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Synthesis Employing Oxidative Insertion of Palladium Atoms into Aryl, Alkyl, and Acyl Carbon–Halogen Bonds. Properties of and Phosphine Trapping of the Nonligand Stabilized RPdX and RCOPdX Intermediates[1,2]

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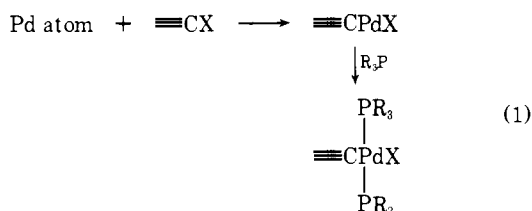
Abstract: Palladium atoms oxidatively insert aryl, alkyl, and acyl carbon–halogen bonds at low temperature to yield a new series of reactive intermediates ArPdX, RPdX, and RCOPdX. Efficiency of the insertion is in the order C–1 > C–Br > C–Cl. These species are formed in the absence of normal stabilizing ligands and their stabilities vary greatly depending on the organic group attached. For example C_6F_5PdBr is stable at room temperature in the air whereas CH_3PdI decomposes at extremely low temperature under vacuum. The stability order is $C_6F_5 > CF_3 \sim CF_3CF_2 \sim CF_3CF_2CF_2 > C_6H_5 \gg CF_2Br > (CF_3)_2CF \sim CH_3 \sim CH_3CH_2$. The ArPdX species decompose thermally to Ar–Ar, Pd, and $PdBr_2$. Some of the RPdX species decompose free radically at low temperature. The RCOPdX species decompose by decarbonylation and have stabilities in the order of $R = CF_3CF_2CF_2 > CF_3 > C_6F_5 > C_6H_5 > CH_3 \sim CH_3CH_2CH_2$. These intermediates, ArPdX, RPdX, and RCOPdX, are highly coordinatively unsaturated and thus extremely reactive with phosphines. In fact many of these materials can be readily trapped with tertiary phosphines to form the bisphosphine adducts $(R_3P)_2Pd(Ar)X$, $=Pd(R)X$, and in some cases $=Pd(RCO)X$. This serves as a rapid method of preparation of these complexes and in some cases quite high yields of these materials can be prepared by simultaneous deposition of palladium atoms, ArX, and Et_3P at $-196°$.

Simple organopalladium salts ArPdX and RCOPdX (no stabilizing ligands) have been proposed as intermediates in a number of important reactions. Heck,[3] Henry,[4] and Maitlis[5] formulate "phenylpalladium chloride (C_6H_5PdCl)" as the reactive intermediate formed in solutions of palladium dichloride with an arylating agent such as phenylmercuric chloride. These solutions have been used for olefin arylations, alkylations, carboalkylations, etc. Similarly, Henry[4] and Tsuji and coworkers[6] discuss RCOPdCl as a likely short-lived species in palladium catalyzed CO insertion

reactions, olefin carbonylation reactions, and reaction mechanisms relating to the Rosenmund reduction.[6] Furthermore, Maitlis and coworkers[5] have reported on interesting chemistry of "lightly stabilized" organopalladium compounds (very weak donating ligands). In light of these works, we thought it would be quite interesting to produce and study "nonligand stabilized" organopalladium compounds (no donating ligands at all).

In this paper we describe the synthesis, isolation, trapping and other studies of a series of nonligand stabilized

ArPdX, RPdX, and RCOPdX species at low temperature, point out the vast differences in stabilities with change in Ar or R, and show how this new series of reactive intermediates can be used in further steps for the synthesis of stable bisphosphine adducts of these species. To carry out these experiments we have employed the "metal atom technique" where free metal atoms have been cocondensed with the organic halides at −196°. The high chemical potential of these atoms, due to the substantial heat of vaporization of palladium, allows facile oxidative insertion into the carbon-halogen bonds at the low temperature employed. The apparatus we use for these experiments is relatively inexpensive

$$\text{Pd atom} + \equiv\!\text{CX} \longrightarrow \equiv\!\text{CPdX}$$
$$\downarrow \text{R}_3\text{P}$$
$$\equiv\!\text{CPdX} \begin{array}{c} \text{PR}_3 \\ | \\ | \\ \text{PR}_3 \end{array} \quad (1)$$

and easy to assemble and has been described in detail.[1] It is quite similar to the apparatus first developed by Skell and Wescott for the study of carbon atom chemistry.[7] Skell,[8] Timms,[9] and von Gustorf[10] and their coworkers are also actively engaged in metal atom chemistry, and Timms[11] has recently reviewed this area.

Results and Discussion

Palladium Vapor. Palladium has a heat of vaporization of 88 kcal/mol, a value that readily allows vaporization of the metal but high enough to induce a significant chemical potential into the system. Mass spectrometric studies have shown that palladium, as well as many other transition metals, vaporize as monatomic species.[12]

The Oxidative Insertion Reaction. We anticipated that the metal atom technique would be ideal for generating and studying the products of the oxidative insertion of palladium atoms into carbon-halogen bonds. These ArPdX, RPdX, and RCOPdX species were expected to be rather unstable due to their extreme coordinative unsaturation. Thus, the low temperature and inert conditions of the reaction matrix provide a unique method for this type of study.[13]
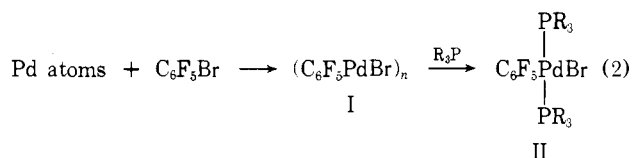
The most desirous starting point for such a study would be to first produce the most stable intermediate possible. Thus, we chose to study the C_6F_5PdBr species first since it is known that the C_6F_5-Pd bond is very stable due to electronegativity effects as well as Pd π^* back-bonding.[14a]

Perfluoroaryl Halides. Palladium atoms cocondensed with C_6F_5Br at −196° yielded an orange-brown solid.[2a] This material had moderate solubility in organic solvents such as benzene, diethyl ether, and methylene chloride and high solubility in acetone. Infrared studies and chlorination experiments indicated the presence of Pd-C σ-bonding, and phosphine trapping experiments confirmed this. Thus, we found that tertiary phosphines reacted with the orange-brown solid to instantaneously form the bisphosphine adducts II, and so we concluded that the orange-brown product was $(C_6F_5PdBr)_n$ (I).[2a] Table I summarizes the phosphine reactions with I that we studied. The rapidity of these phosphine reactions was expected considering the high

Table I. Tabulation of Products and Yields of Palladium Atom Reactions with Organohalides Followed by Tertiary Phosphine Trapping

Organohalide (RX)	Phosphine trapping agent	Temp phosphine[a] added (°C)	$(R'_3P)_2Pd(R)X$ % yield[b]	$(R'_3P)_2PdX_2$[m] % yield	Method[c]
C_6F_5Br	Ph₃P	25	7.6	5.0	B
	Me₂PhP	25	19.7	6.8	B
	Et₃P	25	7.7	4.8[f]	B
	Et₃P	−196	30	20[f]	D
C_6F_5Cl	Ph₃P	25	7.0[g]	0.4[h]	B
	Et₃P	25	15[i]	Trace	B
C_6F_5I	Et₃P	25	23	Trace	C
C_6H_5Br	Et₃P	−116	11	14[f]	B
C_6H_5Cl	Et₃P	−116	1.5[j]	3.0[k]	B
CF_3Cl	Et₃P	25	0	0	B
CF_3Br	Et₃P	−70	4	Trace	B
	Et₃P	25	3.1	Trace	B
	Et₃P	−196	Small	35[f]	D
CF_3I	Et₃P	25	10	Trace	C
C_2F_5I	Et₃P	−90	10	25[i]	B
	Et₃P	25	7.5	1.0[l]	C
$n\text{-}C_3F_7I$	Et₃P	25	8.5	Trace	C
CCl_3Br	Et₃P	0	0	40	B
CF_2BrBr	Et₃P	−78	0	13	B
C_6F_5COCl	Et₃P	25	$(Et_3)P_2Pd(C_6F_5)Cl$,[i] 23	Trace	B
$n\text{-}C_3F_7COCl$	Et₃P	−78	$(Et_3P)_2Pd(C_3F_7CO)Cl$, 9.0	0	B
CF_3COCl	Et₃P	−78	$(Et_3P)_2Pd(CF_3CO)Cl$, 7[d] $(Et_2P)_2Pd(CF_3)Cl$, 4	5	B
C_6H_5COCl	Et₃P	40	0	8[e]	B
$n\text{-}C_3H_7COCl$	Et₃P	0	0	19	B
CH_3COCl	Et₃P	−78	0	17	B

[a] If a substantial yield of RPdX was trapped, this temperature gives an indication of the thermal stability of the RPdX intermediate. [b] These yields are based on palladium vaporized and are uncorrected for metal lost on electrode supports, etc., which is about 20–40% of the total metal. [c] Cf. Experimental Section for detailed description of the methods: briefly, Method A, phosphine was added to the reactor after the excess organohalide was pumped off; B, phosphine added to the acetone extract (outside the reactor, room temperature); since PdI₂ was not acetone soluble, this method did not show how much $(R_3P)_2PdI_2$ was actually formed; C, phosphine, palladium, and organohalide all condensed simultaneously at −196°. [d] In this experiment, the yield of each component in the mixture was estimated from mass spectral evidence. [e] Biphenyl (10%) and chlorobenzene (8%) were also found in this experiment. [f] C. H. S. Hitchcock and F. G. Mann, *J. Chem. Soc.*, 2081 (1958). [g] R. Nyholm, *Quart. Rev., Chem. Soc.*, **24**, 1 (1970). [h] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1622 (1939). [i] F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc. A*, 1326 (1966). [j] R. J. Cross and R. Wardle, *ibid.*, 840 (1970). [k] F. G. Mann and D. J. Puride, *J. Chem. Soc.*, 1549 (1935). [l] Reference 25. [m] Normally, the dihalide complexes were colored (yellow for chloride and bromides, orange for iodides) while the organopalladium complexes were white.

$$\text{Pd atoms} + C_6F_5Br \longrightarrow (C_6F_5PdBr)_n \xrightarrow{R_3P} \overset{\displaystyle PR_3}{\underset{\displaystyle PR_3}{\overset{|}{\underset{|}{C_6F_5PdBr}}}} \quad (2)$$

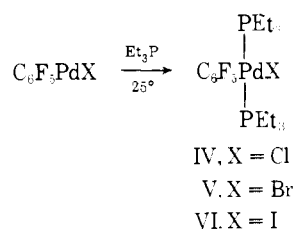$$\text{I} \qquad\qquad\qquad \text{II}$$

coordinative unsaturation of a species such as I. Thus, it seemed quite remarkable to us that I had moderately good resistance to attack by water or air *even at room temperature*. In fact, one useful technique for isolation of I was to wash it out of the reactor with acetone and then filter the solution and pump off the acetone—all of this could be done under atmospheric conditions. Addition of R_3P to the initial fresh acetone solution immediately yielded the bisphosphine adduct II. However, compound I was not indefinitely stable, and in benzene solution we observed slow decomposition over a 4-hr period yielding palladium, palladium dibromide, and decafluorobiphenyl in ratio 1:1:1. This decomposition also took place in ·diethyl ether solution, but

$$2C_6F_5PdBr \xrightarrow[25°]{benzene} C_6F_5C_6F_5 + Pd + PdBr_2 \quad (3)$$
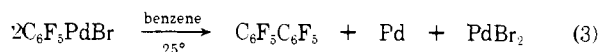
was slowed down considerably in acetone solution or in the solid state. In the solid state I probably exists in dimeric or polymeric form. In diethyl ether solution, however, vapor pressure depression molecular weight studies suggested a monomeric form for I, although this study was complicated by a constant slow decomposition of I.

Choropentafluorobenzene and iodopentafluorobenzene were also codeposited with palladium atoms. Trapping of the C_6F_5PdX intermediate in each case (X = Cl, Br, I) was carried out at room temperature with triethylphosphine yielding *trans*-bis(triethylphosphine)pentafluorophenylpalladium halide (III) in yields of 7% (Cl), 8% (Br), and 23% (I) as shown in Table I. In the case of hexafluorobenzene as substrate (X = F) no reaction took place. Thus, the order of
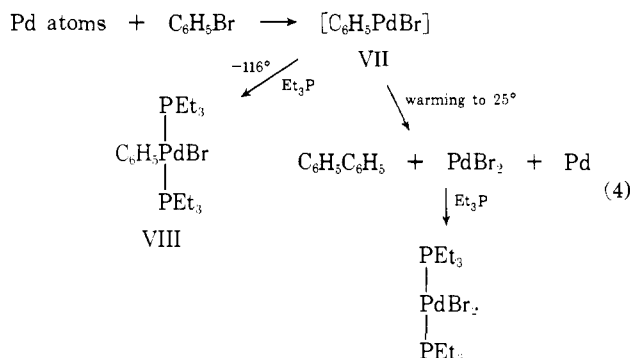
$$C_6F_5PdX \xrightarrow[25°]{Et_3P} \overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{\overset{|}{\underset{|}{C_6F_5PdX}}}}$$

$$\text{IV, X = Cl}$$
$$\text{V, X = Br}$$
$$\text{VI, X = I}$$

efficiency of the palladium atom oxidative insertion in this perfluoroaryl series is in the order C-I > C-Br ≳ C-Cl ≫ C-F. These results parallel those of Parshall who studied oxidative addition of aryl halides to $Pd(PEt_3)_4$.[14b]

In every reaction of Pd atoms with C_6F_5X, some PdX_2 was always formed along with the C_6F_5PdX. Phosphine trapping yielded this product as the bisphosphine adduct $(R_3P)_2PdX_2$ (*cf.* Table I). We do not know the exact mechanism for formation of the secondary product (PdX_2). It could be formed *via* the example shown in eq 3 while still at low temperature. However, since C_6F_5PdX was found to be stable up to room temperature, the operation of eq 3 at low temperature would suggest the momentary existence of a vibrationally excited C_6F_5PdX species[15] or perhaps assistance of the decomposition by another Pd atom. We do not favor direct radical abstraction reactions of X by Pd atoms since we have not been successful at trapping C_6F_5 radicals at low temperature with a hydrogen atom donor such as pivaladehyde.[16]

A small change in technique allowed us to synthesize V in considerably increased yield. That is Pd atoms, Et_3P, and C_6F_5Br were condensed *simultaneously* at −196°. This procedure is a rapid and clean synthesis of V, and the high

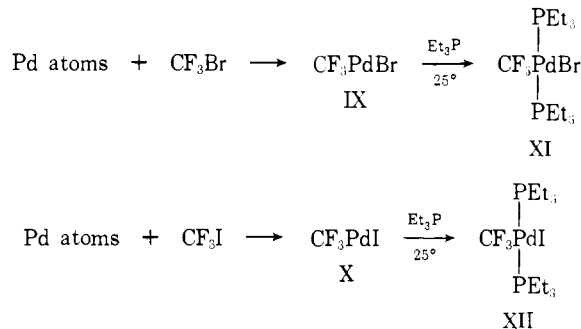yield must be the result of immediate trapping of C_6F_5PdBr upon its formation.[17]

Aryl Halides. Palladium atoms also oxidatively insert normal aryl carbon–halogen bonds. However, the resultant intermediates are much less thermally stable than in the perfluoroaryl cases. Thus, cocondensation of palladium atoms with bromobenzene, followed by warming to room temperature or −78° and then addition of Et_3P trapping reagent yielded $(Et_3P)_2PdBr_2$ as the sole product containing palladium. Biphenyl was also formed. However, if the matrix was only allowed to warm to −116° before phosphine addition, the expected insertion product (VII) was trapped. These experiments show that C_6H_5PdBr (VII) was indeed formed at −116° and was stable at this temperature, but not −78°.

$$\text{Pd atoms} + C_6H_5Br \longrightarrow [C_6H_5PdBr]$$

$$\text{VII}$$

$$\overset{-116°}{\underset{Et_3P}{\swarrow}} \qquad\qquad \overset{\text{warming to 25°}}{\searrow}$$

$$\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{\overset{|}{\underset{|}{C_6H_5PdBr}}}} \qquad C_6H_5C_6H_5 + PdBr_2 + Pd \quad (4)$$

$$\text{VIII} \qquad\qquad\qquad \Big\downarrow Et_3P$$

$$\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{\overset{|}{\underset{|}{PdBr_2}}}}$$

Chlorobenzene did not react with palladium atoms as efficiently as bromobenzene. This was evident from a −116° trapping experiment as in eq 4, and only a small yield of the expected insertion product was found (Table I).

As shown by yields of trapping products, or simply biphenyl yields observed, the efficiency of insertion is in the order C-I > C-Br > C-Cl. We also showed that a mixed biphenyl ($C_6F_5C_6H_5$) could be produced by cocondensing palladium atoms with a 50:50 mixture of C_6F_5I-C_6H_5I and then warming ($C_6F_5C_6F_5$, 9%; $C_6F_5C_6H_5$, 15%; $C_6H_5C_6H_5$, 9%).

Perfluoroalkyl Halides. Palladium vapor was allowed to cocondense at −196° with chlorotrifluoromethane (CF_3Cl), bromotrifluoromethane (CF_3Br), and iodotrifluoromethane (CF_3I) in the usual manner. Phosphine trapping experiments were carried out at −90, −78°, and room temperature. We determined from these experiments that palladium atoms did not react with CF_3Cl but did react with CF_3Br and CF_3I, and CF_3PdBr (IX) and CF_3PdI (X) were found to be moderately stable *at room temperature in the air* and could be trapped with Et_3P to form the bisphosphine adducts (XI and XII). Product yields (Table 1) indicate a reactivity order of C-I > C-Br ≫ C-Cl.

$$\text{Pd atoms} + CF_3Br \longrightarrow CF_3PdBr \xrightarrow[25°]{Et_3P} \overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{\overset{|}{\underset{|}{CF_3PdBr}}}}$$

$$\text{IX} \qquad\qquad\qquad \text{XI}$$

$$\text{Pd atoms} + CF_3I \longrightarrow CF_3PdI \xrightarrow[25°]{Et_3P} \overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{\overset{|}{\underset{|}{CF_3PdI}}}}$$

$$\text{X} \qquad\qquad\qquad \text{XII}$$

A series of perfluoroalkyl iodides was studied. Thus CF_3I, CF_3CF_2I, $CF_3CF_2CF_2I$, and $(CF_3)_2CFI$ were all allowed to react with palladium atoms. In the first three cases the resultant R_fPdI (XIII) species were found to be room

Table II. Nonligand Stabilized Species Produced, Approximate Thermal Stabilities, Thermal Decomposition Products Found, and Infrared Spectra of Stable Species

RPdX^a	Temp at which stable (°C)^b	Ir (cm^{-1}, acetone)	Obsd products of thermal dec under vacuum^d
C_6F_5PdCl	25		
C_6F_5PdBr	25	1670 s, 1520 s, 1505 vs, 1300 s, 1268 s, 1082 vs, 1070 s, 965 s, 800 s, 546 m, 406 m	$C_6F_5C_6F_5$, Pd, PdBr$_2$ (1:1:1)
C_6F_5PdI	25		
C_6H_5PdBr	−116		$C_6H_5C_6H_5$, PdBr$_2$
CF_3PdBr	25		
CF_3PdI	25	1340 w, 1250 m, 1215 m, 1165 m, 1130 m, 1080 vs, 1030 vs, 915 m, 785 s, 650 m, 550 vs, 510 m	C_2F_4 (0.3%), C_2F_6 (9.7%), PdI$_2$
C_2F_5PdI	25	1318 vs, 1270 w, 1211 m, 1180 vs, 1075 vs, 1042 s, 932 vs, 803 w, 749 m, 660 m. 554 s	C_2F_4 (19%), n-C_4F_{10} (25%), PdI$_2$
n-C_3F_7PdI	25	1334 m, 1249 m, 1204 vs, 1171 s, 1104 m, 1090 m, 1060 m, 922 w, 883 w, 818 s, 727 s, 552 s, 473 s	
i-C_3F_7PdI ?	<−78		PdI$_2$
CCl_3PdBr ?	<0		PdClBr, PdCl$_2$, PdBr$_2$
$CF_2BrPdBr$?	−130		PdBr$_2$
CH_3PdI	−130^c	Trace found	C_2H_4 (20%), C_2H_6 (0.2%)
C_2H_5PdI	−130	Trace found	C_2H_4 (4.0%), C_2H_6 (23%), n-C_4H_{10} (3.8%)
$C_6H_5COPdCl$	<−50		CO, C_6H_5PdCl, PdCl$_2$
$CF_3COPdCl$	<−78		CO, PdCl$_2$
n-$C_3F_7COPdCl$	>−78		CO, PdCl$_2$
$C_6H_5COPdCl$?	<−50		$C_6H_5C_6H_5$ (10%), C_6H_5Cl (8%), CO, PdCl$_2$
$CH_3COPdCl$?	<−130^c		CO, PdCl$_2$
n-$C_3H_7COPdCl$?	<−130^c		CO, PdCl$_2$

^{a} In cases where we have no direct trapping evidence for the existence of the intermediate, a question mark is used. ^{b} These temperatures are approximate, and in some of the low temperature cases, only estimates. These values are not necessarily the maximum temperatures at which these species are stable, but simply the temperatures where we observed stability. ^{c} In this experiment, a noncondensable gas was released upon slight warming of the matrix after completion of the experiment. This gas was very likely methane. ^{d} These are only the products found, not necessarily all the products formed. ^{e} CO given off during deposition.

temperature and air stable, and solution phase ir studies were carried out (cf. Table II). Triethylphosphine trapping

$$\begin{array}{ccc} & \overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{\overset{|}{\underset{|}{R_fPdI}}}} & \overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{\overset{|}{\underset{|}{PdI_2}}}} \\ R_fPdI & & \\ XIII & XIV & XV \end{array}$$
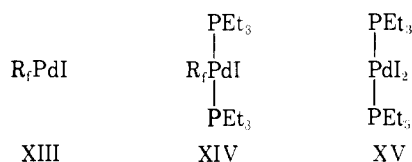
at 25° was successful in each case to yield XIV. However, in the case of (CF$_3$)$_2$CFI, no trace of structure XIII nor of XIV (after Et$_3$P addition at 25 or −78°) was detected. Therefore, either XIII is very unstable when R$_f$ = CF(CF$_3$)$_2$ or other reactions predominate in this particular case. More work is needed in this area before any real conclusions can be made. We note that yields of XV were quite high in general with R$_f$I reactions, which may be quite significant in a mechanistic interpretation. The yields were so high, in fact, that we had difficulty in separating XIV from XV and so developed a slightly modified technique, which made use of the solubility of R$_f$PdI (XIII) in acetone whereas PdI$_2$ was not soluble. Thus, XIII could be extracted out of large amounts of PdI$_2$, and then Et$_3$P added to yield XIV. (This, of course, was not successful when R$_f$ = CF(CF$_3$)$_2$.)

Dibromodifluoromethane (CF$_2$Br$_2$) and bromotrichloromethane (CCl$_3$Br) reacted with palladium atoms. However, only phosphine adducts of PdX$_2$ were isolated after trapping. Thus, it appears that RPdX species containing α-halogen other than fluorine are very thermally unstable.

Decomposition products formed upon pyrolysis of the matrices containing CF$_3$PdI and CF$_3$CF$_2$PdI were examined. Thus, after pump off of excess substrate, the residues of the atom reactions were heated above 150° and the volatiles collected. The results are summarized in Table II.

Alkyl Halides. We quickly determined that palladium atom reactions with normal alkyl halides only produced very unstable organometallic species. Low temperature

phosphine trapping experiments were not successful, and gaseous products were usually formed at well below −78°.
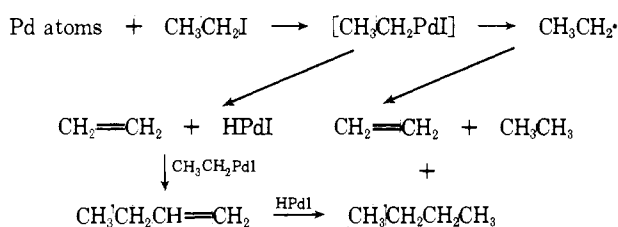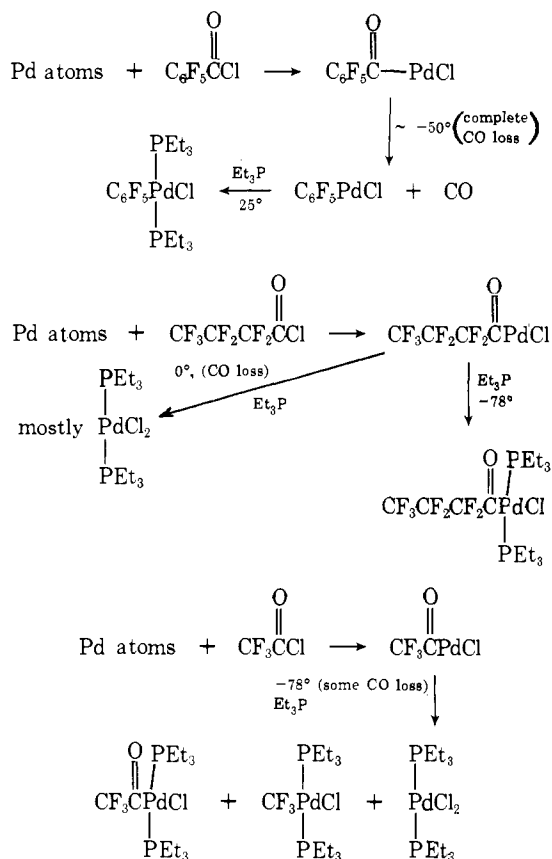
$$Pd\ atoms\ +\ CH_3CH_2I\ \longrightarrow\ [CH_3CH_2PdI]\ \longrightarrow\ CH_3CH_2\cdot$$

Table II summarizes our results with methyl iodide (CH$_3$I) and ethyl iodide (CH$_3$CH$_2$I). The products can be rationalized in terms of either formation of free radicals at low temperature[18] or by HPdI elimination and subsequent reactions.

Perfluoroacyl Halides. Cocondensation of palladium atoms with perfluoroacyl chlorides (R$_f$COCl) allowed oxi-

$$Pd\ atoms\ +\ R_f\overset{\displaystyle O}{\overset{\|}{C}}Cl\ \longrightarrow\ R_f\overset{\displaystyle O}{\overset{\|}{C}}PdCl$$
$$XVI$$
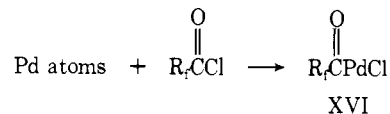
dative insertion into the C–Cl bond to yield XVI. These intermediates of structure XVI were more unstable than corresponding R$_f$PdX species and readily decarbonylated. Also, the exact structure of R$_f$ had a significant effect on stability. Thus, perfluorobenzoyl chloride (R$_f$ = C$_6$F$_5$) yielded a palladium intermediate that decarbonylated at relatively low temperature,[19] whereas perfluorobutyryl chloride (R$_f$ = CF$_3$CF$_2$CF$_2$) yielded a species that was stable at −78° but not at 0°, and, lastly, perfluoroacetyl chloride yielded a palladium intermediate that was moderately unstable at −78°. These results were obtained through Et$_3$P trapping experiments which are summarized below, and yields tabulated in Table I. It is of interest that Stone and coworkers found a somewhat similar stability trend in their solution phase studies of (R$_3$P)$_4$Pd reactions with perfluo-

$$\text{Pd atoms} + C_6F_5\overset{\overset{\displaystyle O}{\|}}{C}Cl \longrightarrow C_6F_5\overset{\overset{\displaystyle O}{\|}}{C}\!-\!PdCl$$

$$\bigg\downarrow \sim -50° \binom{\text{complete}}{\text{CO loss}}$$

$$\underset{\displaystyle PEt_3}{\overset{\displaystyle PEt_3}{C_6F_5PdCl}} \xleftarrow[25°]{Et_3P} C_6F_5PdCl + CO$$

$$\text{Pd atoms} + CF_3CF_2CF_2\overset{\overset{\displaystyle O}{\|}}{C}Cl \longrightarrow CF_3CF_2CF_2\overset{\overset{\displaystyle O}{\|}}{C}PdCl$$

$$\text{mostly } \underset{\displaystyle PEt_3}{\overset{\displaystyle PEt_3}{PdCl_2}} \xleftarrow[Et_3P]{0°, \text{ (CO loss)}} \qquad \bigg\downarrow \overset{Et_3P}{-78°}$$

$$CF_3CF_2CF_2\underset{\displaystyle PEt_3}{\overset{\overset{\displaystyle O}{\|}\, PEt_3}{C}PdCl}$$

$$\text{Pd atoms} + CF_3\overset{\overset{\displaystyle O}{\|}}{C}Cl \longrightarrow CF_3\overset{\overset{\displaystyle O}{\|}}{C}PdCl$$

$$\bigg\downarrow \overset{-78° \text{ (some CO loss)}}{Et_3P}$$

$$CF_3\underset{\displaystyle PEt_3}{\overset{\overset{\displaystyle O}{\|}\, PEt_3}{C}PdCl} + \underset{\displaystyle PEt_3}{\overset{\displaystyle PEt_3}{CF_3PdCl}} + \underset{\displaystyle PEt_3}{\overset{\displaystyle PEt_3}{PdCl_2}}$$

roacyl halides.[20] In our studies decarbonylation occurs *before* phosphine addition, and, so, CO loss can readily take place both from R_fCOPdX (our work) and the R_fCO-$(X) \cdot Pd(PR_2)_4$ system to yield $(R_3P)_2Pd(R_f)X$ (Stone's work).

Acyl Halides. Benzoyl chloride and palladium atoms were allowed to react followed by slow warming to 40° with complete pump off of excess substrate. Biphenyl (10%) and chlorobenzene (8%) were formed and pumped off during this warm-up period. Addition of Et_3P to the remaining residue only yielded the $PdCl_2$ adduct.[19]

$$\text{Pd atoms} + C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}Cl \longrightarrow \underset{\text{XVII}}{C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}PdCl}$$

$$\bigg\downarrow \text{warming}$$

$$\underset{\displaystyle PEt_3}{\overset{\displaystyle PEt_3}{PdCl_2}} \xleftarrow{Et_3P} C_6H_5C_6H_5 + C_6H_5Cl + PdCl_2 + Pd$$
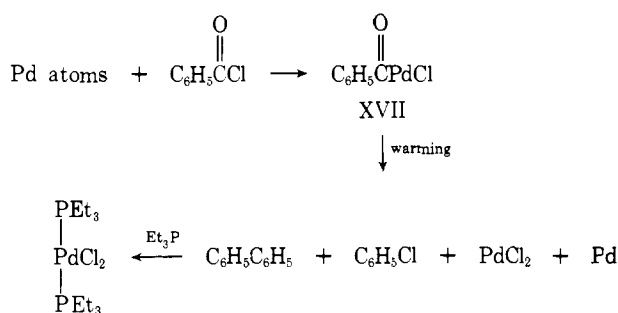
Upon cocondensation of palladium atoms with acetyl chloride or butyryl chloride some carbon monoxide was liberated during the deposition. Warming of the Pd − CH_3COCl matrix to 0° with pumpoff of excess CH_3COCl followed by Et_3P addition yielded only $(Et_3P)_2PdCl_2$. The same result was obtained at −78° with both CH_3COCl and $CH_3CH_2CH_2COCl$. The organopalladium species formed in these reactions were very unstable.

Conclusions

As outlined in the Abstract, we have shown that palladium atoms oxidatively insert carbon–halogen bonds at low temperature. Using this general reaction, we now can say several things regarding the production of ArPdX, RPdX,

and RCOPdX. (1) We have demonstrated the existence of these very coordinatively unsaturated species. (2) We now know a great deal concerning the stabilities of these species with variation of Ar or R. It is interesting that Ar_f and R_f groups impart unexpectedly high thermal and air stabilities to these materials, whereas normal Ar and R groups and groups containing halogen other than fluorine impart poor thermal stabilities. (3) We know what major products are formed from the thermal decompositions of these materials. (4) Since our main interest was in the production and stability determinations for ArPdX, RPdX, and RCOPdX species, not much effort was directed toward optimization of the yields of the phosphine adducts of these materials. However, simultaneous deposition of halide, phosphine, and metal does produce high yields of the desired adducts in the aryl halide systems. As nmr studies show, the phosphine adducts formed are always trans.[2b] Since the trans complexes are sterically favored over the cis, the phosphine must react stepwise and somewhat selectively with the ArPdX, RPdX, and RCOPdX species.

At the present time more work is being directed toward the mechanism of formation and decompositions of the RPdX and RCOPdX species and toward their structure and chemistry. Other metals are also being investigated.

Experimental Section

Analytical Methods. Quantitative elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Analyses of pertinent compounds are listed in Table III. These analyses were obtained primarily as checks on our routinely employed mass spectrometer techniques for structure determination. Thus, all the Et_3P complexes were amenable to study by mass spectrometry, and the major ions observed are summarized in Table III. These palladium complexes yielded very characteristic parent envelopes and fragment envelopes due to the presence of many isotopes of palladium. Theoretical spectra compared very favorably with observed spectra, and the compounds normally had relatively simple fragmentation patterns. We were able to routinely use the mass spectrometer for determining the components of crude reaction mixtures, as well as for characterizing pure compounds.

Vapor depression molecular weight studies of pentafluorophenylpalladium bromide (C_6F_5PdBr) were carried out in diethyl ether according to Shriver.[21] Several experiments with a standard (1,3,5-tribromobenzene) were carried out (av mol wt found = 312, calcd = 314). Seven trials with the C_6F_5PdBr species were carried out yielding values of 350 up to 467 (av = 353). Slow decomposition with the precipitation of Pd and $PdBr_2$ complicated these experiments.

Analysis for Pd was carried out according to Hildebrand, Lundell, Bright, and Hoffman.[22] Palladium dibromide was determined by dissolving in $KBr–H_2O$ solution, filtration, addition of triphenylphosphine, and isolation of the bis(triphenylphosphine)palladium dibromide.

Analyses for decafluorobiphenyl, halobenzenes, and other similar compounds were carried out by glpc on SE-30 analytical columns (30%). Gases were analyzed on SE-30 or Porapak (20%) columns.

Control Experiments. Clean palladium films were produced by depositing palladium atoms alone on the reactor walls or by depositing with an inert substrate such as perfluorocyclobutane. Bromopentafluorobenzene did not react with these films.[23]

Yields. The per cent yields are based on palladium vaporized and are uncorrected for some metal loss (20–40%) to electrode supports, wide spread deposition, etc. Corrections were not made because the metal losses were not consistent from one experiment to the next. (In previous publications corrections were made assuming 40% metal loss.) In general the yields based on metal vaporized are low, but it should be pointed out that the bulk metals are quite cheap, and some wastage can thus be tolerated.[17a]

Metal Atom Apparatus. Our metal atom reactors have been described in detail in a previous publication.[1] In this study palladium vapor was generated by electrical heating of aluminum oxide coat-

Table III. Physical and Spectral Properties of Pertinent New Compounds

Structure (all trans by nmr)[2b,h]	Color	Ir (cm⁻¹) (KBr, polyethylene far-ir)	Pmr (δ) (CDCl₃–TMS)[c]	Mp, °C	Mass spec (24 eV) M = parent, % intensities	Analyses
(Ph₃P)₂Pd(C₆F₅)Br	White	1500 vs, 1460 vs, 1100 s, 1050 s, 950 s, 935 s, 690 vs, 552 s, 429 w, 412 w	7.0 (m, 18 H), 7.2 (t, 12 H)	265–267		Found: C, 57.62; H, 3.45; Br, 9.15 Calcd: C, 57.49; H, 3.44; Br, 9.10
(Me₂PhP)₂Pd(C₆F₅)Br	White	1520 vs, 1480 vs, 1455 vs, 1440 s, 1375 s, 1300 s, 1128 s, 1074 vs, 985 vs, 928 vs, 860 s. 755 vs, 735 s, 710 s, 551 s, 430 m	6.9 (m, 10 H), 1.37 (t, 6 H, $J_{p\text{-}CH_3}$ = 4.0 Hz)	143–144		Found: C, 41.97; H, 3.55; F, 15.14 Calcd: C, 41.96; H, 3.53; F, 15.09
(Et₃P)₂Pd(C₆F₅)Br	White	2990 m. 1511 vs, 1468 vs, 1065 m, 1040 s, 962 vs, 792 m, 770 s, 735 m, 552 s. 408 m	0.9 (q, 6 H, $J_{H,P\text{-}CH_3}$ = 8.0 Hz)	124–125	M (13), M – C₆F₅ (1), (Et₃P)₂Pd (46), Et₃PBr (100), C₆F₅ (20), Et₃P (76)	Found: C, 37.68; H, 5.05; F, 16.03 Calcd: C, 36.66; H, 5.14; F, 16.11
(Et₃P)₂Pd(C₆F₅)I	White	3010 m, 2990 w, 2715 w, 1520 s, 1472 vs, 1400 w, 1370 m, 1265 m, 1072 vs, 1050 vs, 1035 m, 970 vs, 797 s, 780 vs, 740 s, 640 w, 572 m, 550 m, 422 w, 402 w	1.50 (q, 6 H, $J_{H,P\text{-}CH_3}$ = 8.0, 1.7 (m, 4 H)	154–155		
(Et₃P)₂Pd(CF₃)Br	White	3020 m, 1467 m, 1263 m, 1090 vs, 1046 vs, 1002 vs, 778 s, 738 s, 551 s, 406 w	1.18 (q, 6 H, $J_{H,P\text{-}CH_3}$ = 8.0 Hz), 2.0 (m, 4 H)	96–97	M (5), M – CF₃ (4), (Et₃P)₂Pd (24), Et₃PPdPEt₂ (6), Et₃PBr (100), PEt₃ (43)	Found: C, 31.64; H, 6.27; F, 11.54 Calcd: C, 31.75; H, 6.16; F, 11.59
(Et₃P)₂Pd(CF₃)I	White	1265 m, 1083 vs, 1042 vs, 1017 vs, 775 m, 730 w, 640 w, 543 vs, 398 w, 360 w, 325 w	1.18 (q, 6 H, $J_{H,P\text{-}CH_3}$ = 8.5 Hz), 2.1 (m)	111–112	M (6), M – CF₃ (4), M – I (100), (Et₃P)₂Pd (8), Et₃PPdPEt₂ (3), Et₃P (30), CF₃ (6)	
(Et₃P)₂Pd(CF₃CF₂)I	Off white	2978 s, 2940 m, 2845 w, 1466 m, 1427 m, 1385 m, 1301 s, 1245 m, 1200 m, 1190 vs, 1051 vs, 1037 vs, 1015 vs, 910 vs, 765 vs, 732 m, 718 w, 618 w, 600 w, 540 w, 432 w, 408 w	1.15 (q, 6 H, $J_{H,P}$ = 8.0 Hz), 2.1 (m, 4 H)	119–120	M (3), M – I (100), (Et₃P)₂Pd (36)	
(Et₃P)₂Pd(CF₃CF₂CF₂)I	Off white	2990 m, 1467 m, 1422 m, 1335 s, 1222 vs, 1202 vs, 1165 s, 1092 s, 1055 vs, 1040 vs, 1022 vs, 815 s, 772 vs, 730 vs, 537 m	1.15 (q, 6 H, $J_{H,P\text{-}CH_3}$ = 8.0 Hz), 2.1 (m, 4 H)	95–97	M (1), M – I (6), M – C₃F₇ (3), (Et₃P)₂Pd (3), Et₃PI (7), C₃F₇ (100), Et₃P (9)	
(Et₃P)₂Pd(C₃F₇CO)Cl	Yellow	2985, 1695 s, 1470 s, 1430 m, 1390 w, 1342 s, 1235 vs, 1195 vs, 1089 m, 1065 vs, 1042 vs, 1030 vs, 1017 s, 990 m, 815 w, 772 vs, 732 vs, 732 s, 712 s, 645 m, 554 s, 400 m, 319 s, 292 s	1.17 (q, 6 H. $J_{H,P\text{-}CH_3}$ = 8.0 Hz), 1.83 (m, 4 H)	Oil	M (16). M – C₃F₇Cl (100), M – C₃F₇CO (100), (Et₃P)₂Pd (60), Et₃PPdPEt₂ (16), C₃F₇ (7), Et₃P (100), Et₃PH (60)	
(Me₂PhP)₂PdBr₂	Yellow		6.9 (m, 10 H), 1.60 (t, 12 H, $J_{p\text{-}CH_3}$ = 3.5 Hz)			
(Et₃P)₂Pd(C₆H₅)Br	White			103–104[a]	M (6), M – C₆H₅ (3), (Et₃P)₂Pd (53), Et₃PPdPEt₂ (6), Et₃PBr (82), Et₃P (100), C₆H₅ (77)	

[a] Literature reports 89° (ref 24). [b] J. M. Jenkins and B. L. Shaw, *Proc. Chem Soc.*, *London*, 279 (1963); F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc. A*, 1326 (1966). Key: m, multiplet; t, triplet, q, quintet.

ed tungsten crucibles (Sylvania Emmissive Products, CS-1002A). Power input was about 6 V, 65 A. Slight power alterations were required with crucible aging (a crucible's lifetime normally was about 10 experiments).

Reaction Procedures (Methods A, B, C, and D). Method A. For isolation of temperature-stable Ar_fPdX and R_fPdX species, organohalide (about 25 mmol) and palladium vapor (about 3 mmol) were cocondensed at $-196°$ in approximately 30 min. Then the reactor was allowed to slowly warm to 25° with pump off of excess substrate and vented to air (or argon), and the R_fPdX species was washed out with solvent in the air or under an argon atmosphere. The solvent employed was usually spectral grade acetone, but in a few cases dry benzene, methylene chloride, or diethyl ether were used. The resultant solution was filtered to yield a fresh light yellow batch of R_fPdX in solvent which was used immediately for carrying out reactions or for spectral studies.

Method B. For preparation of most $(R_3P)_2Pd(R)X$ complexes, organohalide and palladium were cocondensed as in Method A. After completion of this deposition at $-196°$, the reactor was allowed to slowly warm to a specific desired temperature with pump off of excess substrate (if possible). Then the reactor was usually cooled to -78 or $-116°$ and the phosphine trapping agent added in one of three ways: (1) Ph_3P in benzene allowed to flow in as a liquid and spray out the showerhead inlet thereby washing down the walls of the reactor, (2) vacuum distilling in Me_2PhP or Et_3P, (3) distilling in Et_3P followed by 10 cm³ acetone or methylene chloride to serve as a solvating medium. Then the reactor contents were stirred magnetically at a desired temperature, usually room temperature, the volatiles pumped off, and the remaining solids washed out with solvent.

Example, Preparation of Bis(triethylphoshine)phenylpalladium Bromide, $(Et_3P)_2Pd(C_6H_5)Br$. Palladium vapor (0.479 g, 4.4 mmol) and bromobenzene were cocondensed at $-196°$. After codeposition the liquid nitrogen bath was replaced with an ether slush bath $(-116°)$ and held for 1 hr. Then Et_3P (1 cm³) was distilled in, and the whole mixture was allowed to slowly warm to room temperature. Volatiles were pumped off, the reactor was vented to air, and the solids were washed out with two 10-cm³ portions of methylene chloride. The washings were combined and filtered to yield a dirty black solution which was subsequently decolorized with carbon yielding a clear brownish solution. The solvent was stripped off and the resultant brown oil crystallized and was recrystallized from hexane yielding white bis(triethylphosphine)-phenylpalladium bromide (0.25 g, 11%) mp 103–104° without decomposition, in disagreement with the literature, mp 89°.[24]

From the mother liquor yellow bis(triethylphosphine)palladium dibromide was isolated (0.31 g, 14%).

In a similar experiment the cocondensate was warmed to 25 or $-78°$ before phosphine addition, and only the palladium dibromide complex was isolated.

Method C. For trapping stable R_fPdX species in acetone solution and removing from the reactor, method A was followed, and then phosphine added to the acetone solution of R_fPdX.

Example, Preparation of Bis(triethylphosphine)trifluoromethylpalladium Iodide. Palladium vapor (0.302 g, 2.8 mmol) was codeposited with trifluoromethyl iodide (300 mm in 2-l. bulb, 33 mmol). After deposition the reactor was allowed to slowly warm to 25° with simultaneous pump off of excess substrate. The reactor was vented to the atmosphere and the residue washed with several portions of acetone. These extracts were combined and filtered to yield a light yellow solution, to which was added 1 cm³ of Et_3P. The solution immediately turned almost colorless. The acetone was stripped off on a rotovac, and the resultant faint light yellow solid was recrystallized from methanol to yield white bis(triethylphosphine)trifluoromethylpalladium iodide (0.15 g, 10%) mp 111–112°. This white solid, upon standing in methanol solution for 1 month, turned to an orange solid, bis(triethylphosphine)palladium diiodide, mp 135–137°, lit. 138°.[25]

Similarly, bis(triethylphosphine)pentafluorophenylpalladium iodide was synthesized in 23% yield.

This method allowed isolation of the organopalladium species (R_fPdX) in the absence of most of the PdI_2 also produced, since PdI_2 was not acetone soluble.

Method D. For high yields of perfluoroaryl complexes, the organohalide, palladium vapor, and Et_3P were all condensed together at $-196°$.

Example, Preparation of Bis(triethylphosphine)pentafluorophenyl Bromide. Palladium vapor (0.263 g, 2.5 mmol), bromopentafluorobenzene (5 g, 20 mmol), and Et_3P (2 g, 17 mmol) were all condensed together at $-196°$. (The organohalide and phosphine were inletted from separate containers and only allowed to mix immediately before entering the reactor.) After deposition the reactor was allowed to slowly warm to room temperature with pump off of excess organohalide and phosphine and vented to the atmosphere, and the solid residue was dissolved and washed out with acetone. The acetone solution was filtered and decolorized with carbon, and the acetone was stripped off on a rotovac yielding a light yellow solid which was recrystallized from methanol to afford, first, a crop of white plates of bis(triethylphosphine)pentafluorophenyl-palladium bromide (0.44 g, 30%), mp 124–125° and then a crop of yellow needle-like crystals of bis(triethylphosphine)palladium dibromide (0.26 g, 21%).

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