2O mixture. (Found: C, 22.8; H, 5.7. $C_8H_{23}IP_2Pd$ requires C, 23.2; H, 5.6%).

Reaction of Allyl Chloride with Complex **7**.—To an NMR tube containing complex **7** (30 mg, 0.63 mmol) was added CD_2Cl_2 (0.3 cm^3) by a syringe under argon. Allyl chloride (5.4 mg, 0.71 mmol) was added to the solution at room temperature to give a yellow-orange solution. Measurement of the ^1H NMR spectrum after reaction at room temperature for 12 h showed the formation of allyl phenyl ether in 64% yield. The ^{31}P-$\{^1H\}$ NMR spectrum showed the formation of complex **4**. Reactions of other organic halides with **1** in NMR sample tubes were carried out analogously.

Kinetic Measuremnts.—An NMR sample tube containing complex **1** (25 mg, 0.063 mmol) was capped with a rubber septum. Argon was introduced to the tube through the septum using a syringe. A solution of benzyl methyl ether (internal standard) in $[^2H_8]$toluene (0.800 cm^3) was injected. The sample tube was placed in the NMR probe thermostatted at 33.0 ± 0.2 °C, and allyl chloride (48 mg, 0.63 mmol) was added to the mixture. The increase in the ^1H NMR signal of CH_2S (δ 3.21) compared to the CH_3 signal of benzyl methyl ether (δ 3.08) was monitored: k_{obs} = 7.88 × 10^{-5} (1.05), 8.32 × 10^{-5} (1.55), 1.42 × 10^{-4} (2.04) and 2.18 × 10^{-4} s^{-1} ($[CH_2{=}CHCH_2Cl]_0$ = 3.11 mol dm^{-3}).

X-Ray Crystallogaphy.—Crystals of complex **5** suitable for X-ray crystallography were grown in CH_2Cl_2–Et_2O at −78 °C and mounted in glass capillary tubes under argon. The unit-cell parameters were obtained by least-squares refinement of 2θ values of 21 reflections with 19 ⩽ 2θ ⩽ 22°. Intensities were collected on a Rigaku AFC-5 automated four-circle diffractometer by using Mo-Kα radiation (λ = 0.710 69 Å) and the ω–2θ scan method (scan speed = 4° min^{-1}).

Crystal data. $C_8H_{23}BrP_2Pd$, M = 367.40, crystal size 0.4 × 0.4 × 0.1 mm, orthorhombic, space group *Pbca*, a = 12.306(3), b = 20.078(5), c = 11.753(2) Å, U = 2903.7 $Å^3$, Z = 8, D_c = 1.682 g cm^{-3}, $F(000)$ = 1456, μ = 41.69 cm^{-1}.

Measured reflections (3 ⩽ 2θ ⩽ 45, 0 ⩽ h ⩽ 14, 0 ⩽ k ⩽ 22, 0 ⩽ l ⩽ 13), 2439; observed reflections [$F_o \geqslant 3\sigma(F_o)$], 1869. The standard reflections, monitored after every 200 reflections, showed no decrease in intensity during measurement.

Calculations were carried out with the program system SAPI85[20] on a FACOM A-70 computer. An empirical absorption correction[11] was applied after all the non-hydrogen atoms had been located. The structure was solved by common Fourier methods. A full-matrix least-squares refinement procedure was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located in a Fourier difference map and included in least-squares calculations without refinement of their parameters. Atomic coordinates are listed in Table 4. The weighting scheme, $w = 1/\{\sigma^2(F_o) + [0.020(F_o)]^2\}$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values were 0.036 and 0.042, respectively.

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

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