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Sulphur Substituted Alkylpalladium Compounds.
Part 3.* Reactions of Organothionemethyl–Palladium Compounds with Alkyl Halides

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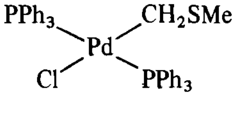
Exchange of halide (or pseudohalide) was found to occur in reactions between $[(PPh_2R)_2Pd(CH_2SR')X]$ *(R = Me or Ph; R' = Me or Ph; X = Cl, Br or SCN) and alkyl halides (MeI, EtI or EtBr) in chloroform solution at room temperature. The reactivity of the alkyl halides was in the sequence MeI > EtI > EtBr. There was no evidence for Pd–C bond cleavage.*

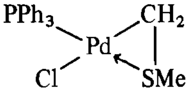
Complexes containing the bidentate CH_2SMe *group, e.g.* $[(PPh_3)Pd(CH_2SMe)X]$ *(X = Cl, Br or I), undergo exchanges with alkyl halides much more slowly.*

Introduction

Various organothiomethyl–palladium complexes are known [1–3] in which the $RSCH_2$ group acts as a mono-dentate ligand as in (*I*) or a bidentate one, as in (*II*).



(*I*)



(*II*)

Reactions of these and related complexes with proton acids indicate a greater reactivity for the monodentate $RSCH_2$ compounds [2]. The greater reactivity of the complexes containing the free sulphur atom suggested that the sulphur may play a role in the reaction as a donor centre for the attacking electrophilic species. To further investigate this, reactions with alkyl halides were studied and the results are now reported.

Experimental

The organopalladium compounds, $[(PPh_2R)_2Pd(CH_2SR')X]$ (R = Me or Ph; R' = Me or Ph; X = Cl, Br, I, SCN, or NO_3) and $[(PPh_3)Pd(CH_2SMe)X]$ (X = Cl, Br or I), were obtained as previously described [1]. Deoxygenated solvents and nitrogen atmospheres were generally used.

Alkyl halides [MeI, EtI and EtBr] were treated with aqueous potassium hydroxide, washed with water and dried over calcium chloride. The samples were stored over calcium chloride and distilled prior to use [4].

Reactions

An equimolar quantity of the alkyl halide was syringed into a solution of the organopalladium compound (0.18–0.23 *M*) in $CDCl_3$. The reaction vessel (NMR tube) was sealed and the reaction monitored by ^1H NMR spectroscopy. At the completion of the reaction, the tube was opened and the volatile components were removed under reduced pressure. The ^1H NMR spectrum of the residue in $CDCl_3$ was obtained. Addition of hexane precipitated the organopalladium product, which was recrystallised from dichloromethane/hexane. Data for the products and reaction times are listed in Table I.

Results and Discussion

Interactions of $[(PPh_2R)_2Pd(CH_2SR')X]$ (*III*) (R = Me or Ph; R' = Me or Ph; X = Cl, Br, SCN or NO_3) and or $[(PPh_3)Pd(CH_2SMe)X]$ (*IV*) (X = Cl, Br or SCN) with equimolar amounts of alkyl halides, R''Y (R''Y = MeI, EtI or EtBr) were investigated in $CDCl_3$ solution at ambient temperature in sealed vessels. Monitoring of the reactions was by ^1H NMR spectroscopy, following the changes in the intensities of the absorptions of R''Y and R''X.

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*Part 2. Ref. [2].

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TABLE I. Reactions of Equimolar $[(PPh_2R)_nPd(CH_2SR')X]$ and Alkyl Halides in $CHCl_3$ Solution at Ambient Temperature.

Palladium Compound	Alkyl[b] Halide	Reaction Time (h)	Reaction Product	Yield (%)	M.p. (℃)	Analysis, Calcd. (Found) C	H	X	δCH_2
$[(PPh_3)_2Pd(CH_2SMe)Cl]$	MeI	2	$[(PPh_3)Pd(CH_2SMe)I]$	75	201–4dec.	43.2 (43.5)	3.6 (3.5)	22.8[I] (22.4)	2.70^c (J 2Hz)
	EtI	16	$[(PPh_3)Pd(CH_2SMe)I]$	70	196–200dec.	43.2 (42.7)	3.6 (3.3)	22.8[I] (22.3)	$2.70d^c$ (J 2Hz)
	EtBr	40	$[(PPh_3)Pd(CH_2SMe)Br]$	71	195–8dec.	47.2 (47.6)	3.9 (4.0)	15.7[Br] (15.0)	$2.70d^c$ (J 2Hz)
$[(PPh_3)_2Pd(CH_2SPh)Cl]$	MeI	3	$[(PPh_3)_2Pd(CH_2SPh)I]$	83	152–5dec.	58.6 (57.8)	4.2 (4.3)	14.4[I] (13.8)	2.92
	EtI	20	$[(PPh_3)_2Pd(CH_2SPh)I]$	88	154–8dec.	58.6 (57.9)	4.2 (4.2)	14.4[I] (14.0)	2.94
	EtBr	40	$[(PPh_3)_2Pd(CH_2SPh)Br]$	70	154–8dec.	61.9 (61.6)	4.4 (4.1)	9.6[Br] (9.2)	2.73
$[(PPh_3)_2Pd(CH_2SPh)SCN]$	MeI	4	$[(PPh_3)_2Pd(CH_2SPh)I]$	70	153–7dec.	58.6 (59.0)	4.2 (4.5)	14.4[I] (15.0)	2.94
	EtI	40	$[(PPh_3)_2Pd(CH_2SPh)I]$	78	152–5dec.	58.6 (58.8)	4.2 (4.3)	14.4[I] (14.1)	2.94
	EtBr	120	$[(PPh_3)_2Pd(CH_2SPh)Br]$	78	155–8dec.	61.9 (61.8)	4.4 (4.2)	9.6[Br] (9.3)	2.73
$[(PPh_3)_2Pd(CH_2SMe)SCN]$	MeI	2	$[(PPh_3)Pd(CH_2SMe)I]$	72	199–202dec.	43.2 (42.8)	3.6 (3.3)	22.8[I] (22.4)	2.70^c
	EtI	40	$[(PPh_3)Pd(CH_2SMe)I]$	75	198–200dec.	43.2 (43.7)	3.6 (3.7)	22.8[I] (22.6)	2.70^c
	EtBr	90	$[(PPh_3)Pd(CH_2SMe)Br]$	80	195–8dec	47.2 (47.5)	3.9 (3.5)	15.7[Br] (15.2)	2.70^c
$[(PPh_3)_2Pd(CH_2SPh)Br]$	MeI	2	$[(PPh_3)_2Pd(CH_2SPh)I]$	70	155–8dec.	58.6 (58.8)	4.2 (4.2)	14.4[I] (14.2)	2.94
	EtI	40	$[(PPh_3)_2Pd(CH_2SPh)I]$	73	155–6dec.	58.6 (58.9)	4.2 (4.0)	14.4[I] (14.5)	2.92
$[(PPh_2Me)_2Pd(CH_2SMe)Cl]$	MeI	<1	$[(PPh_2Me)_2Pd(CH_2SMe)I]$	81	161–3dec.	48.4 (48.6)	4.5 (4.8)	18.3[I] (18.8)	3.18^d
	EtI	6	$[(PPh_2Me)_2Pd(CH_2SMe)I]$	78	159–62dec.	48.4 (48.9)	4.5 (4.2)	18.3[I] (18.5)	3.16^d
	EtBr	36	$[(PPh_2Me)_2Pd(CH_2SMe)Br]$	78	167–70dec.	51.9 (51.5)	4.8 (4.4)	12.4[Br] (12.2)	2.98^e
$[(PPh_2Me)_2Pd(CH_2SMe)Br]$	MeI	<1	$[(PPh_2Me)_2Pd(CH_2SMe)I]$	81	160–3dec.	48.4 (48.2)	4.5 (3.9)	18.3[I] (18.7)	3.16^d
	EtI	6	$[(PPh_2Me)_2Pd(CH_2SMe)I]$	86	159–63dec.	48.4 (48.6)	4.5 (4.2)	18.3[I] (18.5)	3.18^d
$[(PPh_3)Pd(CH_2SMe)Cl]$	MeI	36	$[(PPh_3)Pd(CH_2SMe)I]$	83	198–201dec.	43.2 (43.8)	3.6 (3.6)	22.8[I] (22.3)	$2.70d^c$ (J 2Hz)
$[(PPh_3)Pd(CH_2SMe)Br]$	MeI	36	$[(PPh_3)Pd(CH_2SMe)I]$	86	199–202dec.	43.2 (42.8)	3.6 (3.1)	22.8[I] (23.4)	$2.70d^c$

[a] 0.18–0.23 *M*. [b] $\delta\,^1H$ MeCl 3.00; MeBr 2.64; MeI 2.15; MeSCN 2.54; CH_3CH_2Cl 1.49t; 3.56q; CH_3CH_2Br 1.66t, 3.41q; CH_3CH_2I 1.82t, 3.20q; CH_3CH_2SCN 1.54t, 2.97q. [c] $\delta\,^1H$ CH_2SMe 2.32 (J = 4 Hz). [d] $\delta\,^1H$ P–Me 1.92d(J 8 Hz); CH_2SMe 2.40. [e] $\delta\,^1H$ P–Me 1.98d (J 8 Hz); CH_2SMe 2.36.

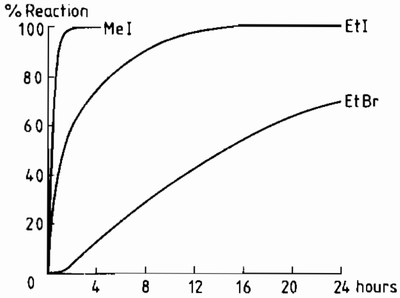


Fig. 1. Reactions of [$(PPh_3)_2Pd(CH_2SMe)Cl$] (0.183 *M*) and alkyl halides (0.183 *M*) in $CDCl_3$ solution at 20 ± 1 °C.

$$[(PPh_2R)_2Pd(CH_2SR')X] + R''Y \longrightarrow [(PPh_2R)_2Pd(CH_2SR')Y] + R''X \qquad (1)$$

$X = Cl$ or Br

For all (*III*), except $X = NO_3$, exchange cleanly occurred, eqn. 1. No evidence was gained for cleavage of the Pd–C band in any reaction. For reactions of (*III*; $X = NO_3$), slow decomposition occurred as shown by the solutions becoming darker in colour and the ^1H NMR spectra becoming broader.

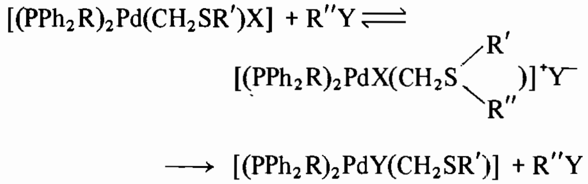
The reactivity of the alkyl halides was in the sequence MeI > EtI > EtBr–that expected for reactions of alkyl halides with metal derivatives (see Table I and Fig. 1). Little differences in reactivity were found for X = Cl or Br in any of the series (*III*); the SCN derivatives were less reactive. Another comparison showed that the PPh_2Me derivatives were more reactive than the PPh_3 analogues.

At the completion of each reaction, the organopalladium product was precipitated from the reaction media by the addition of hexane and recrystallised from dichloromethane/hexane; data are presented in the Table. Yields of recrystallised compounds were greater than 80%.

The complexes (*IV*) containing the bidentate $MeSCH_2$ group also reacted with MeI at ambient temperature. However (*IV*) were much less reactive than (III),

$$[(PPh_3)Pd(CH_2SMe)X] + MeI \longrightarrow \underset{(IV)}{} \quad [(PPh_3)Pd(CH_2SMe)I] \qquad (2)$$

see Table I, *e.g.* compare the 1 h reaction time required for [$(PPh_3)_2Pd(CH_2SMe)Cl$] with the 36 h needed for [$(PPh_3)Pd(CH_2SMe)Cl$]. Furthermore, reaction of (*IV*, X = Cl) with EtI was only 50% complete after 6 weeks and EtBr was found to be unreactive towards (*IV*, X = Cl), Such data clearly point to an enhanced reactivity when the donor centre, the sulphur atom, is not coordinated to the palladium and hence is able to interact with the alkyl halide (or the proton). We envisage the mechanism for these alkyl halide reactions with (*III*) to involve the intermediacy of sulphonium salts:



$$[(PPh_2R)_2Pd(CH_2SR')X] + R''Y \rightleftharpoons [(PPh_2R)_2PdX(CH_2S\genfrac{}{}{0pt}{}{R'}{R''})]^+Y^- \longrightarrow [(PPh_2R)_2PdY(CH_2SR')] + R''Y$$

Such a mechanism is not possible with (*IV*) since the sulphur is already coordinated. For compounds (*IV*), an alternative mechanism has to be followed, such as one involving oxidative addition of R″Y to give intermediate Pd(IV) species, [$(PPh_3)Pd^{IV}(CH_2SMe)XR''Y$], followed by reductive elimination of R″X and formation of [$(PR_3Pd^{II}(CH_2SMe)Y$]. Okawara *et al.* [5] have shown that the organoplatinum analogues of (*III*) and $MeOSO_2OF$ form isolatable sulphonium salts, *e.g.* [$(PPh_3)_2Pt(CH_2SMe_2)X$]OSO_2F [5].

Reactions of alkyl halides with organopalladium compounds can be complex, *e.g.* reaction of [(dpe)$PtEt_2$] with MeI at room temperature provides CH_4, $CH_2{=}CH_2$, CH_3CH_3, $CH_3CH_2CH_3$, $CH_3CH_2CH_2CH_4$ and EtI. It was suggested that some of the products may arise from a Pd^{IV} intermediate [6]. Reaction of [(dpe)$PtMe_2$] and excess MeI at room temperature was simpler giving CH_3CH_3 with only a trace of CH_4 also present. Another type of reaction, exchange of organic ligand, was found by Maitlis and Stone [7] in the reaction of [(bipy)$PdMe_2$] and C_3F_7I, which provided [(bipy)Pd(C_3F_7)Me] or [(bipy)Pd$(C_3F_7)_2$] if excess C_3F_7I was used.

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