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Alkylthiomethylpalladium Compounds

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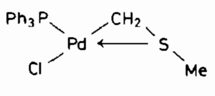
Syntheses of $[PPh_2R)_2Pd(CH_2SR')Cl]$ *(R = Ph, R' = Me or Ph; R = Me, R' = Me) were obtained by oxidative addition of* $R'SCH_2Cl$ *to* $(PPh_2R)_4Pd$*. Metathetic reactions of* $[(PPh_2R)_2Pd(CH_2SR')Cl]$ *with MX (KBr, KI, KSCN or* $AgNO_3$*) provide* $[(PPh_2R)_2Pd(CH_2SR')X]$ *or* $[(PPh_3)Pd(CH_2SMe)X]$ *(X = Br or I). Extensive dissociation of* $[(PPh_2R)_2Pd(CH_2SR')Cl]$ *occurs in solution. Exchange occurs between* $[(PPh_2R)_2Pd(CH_2SR')X]$ *and phosphines or phosphites.*

Reactions with halogens (Y_2) *were also studied, the organosulphur products of* $[(PPh_2R)Pd(CH_2SR')X]$ *(n = 1 or 2) were generally found to be* YCH_2SR' *and* XCH_2SR' *from each reaction.*

Introduction

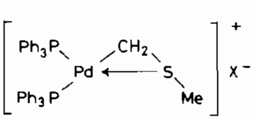
Organopalladium compounds containing CH_2SR ligands have been variously reported in the past few years [1–9]. A CH_2SR ligand can act both as a bidentate ligand as in (*I*)–(*III*) and as a monodentate unit, as in (*IV*).



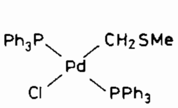
(I) [3]

$[Pd(CH_2SPh)_2]_4\,CH_2Cl_2$

(II) [4]



(III) X = PF_6 or ClO_4 [1]



(IV) [2]

Simply by recrystallisation can (*IV*) be converted to (*I*) [6]. In CH_2Cl_2 solution, (*IV*) has been found to be partially dissociated [6].

Much of the interest with these compounds has centred on structures in the solid state; crystal structures of (*I*)–(*IV*) have been determined [1–4]. Less mention has been made of solution properties and of reactions. We have made a brief report on some reactions of (*IV*) and related compounds with halogens, alkyl halides and proton acids [7]. Other reactions to have been reported upon include (i) metathetic exchange of Cl in (*IV*) using KBr or KI [6], (ii) formation of cationic complexes (*III*) from (*IV*), *e.g.* using $NH_4^+PF_6^-$ or $Et_3O^+BF_4^-$ [1, 6, 8], (iii) reactions of (*I*) with AgO_2CCF_3 to give $[(PPh_3)Pd(CH_2SMe)O_2CCF_3]$ (*V*), (iv) reaction of (*I*) with TlCp to give $[(PPh_3)Pd(Cp)CH_2SMe]$ and (v) insertion reactions of (*V*) (into Pd–C) using $MeO_2CC{\equiv}CCO_2Me$ or norbornadiene.

In this paper, we wish to report on further preparations of Pd–CH_2SR compounds and on reactions with halogens.

Results and Discussion

Compounds $[(PPh_2R)_2Pd(CH_2SR')Cl]$ (R = Ph, R' = Me (*IV*); R = R' = Ph, R = R' = Me] were prepared from $(PPh_2R)_4Pd$ and $ClCH_2SR'$ in essentially the same manner as that previously reported [6]. The compound $[(PPh_2Me)_2Pd(CH_2SMe)Cl]$, was assigned a *cis*-structure in solution from the doublet (J(PH) 8 Hz) for P–Me in the ^1H NMR spectrum. The preparation of $[(PPh_2R)_2Pd(CH_2SR')Cl]$ *via* oxidative addition of $ClCH_2SR'$ to $(PPh_2R)_4Pd$ contrasts with failure to obtain $\{(PPh_3)_2Pd[(CH_2)_nSR]X\}$ (n = 2, 3; X = Cl, Br or I) by similar reactions. Colour changes did indicate some interaction between $X(CH_2)_nSR$ and $(PPh_3)_4Pd$ but none of the desired products were obtained. Attempts to prepare $[(PPh_2Me)_2Pd(CH_2SPh)Cl]$ by this oxidative addition route were not successful since the major product obtained was *cis*-$[(PPh_2Me)_2PdCl_2]$. No reaction occurred with $[P(OEt)_3]_4Pd$. Complete recovery of $[P(OEt)_3]_4Pd$ was obtained from mixtures of $[P(OEt)_3]_4Pd$ and

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TABLE I. Molecular Weight and Molar Conductivity of $[(Ph_2RP)_2Pd(CH_2SR')Cl]$ in Solution.

Compound	Molecular Weight in $CHCl_3$ at 25 °C			Molar Conductivity in CH_2Cl_2 at 25 °C	
	Calc.	Found	Conc. 10^3 mol l^{-1}	Ω^{-1} cm^2 mol^{-1}	Conc. 10^3 mol l^{-1}
$[(PPh_3)_2Pd(CH_2SMe)Cl]$	726.5	470	1.40	5.5	1.8
$[(PPh_3)_2Pd(CH_2SPh)Cl]$	785.5	455	1.26	4.2	1.8
$[(PPh_2Me)_2Pd(CH_2SMe)Cl]$	602.5	490	2.37		

TABLE II. ^1H Chemical Shifts of $PdCH_2SMe$ in Solutions of $[(Ph_3P)Pd(CH_2SMe)X]$ and Ligands, L, in $CDCl_3$ Solution at 34 °C.

	Equivalents of L	PPh_3		$PPhMe_2$[a]		PPh_2Me[b]		$P(OMe)_3$[c]	
		δCH_2	δCH_3	δCH_2	δCH_3	δCH_2	δCH_3	δCH_2	δCH_3
$[(Ph_3P)Pd(CH_2SMe)Cl]$	0	2.68	2.33						
	0.2	3.04	2.31	2.94br	2.24	2.86	2.31	3.22	2.33
	0.4	3.12	2.29	2.96br	2.24	2.91	2.31	3.36	2.36
	0.6	3.18	2.29	2.98br	2.16	3.13	2.27	3.44	2.38
	1.0	3.20	2.24	2.87br	2.09	3.18	2.20	3.47	2.44
	2.0	3.40	2.24	2.16br	2.07	2.76br	2.11	3.33	2.47
	>5	3.42	2.24	d	d	2.72br	2.11	3.11	2.47
$[(Ph_3P)Pd(CH_2SMe)Br]$	0	2.72	2.36						
	0.2	3.04	2.33	2.92	2.36			2.93	2.33
	0.4	3.33	2.31	3.14	2.34			3.04	2.33
	0.6	3.33	2.31	3.26	2.32			3.22	2.36
	1.0	3.44	2.31	3.17br	2.28			3.40	2.40
	2.0	3.49	2.29	2.45	2.06			2.53	2.50
	>5	3.51	2.31	2.32	1.92			d	2.53
$[(Ph_3P)Pd(CH_2SMe)I]$	0	2.72	2.36						
	0.2	2.89	2.31	2.96	2.33			2.89	2.31
	0.4	3.27	2.27	3.16	2.36			3.02	2.31
	0.6	3.31	2.24	3.22	2.33			3.20	2.33
	1.0	3.40	2.27	3.13br	2.20			3.28	2.47
	2.0	3.44	2.27	2.49	2.00			3.51	2.47
	>5	3.49	2.24	2.36	1.84			3.49	2.47

[a] Free $PPhMe_2$: δ 1.27 d J_{PH} 2.0 Hz: change on complexation to δ1.80br. [b] Free PPh_2Me: δ 1.60 d J_{PH} 1.5 Hz: change on complexation to δ 1.98 dJ_{PH} 8.0 Hz. [c] Free $P(OMe)_3$: δ 3.51 d J_{PH} 10.7 Hz: change on complexation to δ 3.6–3.7 dJ_{PH} 10.7 Hz. [d] Obscured.

$ClCH_2SR'$. All $[(PPh_2R)_2Pd(CH_2SR')Cl]$ were stable both as solids (at least for weeks) and in solution (at least for days); decomposition does occur on melting.

As reported, repeated recrystallisation of (*IV*) leads to formation of (*I*).

$$\underset{(IV)}{[(PPh_3)_2Pd(CH_2SMe)Cl]} \xrightarrow{-PPh_3} \underset{(I)}{[(PPh_3)Pd(CH_2SMe)Cl]}$$

Analogous situations did not arise with $[(PPh_3)_2Pd(CH_2SPh)Cl]$ or $[(PPh_2Me)_2Pd(CH_2SMe)Cl]$. Recovery of these diphosphine compounds was always achieved on recrystallisation despite the considerable dissociation of these compounds in solution. Okawara *et al.* [6] studied the dissociation of (*IV*) in CH_2Cl_2 at 25 °C and $[(PPh_3)_2Pd(CH_2SMe)Br]$ in $CHCl_3$ at 37 °C by an osmotic molecular weight method. Similarly in this study dissociation was found to occur in $CHCl_3$ solution at 25 °C for (*IV*), $[(PPh_3)_2Pd(CH_2SPh)Cl]$ and $[(PPh_2Me)_2Pd(CH_2SMe)Cl]$, see Table I. The greater dissociation of PPh_3 compared to PPh_2Me is that expected from other results [10]. Molar conductivities were also determined by us and found to be low with

TABLE III. ^1H Chemical Shifts of $PdCH_2SR'$ in Solutions of $[(Ph_2RP)_2Pd(CH_2SR')Cl]$ and Ligands, L, in $CDCl_3$ Solution at 34 °C.

	Equivalents of L	Ligand L		
		PPh_3 δCH_2	PMe_2Ph[a] δCH_2	$P(OMe)_3$[b] δCH_2
$[(Ph_3P)_2Pd(CH_2SPh)Cl]$	0	2.42		
	0.2	2.35	2.40	2.44
	0.4	2.33	2.38	2.82
	0.6	2.29	2.38	3.18
	1.0	2.29	2.33	3.20
	2.0	2.24br	2.24	3.22
	>5	2.20br	2.09	3.22
$[(Ph_3P)_2Pd(CH_2SMe)Cl]$	0	3.26		
	0.2	3.26	3.28	3.31
	0.4	3.27	3.30	3.44
	0.6	3.33	3.30	3.44
	1.0	3.38	2.87	3.47
	2.0	3.40	1.76	3.42
	>5	3.42	2.02	3.42
$[(Ph_3P)_2Pd(CH_2SMe)Cl]$	0	2.71		
	0.2	2.82	2.73	2.76
	0.4	2.82	2.62	2.80
	0.6	2.82	2.51	2.87
	1.0	2.89	2.42	2.87
	2.0	2.91	2.27	2.93
	>5	2.91	2.20	3.04

[a] Free PMe_2Ph: δ 1.27 d J_{PH} 2.0 Hz: change on complexation to 1.7–1.9. [b] Free $P(OMe)_3$: δ 3.51 d J_{PH} 10.7 Hz: change on complexation to 3.6–3.7.

values for (*IV*) and $[(PPh_3)_2Pd(CH_2SPh)Cl]$ in CH_2Cl_2 solution of 5.5 and 4.2 cm^2 Ω^{-1} mol^{-1} respectively at 1.8×10^{-3} mol l^{-1}, compared to a value of 7 cm^2 Ω^{-1} mol^{-1} for (*IV*) obtained by Okawara *et al.* [6] at 1.08×10^{-3} mol^{-1} l^{-1}. In our view, the molar conductivity and molecular weight data are best accommodated by dissociation as the major process of Ph_2RP from $[(PPh_2R)_2Pd(CH_2SR')Cl]$

$$[(PPh_2R)_2Pd(CH_2SR')Cl] \rightleftharpoons$$

$$[(PPh_2R)Pd(CH_2SR')Cl] + PPh_2R \qquad (1)$$

in solution to provide neutral (*IV*) and $[(PPh_2R)Pd(CH_2SR')Cl]$ rather than dissociation of Cl^- as suggested by Okawara *et al.* [6] as another dominant process. Free ions arising from the latter process are not present to any significant extent, as shown by the conductivity data, and the presence of ion-pairs of $[(Ph_2RP)_2Pd(CH_2SR')]^+$, Cl^- (*VI*) would not satisfy the molecular weight data. Of course free ions and ion pairs (*VI*) could be present to small extents. Addition of PPh_3 to (*IV*) and to $[(PPh_3)_2Pd(CH_2SPh)Cl]$ in CH_2Cl_2 solution leads to increasing conductivity, *e.g.* to 38 and 10.8 cm^2 Ω^{-1} mol^{-1} for (*IV*) and $[(PPh_3)_2Pd(CH_2SPh)Cl]$ with 12 equivs of PPh_3 present. This we feel is due to equilibrium (2) being displaced further to the right, although it must be pointed out that the molar conductivities are still low and the amounts of free ions in solution are very small.

$$[(PPh_3)_2Pd(CH_2SR)Cl] + (PPh_3) \rightleftharpoons$$

$$[(PPh_3)_3PdCH_2SR]^+ + Cl^- \qquad (2)$$

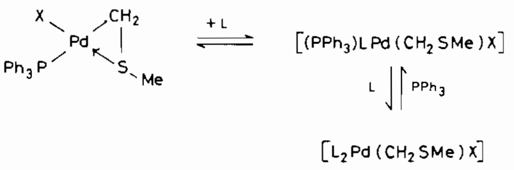
or ion pairs

Various neutral ligands, L, in addition to PPh_3, were added to solutions of $[(PPh_2R)_2Pd(CH_2SR')Cl]$ and $[(PPh_3)Pd(CH_2SMe)X]$ in $CDCl_3$ and the interactions were monitored by ^1H NMR spectroscopy. Changes in δCH_2 in the ^1H NMR spectra were observed for additions of phosphines ($PRh_{3-n}Me_n$) and phosphites, $P(OMe)_3$ or $P(OEt)_3$, but not for other ligands such as Ph_3Sb, Ph_3SbO, Ph_3AsO, Et_3N, $PhNH_2$, MeSPh or Me_2SO (see Tables II and III).

TABLE IV. Estimated ^1H Chemical Shift Values for $PdCH_2SMe$ for undissociated $[L_2Pd(CH_2SMe)X]$ in $CDCl_3$ Solution δCH_2 of $[L_2Pd(CH_2SMe)X]$.

L_2	Cl	X	
		Br	I
$(PPh_3)_2$	3.46	3.51	3.49
$(PPh_2Me)_2$	2.72		
$(PPhMe_2)_2$	2.18	2.32	2.36
$[P(OMe)_3]_2$	3.42	3.53	3.49
$(PMe_2Ph)(PPh_3)$	3.2	3.4	3.3
$(PMePh_2)(PPh_3)$	3.2		
$[P(OMe)_3](PPh_3)$	3.5		
$(PMe_2Ph)(PMePh_2)$	2.2		

Addition of L to $[(PPh_3)Pd(CH_2SMe)X]$ produced successively $[(PPh_3)LPd(CH_2SMe)X]$ and $[L_2Pd(CH_2SMe)X]$ complexes with monodentate CH_2SMe groups.



As already mentioned, $[(PPh_2R)_2Pd(CH_2SR')X]$, is partially dissociated in solution. The values of δCH_2 so found for solutions of $[(PPh_2R)_2Pd(CH_2SR')X]$ are thus average values for the amounts of undissociated compound and $[(PPh_2R)Pd(CH_2SR')$-

TABLE V. Organopalladium Products from Reaction of $[(PPh_2R)_2Pd(CH_2SR')Cl]$ with MX in THF/H_2O.

MX	Product	M.p. (°C) (dec.)	Anal. Calc. (Found)				ν (cm^{-1})	^1H	
			C	H	X	S		δCH_2[a]	δCH_3[a,b]
From $[(PPh_3)_2Pd(CH_2SPh)Cl]$									
KBr	$[(PPh_3)_2Pd(CH_2SPh)Br]$	155–60	61.9 (61.2)	4.4 (4.9)	9.6 [Br] (10.4)			2.73	
KI	$[(PPh_3)_2Pd(CH_2SPh)I]$	155–8	60.0 (59.3)	4.2 (3.7)	14.4 [I] (14.8)			2.94	
KSCN	$[(PPh_3)_2Pd(CH_2SPh)SCN]$	144–8	63.6 (63.7)	4.6 (4.3)	1.7 [N] (1.9)		2080(CN)	2.47	
$AgNO_3$	$[(PPh_3)_2Pd(CH_2SPh)NO_3]$						1635(ONO_2) 1260	3.42	
$SnCl_2$	$[(PPh_3)_2Pd(CH_2SPh)SnCl_3]$	156–8	52.7 (52.9)	3.8 (3.8)	10.9 [Cl] (11.2)		360(Sn–Cl) 305	3.47	
From $[(PPh_3)_2Pd(CH_2SMe)Br]$									
KBr	$[(PPh_3)Pd(CH_2SMe)Br]$	198–200	47.2 (47.1)	3.9 (4.2)	15.7 [Br] (15.4)	(6.3) (6.0)		2.70 J_{PH} 2Hz	2.34 J_{PH} 4.0Hz
KI	$[(PPh_3)Pd(CH_2SMe)I]$	200–3	43.2 (42.8)	3.6 (3.6)	22.8 [I] (23.0)	5.8 (6.0)		2.70 J_{PH} 2Hz	2.34 J_{PH} 4.0Hz
KSCN	$[(PPh_3)_2Pd(CH_2SMe)SCN]$	167–70	62.5 (62.3)	4.7 (4.9)	1.9 [N] (2.0)	4.3 (4.2)	2090(CN) 320(Pd–S)	3.13	2.42
$SnCl_2$	$[(PPh_3)_2Pd(CH_2SMe)SnCl_3]$	163–6	49.8 (49.5)	3.8 (3.8)	11.6 [Cl] (11.9)	3.5 (3.9)	350(Sn–Cl) 300	3.37	2.18
$AgNO_3$	$[(PPh_3)_2Pd(CH_2SMe)NO_3]$						1630(ONO_2) 1260	3.13	2.22
From $[(PPh_2Me)_2Pd(CH_2SMe)Cl]$									
KBr	$[(PPh_2Me)_2Pd(CH_2SMe)Br]$	168–70	51.9 (51.6)	4.8 (4.7)	12.4 [Br] (11.9)	5.0 (4.5)		2.98	2.36[c]
KI	$[(PPh_2Me)_2Pd(CH_2SMe)I]$	160–2	48.4 (48.5)	4.5 (4.3)	18.3 [I] (18.0)	4.6 (4.3)		3.18	2.40[d]

[a] In $CDCl_3$ solution. [b] CH_3 group in CH_2SCH_3. [c] ^1H $P(MePh_2)$ δ 1.98 (J_{PH} 8 Hz). [d] ^1H $P(MePh_2)$ δ 1.93 (J_{PH} 8 Hz).

TABLE VI. Organosulphur Products from Reaction of $[(PPh_2R)_nPd(CH_2SR')X]$ with Halogens in $CDCl_3$ Solution.

Reagents		Relative Yields of Organosulphur Products
$[(PPh_2R)_nPd(CH_2SR')X]$	*Halogen*	
$[(PPh_3)_2Pd(CH_2SMe)Cl]$	Br_2	$ClCH_2SMe$ (20) + $BrCH_2SMe$ (80)
	I_2	$ClCH_2SMe$ (50) + ICH_2SMe (50)
$[(PPh_3)_2Pd(CH_2SMe)SCN]$	Br_2	$(SCN)CH_2SMe$ (50) + $BrCH_2SMe$ (50)
	I_2	$(SCN)CH_2SMe$ (20) + ICH_2SMe (80)
$[(PPh_3)_2Pd(CH_2SMe)SnCl_3]$	Br_2	$ClCH_2SMe$ (65) + $BrCH_2SMe$ (35)
	I_2	$ClCH_2SMe$ (65) + $BrCH_2SMe$ (35)
$[(PPh_3)_2Pd(CH_2SMe)NO_3]$	Br_2	$(NO_3)CH_2SMe$ (45) + $BrCH_2SMe$ (55)
	I_2	$(NO_3)CH_2SMe$ (100)
$[(PPh_2Me)_2Pd(CH_2SMe)Cl]$	Br_2	$ClCH_2SMe$ (100)
	I_2	$ClCH_2SMe$ (85) + ICH_2SMe (15)
$[(PPh_2Me)_2Pd(CH_2SMe)Br]$	Br_2	$BrCH_2SMe$
	I_2	$BrCH_2SMe$ (90) + ICH_2SMe (10)
$[(PPh_2Me)_2Pd(CH_2SMe)I]$	Br_2	ICH_2SMe (10) + $BrCH_2Me$ (90)
$[(PPh_3)_2Pd(CH_2SPh)Cl]$	Br_2	$ClCH_2SPh$ (100)
	I_2	$ClCH_2SPh$ (60) + ICH_2SPh (40)
$[(PPh_3)_2Pd(CH_2SPh)Br]$	I_2	$BrCH_2SPh$ (80) + ICH_2SPh (20)
$[(PPh_3)_2Pd(CH_2SPh)I]$	Br_2	ICH_2SPh (20) + $BrCH_2SPh$ (80)
$[(PPh_3)_2Pd(CH_2SPh)SCN]$	Br_2	$(SCN)CH_2SPh$ (70) + $BrCH_2SPh$ (30)
	I_2	$(SCN)CH_2SPh$ (55) + ICH_2SPh (45)
$[(PPh_3)_2Pd(CH_2SPh)SnCl_3]$	Br_2	$ClCH_2SPh$ (60) + $BrCH_2SPh$ (40)
	I_2	$ClCH_2SPh$ (75) + ICH_2SPh (25)
$[(PPh_3)_2Pd(CH_2SPh)NO_3]$	Br_2	$(NO_3)CH_2SPh$ (35) + $BrCH_2SPh$ (65)
	I_2	$(NO_3)CH_2SPh$ (100)
$[(PPh_3)Pd(CH_2SMe)Cl]$	Br_2	$ClCH_2SMe$ (20) + $BrCH_2SMe$ (80)
	I_2	$ClCH_2SMe$ (50) + ICH_2SMe (50)
$[(PPh_3)Pd(CH_2SMe)Br]$	I_2	$BrCH_2SMe$ (95) + ICH_2SMe (5)
$[(PPh_3)Pd(CH_2SMe)I]$	Br_2	ICH_2SMe (5) + $BrCH_2SMe$ (95)

X] present in solution. By adding PPh_2R to solutions of $[(PPh_2R)_2Pd(CH_2SR')X]$, it was possible to obtain δCH_2 for completely undissociated $[(PPh_2R)_2Pd(CH_2SR')X]$. Values of δCH_2 for undissociated species are listed in Table IV. Other processes recognized were phosphine exchanges in $[(PPh_2R)_2Pd(CH_2SR')Cl]/L$ systems.

Metathetic reactions of $[(PPh_2R)_2Pd(CH_2SR')Cl]$ have been reported using salts such as KBr [6], $NH_4^+PF_6^-$, $Ag^+PF_6^-$ and $[Et_3O]^+BF_4^-$. We have extended the range of these reactions; eqns. (3) and (4).

$$[(PPh_2R)_2Pd(CH_2SR')Cl] + MX \longrightarrow [(PPh_2R)_2Pd(CH_2SR')X] \qquad (3)$$

$X = Br, I, NO_3, SCN$

$$[(PPh_2R)_2Pd(CH_2SR')Cl] + SnCl_2 \longrightarrow [(PPh_2R)_2Pd(CH_2SR')SnCl_3] \qquad (4)$$

However from the reaction of (*IV*) with KBr or KI, only the monophosphine complexes, $[(PPh_3)Pd(CH_2SMe)X]$, X = Br or I, were isolated from the reaction solutions.

$$[(PPh_3)_2Pd(CH_2SMe)Cl] + KX \xrightarrow{-KCl} [(PPh_3)Pd(CH_2SMe)X] \qquad (5)$$

In the main, satisfactory spectral and analytical data were obtained (see Table V). The NO_3 product could not be crystallised but spectral data of the oily product indicated its formation. Reactions of (*IV*) with KCN did not lead to any isolatable product.

Reactions with Halogens

Halogens are known to cleave palladium–carbon bonds [11]. Exothermic reactions occurred between $[(PPh_2R)_nPd(CH_2SR')X]$ (n = 1 or 2) and equimolar Br_2 or I_2 in $CDCl_3$ solution. Precipitates of phosphine palladium dihalides rapidly formed and complete cleavage of the Pd–C bond resulted in very short reaction times. The organic products, YCH_2SR' (Y = Br, I or X) were detected by ^1H NMR

$$[(PPh_2R)_2Pd^{II}(CH_2SR')X] + Y_2 \longrightarrow$$
$$[(PPh_2R)_2Pd^{IV}(CH_2SR')XY_2] \longrightarrow$$
$$[(PPh_2R)_2Pd^{II}XY] + YCH_2SR' +$$
$$+ [(PPh_2R)_2Pd^{II}Y_2] + XCH_2SR' \qquad (6)$$

spectroscopy and the relative yields are quoted in Table VI. As shown in Table VI and in eqn. 6, two organosulphur products, YCH_2SR', were frequently obtained in which Y was derived both from the organopalladium reagent and from the reacting halogen. These products derive from the transient intermediate oxidative addition species $[(PPh_2R)_nPd(CH_2SR')XY_2]$ (*VII*) by reductive elimination. From the relative Pd–halogen bond strengths, *viz.* Pd–I > Pd–Br > Pd–Cl, it would be expected that the preferred sequence of formation of products would be $ClCH_2SR > BrCH_2Sr > ICH_2SR$. The observed ratio of products clearly indicate that factors in addition to bond strengths must also play roles. An important factor must be the arrangement of the halogens in the octahedral intermediate (*VII*).

Experimental

Solvents used were deoxygenated and redistilled prior to use. A nitrogen atmosphere was employed.

Chloromethyl methyl sulphide was a commercial sample. Chloromethyl phenyl sulphide and chloromethyl *p*-tolyl sulphide were prepared by treatment of the appropriate methyl aryl sulphoxide with a saturated solution of hydrogen chloride in Et_2O in the presence of 3A molecule sieves [12] for 2 h. After decanting off the molecular sieves, the solvent was removed and the yellow residue was distilled under reduced pressure. Analysis and ^1H NMR spectral data were as expected.

Compounds, $(Ph_3P)_4Pd$ [13], $(Ph_2MeP)_4Pd$ [10] and $[(EtO)_3P]_4Pd$ [14] were prepared according to literature procedures.

Preparation of [(Ph₂RP)₂Pd(CH₂SR')Cl]

To a suspension of tetrakis(triorganophosphine)-palladium, $(Ph_2RP)_4Pd$, in de-oxygenated PhH, was added dropwise $ClCH_2SR'$ (5 equiv.) in de-oxygenated PhH. The reaction mixture was stirred under N_2 for 3 h at R.T. The solvent volume was reduced and hexane added, precipitating a yellow solid, which was recrystallised from CH_2Cl_2/hexane. Yields were greater than 90%.

Products

trans-*[Chloro(methylthiomethyl)bis(triphenylphosphine)palladium(II)]·dichloromethane*

trans-$[(Ph_3P)_2Pd(CH_2SMe)Cl]\cdot CH_2Cl_2$, m.p. 143–4 °C (lit. m.p. 144 °C dec [5, 6]). ν(Pd–Cl) 275 cm^{-1}. *Anal.* $C_{39}H_{37}Cl_3SP_2Pd$ Calcd: C, 57.7; H, 4.5; S, 3.9; Cl 13.1%. Found: C, 57.8, H, 4.3; S, 3.5; Cl, 13.1%.

[Chloro(phenylthiomethyl)bis(triphenylphosphine)palladium(II)]

$[(PPh_3)_2Pd(CH_2SPh)Cl]$, m.p. 180–3 °C dec. ^1H NMR spectrum (100 MHz. $CDCl_3$): δ 2.42 (2H, s), 6.94 (5H, m), 7.30 and 7.64 (30H, 2 m). ν(Pd–Cl) 285 cm^{-1}. *Anal.* $C_{43}H_{37}ClSP_2Pd$. Calcd. C, 65.4; H, 4.7; S, 4.1; Cl, 4.5%. Found: C, 65.2; H, 4.5; S, 3.9, Cl, 4.4%.

[Chloro(methylthiomethyl)bis(methyldiphenylphosphine)palladium(II)]

$[(PPh_2Me)_2Pd(CH_2SMe)Cl]$, m.p. 163–6 °C dec (lit. [6] 167 °C dec.). ^1H NMR (60 MHz, $CDCl_3$) δ 2.06 (6H, d, J_{PH} 8.0 Hz), 2.11 (3H, s), 2.71 (2H, s), 7.40 and 7.60 (20H, 2m). ν(Pd–Cl) 280 cm^{-1}. *Anal.* $C_{28}H_{31}ClSP_2Pd$. C, 53.8; H, 4.6; S, 5.3; Cl, 5.9%. Found: C, 53.1; H, 5.0; S, 4.9; Cl, 6.1%. [*Chloro(*p-*tolylthiomethyl)bis(triphenylphosphine)-palladium(II)*] was also prepared as an oil but could not be crystallised. ^1H NMR (60 MHz, $CDCl_3$) δ 2.29 (3H, s), 2.78 (2H, s), 7.11, 7.38 and 7.62 (34H, m).

Tetrakis(triethylphosphine)palladium(0) was recovered (>80%) from a refluxed PhH solution of $[(EtO)_3P]_4Pd$ and $ClCH_2SMe$.

Preparation of chloro(methylthiomethyl)(triphenylphosphine)palladium(II) [(PPh₃)Pd(CH₂SMe)Cl]

trans-Chloro(methylthiomethyl)bis(triphenylphosphine)palladium(II) (10 g, 1.4 × 10^{-3} mol) was dissolved in the minimum volume of CH_2Cl_2 and Et_2O was added until the solution became cloudy. Crystals were collected after leaving overnight at 0 °C. Repeated recrystallisation from Et_2O/CH_2Cl_2 gave $[(PPh_3)Pd(CH_2SMe)Cl]$, m.p. 209–211 °C dec. (lit. [6] 210 °C dec. ^1H NMR (60 MHz, $CDCl_3$, 35 °C] δ 2.34 (3H, s), 2.68 (2H, s), 7.42 and 7.76 (15H, m).

^1H NMR (60 MHz, $CDCl_3$, –40 °C) δ 2.34 (3H, d, J 4.0 Hz), 2.68 (2H, d J 2.0 Hz), 7.42 and 7.76 (15H, m). ν(Pd–Cl) 273 cm^{-1}. *Anal.* $C_{20}H_{20}ClSPPd$. Calcd. C, 51.7; H, 4.3; S, 6.9; Cl, 7.6%. Found: C, 51.4; H, 4.4; S, 6.6, Cl, 7.8%.

Interactions of [(Ph₂RP)₂Pd(CH₂SR')Cl] or [(Ph₃P)Pd(CH₂SMe)X] with Phosphines and other Neutral Ligands

To a solution of the organopalladium compound [*ca.* 6–8 × 10^{-5} mol] in $CDCl_3$ (0.5 ml) were added known amounts of the ligand (L).

The interactions were monitored by 60 MHz ^{1}H NMR spectroscopy. (see Tables II and III).

Reactions of [(Ph$_2$RP)$_2$Pd(CH$_2$SR')Cl] with Inorganic Salts

To a solution of the organopalladium compound (2.75×10^{-4} mol) in THF (20 ml) was added the inorganic salt (2 equiv.) in H_2O (3 ml). The reaction mixture was stirred for ½ h at R.T. and the solvent was then removed under reduced pressure. The residue was recrystallised from CH_2Cl_2/hexane. Products, analyses and some spectral data are listed in Table V. Reaction with KCN however did not provide [(Ph$_2$RP)$_2$Pd(CH$_2$SR')CN]. Reaction with $AgNO_3$ did proceed but the [(Ph$_2$RP)$_2$Pd(CH$_2$SR')NO$_3$] product would not crystallise.

Reactions of [(Ph$_2$RP)$_2$Pd(CH$_2$SR')X] or [(Ph$_3$P)Pd(CH$_2$SMe)X] with Halogens

The halogen was added to a solution of equimolar [(Ph$_2$RP)$_2$Pd(CH$_2$SR')X] (6.88×10^{-5} mol) or [(Ph$_3$P)Pd(CH$_2$SMe)X] (7.8×10^{-5} mol) in $CDCl_3$ (0.3 ml). The bromine reactions were exothermic, the iodine ones less so. Brown precipitates formed immediately. The organosulphur products were identified by ^{1}H NMR spectroscopy, see Table VI.

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