*Journal of Organometallic Chemistry*, 137 (1977) 113—130
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

# A Mechanistic Investigation of the Oxidative Addition of Alkyl Halides to Palladium Atoms

Kenneth J. Klabunde and John S. Roberts
Department of Chemistry
University of North Dakota
Grand Forks, N. D. 58202 (U.S.A.)

(Received April 15th, 1977)

## Summary

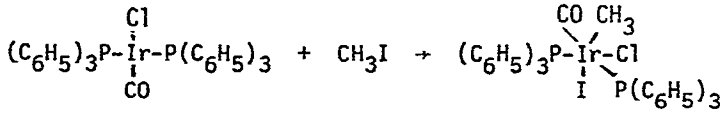
Palladium atoms (vapor) have been cocondensed at low temperature with a series of alkyl halides. Oxidative addition to form RMX occurs. Trapping experiments, free radical scavenging experiments, and decomposition product distributions suggest that the metal atom C-X bond insertion occurs directly via a caged radical pair.

---

## Introduction

Some transition metal complexes exhibit interesting chemistry and catalytic activity because of their ability to undergo oxidative addition and reductive elimination reactions in a facile manner.[1] An example of oxidative addition to a transition metal complex by an alkyl iodide is shown below for Vaska's complex:[2]

general $M + X\text{-}Y \rightarrow X\text{-}M\text{-}Y$



$$(C_6H_5)_3P\text{-}\overset{Cl}{\underset{CO}{Ir}}\text{-}P(C_6H_5)_3 + CH_3I \rightarrow (C_6H_5)_3P\text{-}\overset{CO\ CH_3}{\underset{I}{Ir}}\text{-}Cl\ P(C_6H_5)_3$$

Detailed studies on such reactions have been prevalent in recent years, particularly with regard to mechanistic studies utilizing kinetic and stereochemical probes.[3] The results of these studies indicate a very complex situation where the exact mechanism of the addition (direct insertion, $S_N2$, $S_N1$, free radical pair or free radical chain) is quite dependent on M, ligands attached to M, and on the nature of X-Y. Even a simple change from one alkyl halide (X-Y) to another can cause a change in mechanism.[4] Thus, steric effects, reaction centers involved, and solvent effects are all important.

Our study of the mechanism of oxidative addition to palladium atoms was undertaken for several reasons: (1) it represents an example of a sterically unhindered metal center; (2) solvent effects and ligand effects would be eliminated; (3) the results may have implications regarding oxidative addition to surface metal atoms; (4) we have already obtained substantial chemical information about RPdX compounds that can be formed in this way,[5,6] and thereby have developed broad knowledge in this area.

$$\text{R-X} + \text{Pd atoms} \rightarrow \text{R-Pd-X}$$

$$R = CH_3,\ C_2H_5,\ (CH_3)_3C,\ (CH_3)_3CCH_2,\ CF_3,\ C_2F_5$$

$$X = Br,\ I$$

## Results

### Isolable RPdX Species

Previous work in our laboratory showed the compounds $(CF_3PdI)_n$, $(C_2F_5PdI)_n$, and $(n\text{-}C_3F_7PdI)_n$ are stable, albeit reactive, compounds which can be prepared by codeposition of Pd vapor with the respective $R_fI$ substrate.[5,7] A search for other products was made, in particular $PdI_2$ and gaseous coupling and disproportionation products, $R_fF$ and $R_fR_f$. For the $CF_3I$-Pd system, no $CF_4$, $C_2F_6$, or $C_2F_4$ were formed when Pd vapor was condensed with $CF_3I$ at -196°C, with subsequent slow warming to room temperature. Based on Pd vaporized, the products found were $(CF_3PdI)$ (23% and 20%) and $PdI_2$ (29% and 33%) for two identical experiments. The high yields of $PdI_2$ were confusing in light of the apparent absence of $CF_3$ derived products other than $CF_3PdI$. We have not observed $(CF_3)_2Pd$ by nmr, and we believe $CF_3$ loss is due to polymer formation or decomposition and loss on the Pd-$PdI_2$ residue (cf. analogous behavior of $CH_3I$

discussed later). For the analogous $C_2F_5I$-Pd system, again no gaseous products, $C_2F_6$, $C_2F_4$, or $C_4F_{10}$, were observed. The yields of $C_2F_5PdI$ were quite high (66% and 49%), but still significant amounts of $PdI_2$ (17% and 6%) were formed. These experiments do point out that RPdX can be formed directly without formation of gaseous decomposition products. Therefore, in cases where gaseous products are formed, they probably come from decomposition of RPdX rather than from the process of formation of RPdX.

Non-Isolable RPdX Species

Many $CH_3I$-Pd depositions were studied. Yields of products, $CH_4$ and $C_2H_6$, were rather erratic, until it was discovered that not all of the gaseous products were released unless the reaction residue was pyrolyzed at approximately 100°C. A study was made in which the composition and yields of products were determined upon matrix warmup (-196°C → 25°; no $CH_4$ was formed during codeposition at -196°C) and then upon residue pyrolysis. Identical experiments showed good reproducibility. An average of three experiments is tabulated below:

Table I. Products from $CH_3I$-Pd Reactions

| Product | % Yield | |
|---|---|---|
| | Released→25°C | Released→100° |
| $CH_4$ | 2.8 | 13 |
| $C_2H_6$ | 0.21 | 2.3 |
| $C_2H_4$ | 0.0 | 0.18 |
| $PdI_2$ | 12 | |

We have not been successful in isolating the unstable intermediate, $CH_3PdI$, or even in trapping it as its $Et_3P$ adduct. Therefore, the release of $CH_4$ upon pyrolsis probably is due to $CH_3$, $CH_3I$, or $CH_4$ being bound to or adsorbed tightly on the Pd-$PdI_2$ solid residue remaining after matrix warmup. Alternatively, $CH_3PdI$ may decompose intermolecularly to $CH_3(Pd)n$ + $PdI_2$ with just partial release of organic products, thus rationalizing the higher yield of $PdI_2$ than $CH_4$. A small amount of $CH_3CH_2I$ also was observed as a product, which suggests that $CH_2$ may also be a decomposition product. Similar experiments utilizing $CH_3Br$ gave similar product distributions, although the bulk of the product gases were released at 25°C or lower. ($CH_4$ 9.4%, $C_2H_6$ 1.8%, $CH_2 = CH_2$ 0.29%, $PdBr_2$ 7.0%) It is possible that Pd-$PdI_2$ residues "tie up" $CH_3$ fragments more effectively than Pd-$PdBr_2$ residues.

Reaction of ethyl iodide with Pd yielded more informative results than the $CH_3I$-Pd system. Three pertinent experiments were carried out: (1) codeposition of EtI with Pd followed by warming to room temperature and product removal, (2) deposition of Pd with EtI and HCl together and, (3) deposition of Pd with HCl followed by EtI addition. The latter two experiments were carried out in order to show whether HPdX (HPdCl or HPdI) could be a decomposition product enroute to the final products. The experiments do indicate that HPdX is important, particularly in formation of ethane. Similar results were obtained for EtBr employing the same experiments. In this case the presence of HCl caused increased ethane yields and decreased ethylene yields (HCl and HBr behaved similarly).

Table II. Yields of Products from Various Reactions Involving Cocondensation of Palladium Vapors with Ethyl Iodide and Ethyl Bromide

| Reaction | $C_2H_6$(%) | $C_2H_4$(%) | $PdX_2$(%) |
|---|---|---|---|
| Pd + EtI | 6.7 | 18 | 28 |
| Pd + EtI + HCl | 42 | 40 | -- |
| Pd + HCl followed by EtI | 20 | 8.3 | -- |
| Pd + EtBr | 13 | 11 | 10 |
| Pd + EtBr + HCl | 21 | 4.5 | 4.5 |
| Pd + HCl followed by EtBr | 3.6 | 1.3 | -- |

In none of these experiments was butane observed as a product. This shows conclusively that ethyl radicals were not "free" in the matrix since if that were true, some quantity of butane would be observed even if disproportionation were the favored process.

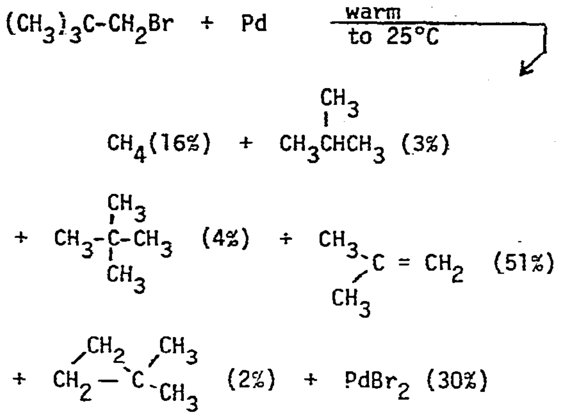
The deposition of t-butyl bromide with Pd vapor was studied since in this case formation of RPdX probably would not occur by an $S_N2$ type mechanism, and if free t-butyl radicals were formed, they would be expected to disproportionate to give about equal yields of 2-methylpropane and 2-methylpropene. Experiments with t-butyl bromide-HCl mixtures also were carried out as shown in Table III. These experiments again showed that HPdX could reduce R-X to RH,[16] but in this case the presence of HCl during the deposition of $(CH_3)_3CBr$ did not affect the $(CH_3)_2C = CH_2$ yield. Overall, product yields with t-BuBr were quite high, which indicates the absence of an $S_N2$ process or other backside attack process. Even though a Pd atom is quite unhindered, at least a slight lowering in reaction efficiency would be expected if an $S_N2$ were operating.‡

Table III. Yields of Gaseous Products from the Cocondensation of t-Butyl with Palladium Vapor

| Reaction | 2-methyl propane | 2-methyl propene |
|---|---|---|
| Pd + $(CH_3)_3CBr$ | 8.5 | 38 |
| Pd + $(CH_3)_3CBr$ + HCl | 16 | 40 |
| Pd + HCl followed by $(CH_3)_3CBr$ | 7.0 | 0.0 |

‡In addition, an $S_N2$ process is probably not reasonable since a Pd atom ($d^{10}$) would be expected to be electrophilic, not nucleophilic.

Our most detailed studies involved neopentyl bromide (1-bromide-2, 2-dimethylpropane) and palladium vapor. An average of several determinations indicated products as shown below:



The main products of the reaction were $CH_4$ and $(CH_3)_2C = CH_2$. The actual $CH_4$ yield was probably somewhat higher, as we had difficulty in trapping this product quantitatively, and also have previously observed the tendency of $CH_3$ and/or $CH_4$ to be adsorbed on the (Pd)n residues. A study of product distribution changes when certain additives were incorporated was made. The additives used were NO (a good free radical scavenger), $C_6H_5CH_3$ (a good radical terminating agent since the $CH_2$-H bond is relatively weak), and $PEt_3$ (as a trap of radicals and/or RPdX). Yields are shown in Table IV. With NO as additive, no change whatever in product distribution was observed. This result precludes a radical chain process for the formation of the observed products. With toluene a slight decrease in $(CH_3)_2C{=}CH_2$ and a slight increase in $(CH_3)_3CH$ was observed. This change is in the expected direction if toluene were trapping t-butyl radicals by H donation. However, the effect is quite small. And curiously, the neopentane yield was not increased, and in fact decreased slightly. The toluene results reinforce the idea that radicals, if formed, are not free to migrate in the matrix. Employing $PEt_3$ as an additive, the $(CH_3)_2C{=}CH_2$ yield was decreased moderately while the $CH_4$ yield increased a greatly. This increased $CH_4$ yield may be due to displacement of adsorbed $CH_3$ or $CH_4$ from bulk Pd-$PdBr_2$. The $C_2H_6$ and $C_2H_4$ are most likely products of metal atom reactions with $PEt_3$, reactions which have been observed before.[8] (Note that $CH_3PdBr(PEt_3)_2$ was not formed, which indicates it is unlikely that neopentylpalladium bromide decomposed directly to yield methylpalladium bromide.)

The fact that the neopentyl moiety is fragmented to give isobutylene and methane (from $CH_3$) indicates that a fast radical type process must be important. Careful studies on the thermochemistry of free radicals[9] and on the generation of "hot" free radicals[10] have shown that $CH_3$ eliminations are facile, but any C-C cleavage requires 26-40 kcal/mole. Thus, the starting radical must be significantly vibrationally excited to allow C-C cleavage to occur. However, at the same time we cannot eliminate a direct frontside insertion mechanism followed by RPdX decomposition or rearrangement. Based on later discussion, this seems more unlikely however.

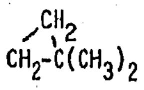
We have studied several alkyl halides containing alkenyl or aryl functional groups, which have led to the synthesis of a number of unusual RMX and $R_2M$ compounds, but which have been of little help in terms of mechanistic information regarding the RX/Pd reaction. For example benzyl chloride yields $\eta^3$-benzylpalladium chloride dimer.[11] In this case neither $PdCl_2$ or bibenzyl were formed, seemingly precluding an uncaged radical type mechanism.[12] Visual observations were such that it seemed likely that upon cocondensation of benzyl chloride and Pd vapor a $\pi$-complex formed first with subsequent C-Cl bond insertion during warmup. Thus, a deep red matrix immediately formed which changed in appearance considerably upon warming, a sequence followed very similar to many M-arene matrices.[‡] We believe $\pi$-complexation, followed by C-X insertion on warming, occurs in aryl halide systems as well,[5,13] for example in the formation of $C_6F_5PdBr$.

The problem with the aryl and aryl-substituted alkyl halides in

---

[‡] Whenever arene ligands (toluene, bromobenzene, bromopentafluorobenzene, xylene, etc.) are cocondensed with Pd (or other transition metals) colored complexes are believed to form. On warming C-X insertion can occur if C-X is available. If it is not, large metal clusters form (cf. ref. 6 and K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. Roppel, J. Amer. Chem. Soc., 98, 1021 (1976)).

Table IV. Effect of Additives on the Product Yields for Neopentyl Bromide-Pd Vapor Reactions

| Additive | $C_2H_6 + C_2H_4$ | $n\text{-}C_4H_{10}$ | $CH_4$ | $(CH_3)_2C{=}CH_2$ | $(CH_3)_3CH$ | $(CH_3)_4C$ |  | $PdBr_2$ |
|---|---|---|---|---|---|---|---|---|
| NO | 0 | 0 | 15 | 48 | 2.3 | 4.3 | 0 | 33 |
| $C_6H_5CH_3$ | 0 | 0 | 14 | 48 | 4.1 | 5.4 | 2.5 | 38 |
| $PEt_3$ | 15 | 10 | 26 | 32 | 2.1 | 2.2 | 0.80 | -- |

the present context is that these unsaturated groups very probably could cause a change in the C-X insertion mechanism compared to saturated R-X substrates. This idea is nicely illustrated by our work with 6-bromo-1-hexene with Pd vapor. Here, it seemed likely that a prior π-complex formed since a clear condensate was produced which changed to yellow and then to brown on warming. The 6-bromo-1-hexene was converted catalytically to 6-bromo-2-hexene, but no $PdBr_2$ or other products attributable to R-Pd-Br formation were observed!

Since the heated crucible in which the metal atoms are generated is white hot and radiating much light during a metal atom reaction, we anticipated possible photoeffects in RX-Pd reactions. A shielded crucible (with Kaowool) was employed in a EtI-Pd reaction. Table V shows product yields for identical experiments employing unshielded and shielded crucibles. The results are essentially identical, and so at least in this case photolysis has no effect.[14]

Table V. Ethane and Ethylene Yields for a EtI-Pd Reaction Employing Shielded and Unshielded Crucibles

| | Ethane(%) | Ethylene(%) |
|---|---|---|
| Shielded | 5.6 | 19 |
| Unshielded | 6.7 | 18 |

## Discussion and Conclusions

There are a number of points that have to be reconciled in order to predict a mechanistic pathway:

1. (1) Coupling and disproportionation reactions of R radicals is a minor process and usually totally absent. Therefore, radicals, if formed are not free to migrate in the matrix.
2. (2) Radical scavengers have no effect on products yields or distributions. Therefore a radical chain process is not important in product formations.

(3) Photolysis by the crucible has no effect, at least in the case of a saturated alkyl halide such at EtI.[‡]

(4) t-Alkyl halides react as effectively as primary halides, indicating a non-backside attack mechanism, such as $S_N2$.

(5) Vibrationally excited radicals probably are formed.

(6) HPdX is an important, reactive intermediate product capable of reducing R-X to R-H.

(7) Gaseous products come from decomposition of RPdX rather than from the process of formation of RPdX. Thus, if RPdX is stable, that is the only organic product found.

(8) Unsaturated alkyl halides react first by π-complexation followed by C-X oxidative addition, probably on matrix warmup.

(9) Based on our previous work with R-X--Ag vapor reactions,[15] it is likely that complexation to form RX--M occurs first at -196°C, and on warmup oxidative addition occurs. This previous work[14] showed that in the reaction $2Ag + RX \rightarrow AgX + RAg$ high RX/Ag ratios favored RAg formation, thus indicating prior RX-Ag complexation before <u>slow</u> reaction to form R· + AgX in warmup. The R· could then quickly trap Ag from still existing RX--Ag complexes.

A mechanism that fits all of these observations is shown below. In brief, upon cocondensation of an excess of RX with Pd atoms, a σ-complex forms[14,15] which is stable at that low temperature. Upon matrix warmup, a caged radical pair forms and at the exact moment of its formation, the R· portion possesses enough excess vibrational energy that decomposition processes <u>may</u> occur. The radicals do not separate, but recombine to form RPdX, which, if it is stable, can be isolated. If RPdX is not stable, it decomposes on warming, yielding various products, depending on the nature of RPdX.[‡] [‡‡] Thus, when possible, HPdX and alkene are formed, and the HPdX can react with RX to form RH and $PdX_2$. The formation of HPdX is so favorable that in the case of $CH_3PdI$, come $CH_2$ appears to be formed, which reacts with $CH_3I$ to form $CH_3CH_2I$. In the case of neopentyl bromide, isobutylene and $CH_3$ are formed. It is unlikely that the $CH_3$ combines with PdBr in this case since there are significant differences in products and yields for the $CH_3Br$ + Pd experiment when compared with the $(CH_3)_3CCH_2Br$ + Pd experiment ($CH_4$ 9.4%, $CH_3CH_3$ 1.8%, $CH_2 = CH_2$ 0.09%, $PdBr_2$ 7.0% for $CH_3Br$ experiment and $CH_4$ 15%, $CH_3CH_3$ 0.0%, $CH_2 = CH_2$ 0.0%, $PdBr_2$ 33% for $(CH_3)_3CCH_2Br$ experiment).

Whenever a β-H elimination is possible, cleaner reaction product mixtures are found. In the case of $CH_3X$, complex and competing reaction patterns are observed. These include retention of $\cdot CH_3$ by the $Pd\text{-}PdX_2$ residue, particularly in the case of $Pd\text{-}PdI_2$. It also is noted that whenever RI is used, the $PdI_2$ yields are much higher than would be predicted from the stoichiometry: $2RI + Pd \rightarrow PdI_2 + 2R$ (organic products). This further reinforces the idea that the $Pd\text{-}PdI_2$ residue retain organic species, with some of them possibly being converted to polymeric products which will be non-recoverable. Thus, the presence of <u>iodide</u> and <u>$CH_3$</u> groups are complicating features. Note that for EtBr, t-BuBr, and $Me_3CCH_2Br$, the reaction stoichiometry is approximately correct, as shown in Table VI.

$2RBr + Pd \rightarrow PdBr_2 + 2R$ (organic products)

---

[†] We do have evidence for photolytic effects in other systems, which will be presented in later publications.

---

[‡] In the cases where RPdX was not trappable (such as $CH_3$), the implicide assumption is made that it did exist at least momentarily.

[‡‡] An alternative, which cannot be eliminated, it that some RPdX species, in particular t-butyl PdBr, were formed by direct front side attack (three centered).

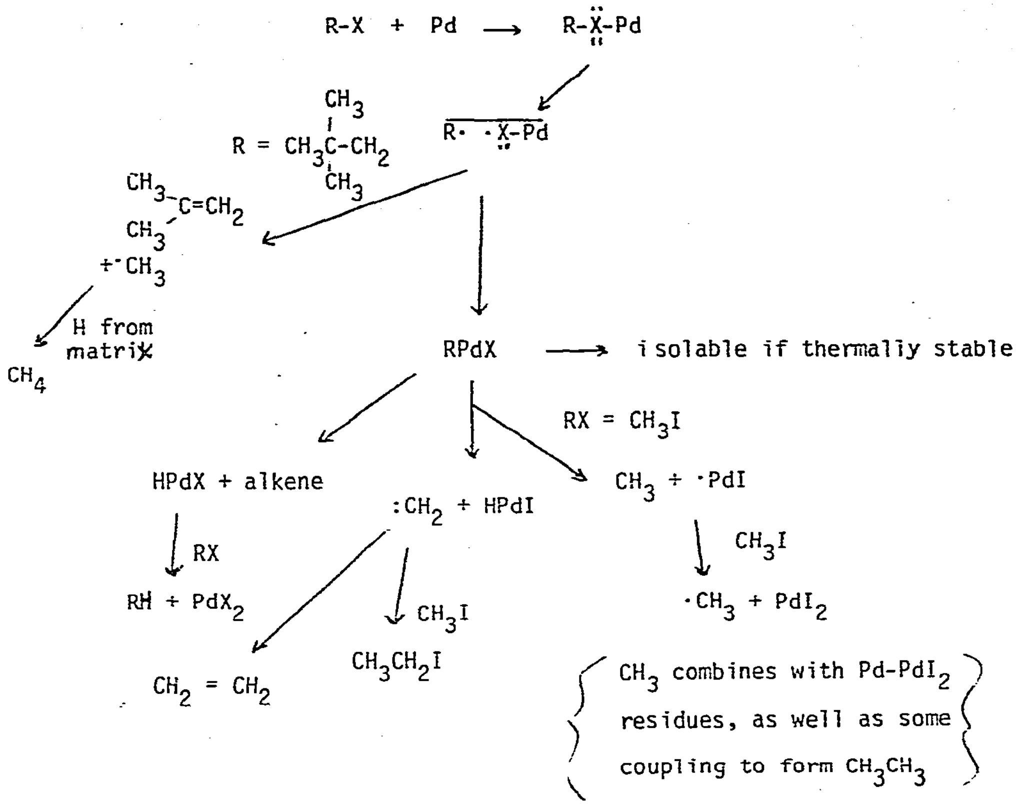


Table VI. Stoichiometry Comparisions for

R-X + Pd Reactions (% Yields)

| | $PdX_2$ | Combined yield of organics |
|---|---|---|
| $CH_3Br$ | 7 | 12 |
| $CH_3CH_2Br$ | 10 | 24 |
| $(CH_3)_3CBr$ | 29 | 55[a] |
| $(CH_3)_3CCH_2Br$ | 30 | 60[b] |
| $CH_3I$ | 12 | 19[c] |
| $CH_3CH_2I$ | 28 | 25 |

[a] Average value.

[b] $CH_4$ not included since isobutylene and $CH_4$ come from same molecule.

[c] Heating needed to release most of organics.

## Experimental Section

General. All reactions were carried out in metal vapor reactors built in this laboratory which have been previously described.[6] Gas chromatography for gaseous samples was performed on a gas chromatograph built in this laboratory. Gas chromatographic analysis of liquid samples was performed on a Varian Aerograph, Model 90P-3. All columns were prepared in this laboratory. All liquid phase columns were supported on 80-100 mesh Chromosorb P. All RX-Pd depositions employed ca. 30:1 RX-Pd ratios.

Reaction of $CF_3I$ with Pd Vapor. Palladium vapor (0.683g, 6.42 mmol) was cocondensed at -196° with $CF_3I$, which was present in a great excess (ca 30 mmol). The reactor was warmed to room temperature while the volatile contents were being removed under vacuum to a -196° trap. The materials were distilled through a -131° trap. Gas chromatography of the contents of both traps revealed only $CF_3I$. The nonvolative contents of the reactor were dissolved by adding 50 ml of acetone (dried over $P_2O_5$) and stirring. The resulting solution was removed by syringe to an inert atmosphere filtration apparatus. The solution was filtered and the acetone solution concentrated. Addition of 10 ml of pentane resulted in the formation of a red powder (0.38 g, 20% yield) which was identified as $(CF_3PdI)n$ by its infrared spectrum.[13]

The remaining reactor residues were treated with an aqueous KI solution. After three recrystallizations from aqueous solution, 1.48 g of $K_2PdI_4$ (33% yield) was obtained.

Reaction of Pentafluoroethyl Iodide with Palladium Vapor. By the same procedure as above $C_2F_5I$ was cocondensed with palladium vapor (0.0811 g, 0.76 mmol). A red powder, $(C_2F_5PdI)n$ (0.132 g, 49% yield) was isolated. The infrared spectrum of this compound compared favorably with the previously reported spectrum.[13] A 6% yield of $K_2PdI_4$ (0.032 g) was obtained.

Reaction of Methyl Iodide with Palladium Vapor: Pyrolysis. Palladium vapor (0.633 g, 6.23 mmol) was cocondensed with methyl iodide. A silica gel-filled demountable trap, preceded by a second demountable trap, both cooled to -196°, was used to trap non-condensible gases formed during the reaction and after warm up to 25°. Upon removal of all volatiles it was possible to release methane by warming the silica gel trap to ∿40°. The gas was adsorbed onto silica gel in a sample tube and transferred to a vacuum line fitted for gas chromatography. Methane was identified by its retention time on a molecular sieve column and by its infrared spectrum. (3.2% yield).

The contents of the second demountable trap were distilled through a -131° trap. This trap retained only methyl iodide. The distilled gas, with methyl iodide removed, was transferred to a gas chromatograph where ethane (0.25%) was identified using a 5' X 1/4", 20% hexanedione column (no ethylene was found).

The traps (silica gel trap and first demountable trap) again where cooled to -196° and the reaction vessel was heated to ∿100°. Yields after pyrolysis were as follows: methane, 15%; ethane, 2.8%; ethylene, 0.2%.

The reactor residues were analyzed by formation of the triethylphosphine complex of palladium diiodide. Triethylphosphine (6 ml) was condensed into the reactor which had been cooled to -196°. After warming the reactor to room temperature, it was vented to the air and washed thoroughly with hexane. The hexane washed were combined, decolorized, and filtered. Upon blowing argon over the hexane solution, crystals of <u>trans</u>-$(PEt_3)_2PdI_2$ were isolated in 15% yield (0.576 g).

<u>Reaction of Other Alkyl Halides with Palladium Vapor</u>. The reactions of ethyl iodide, ethyl bromide and <u>t</u>-butyl bromide were all carried out similarly. The reaction of ethyl iodide will be used as an example.

<u>Reaction of Ethyl Iodide with Palladium Vapor</u>. Palladium vapor (0.468 g, 4.39 mmol) was cocondensed with ethyl iodide. The reactor was warmed to room temperature while the contents of the reactor were being transferred to a -196° trap. The contents of the -196° trap were distilled through a -131° trap. The 131° trap contained only ethyl iodide, while the -196° trap contained ethane (6.7%) and ethylene (18%). Triethyl-

phosphine was added to the reactor residues, producing trans-bis(triethylphosphine) palladium diiodide in 28% yield.

Reaction of Ethyl Iodide and HCl gas with Palladium Vapor. Palladium vapor (0.100 g, 0.937 mmol) was cocondensed with HCl and ethyl iodide. (The HCl was stored in a 2 ℓ bulb and was connected to the substrate inlet through a bubbler to control the rate of addition.) After the codeposition was complete, the reactor was warmed to room temperature, while the contents of the reactor were transferred to a -196° trap. The -196° trap contents were distilled through a -131° trap into a -196° trap. The -131° trap contained only ethyl iodide. The contents of the -196° trap were equilibrated over NaOH pellets to remove excess HCl. Ethane (42%) and ethylene (40%) were observed.

Reaction of HCl and Palladium Vapor. Addition of Ethyl Iodide after Cocondensation. Palladium vapor (0.11 g, 1.04 mmol) was cocondensed with HCl. After the cocondensation was complete, ethyl iodide was on top of the Pd-HCl matrix. The reaction was warmed to room temperature while the volatile contents were removed to a -196° trap. The -196° trap contents were distilled through a -78° trap and a -131° trap. The -78° trap contained ethyl iodide, and the -131° trap contained HCl. The -196° trap contained ethane (20%) and ethylene (8.3%) after equilibration over NaOH pellets.

Reaction of Neopentyl Bromide with Palladium Vapor. Neopentyl bromide was cocondensed with palladium vapor (0.429 g, 4.03 mmol). Noncondensible gases were given off during the reaction. These gases were trapped in a silica trap cooled to -196°. The reactor was warmed to room temperature while any volatile materials were removed to either a -196° trap or a silica gel trap. The silica gel trap contained methane (17%). The -196° trap was fractionated through a -78° trap. The -78° trap contained only neopentyl bromide. The -196° trap contained 2-methylpropene (54%) and smaller amounts of 2-methylpropane (3.2%) and neopentane (4.7%) as identified using a 5' X 1/4", 20% HMPA column. The addition of triphenylphosphine to the reactor resulted in a 6.3% yield of trans-bis(triphenylphosphine)palladium dibromide.

Reaction of Neopentyl Bromide with Palladium Vapor. Nitric Oxide Additive. Palladium vapor (0.281 g, 2.65 mmol) was cocondensed with neopentyl bromide and nitric oxide (0.09 mmol). The nitric oxide was contained in a separate container isolated form the substrate inlet by a bubbler. The remainder of the reaction was carried out as above yielding methane, 15%; 2-methylpropene, 48%; neopentane, 4.3% 2-methylpropane, 2.3%; and trans-$(P(C_2H_5)_3)_2PdBr_2$, 33%.

Reaction of Neopentyl Bromide with Palladium Vapor. Toluene Additive. Palladium vapor (0.347 g, 3.26 mol) was cocondensed with a 35 mol % mixture of toluene in neopentyl bromide. The reaction was carried out as above yielding: methane, 14%; 2-methylpropene, 48%; 2-methylpropane, 4.1%; neopentane, 5.4% and trans-$(P(C_2H_5)_3)_2PdBr_2$, 38%. (ca. 2 cc)

Reaction of Neopentyl Bromide with Palladium Vapor. Triethylphosphine Additive. Palladium vapor (0.092 g, 0.086 mmol) was cocondensed with triethylphosphine and neopentyl bromide. Both the triethylphosphine container and neopentyl bromide container were isolated from the substrate inlet to avoid phosphonium salt formation in the pure samples. The reaction was carried out as above, yielding methane, 26%; 2-methyl-propene, 32%; neopentane, 2.2%; 2-methylpropane, 2.1%; ethylene and ethane, 15%; and butane, 10%.

Reaction of 6-Bromo-1-hexene with Palladium Vapor. Palladium vapor (0.288 g, 2.15 mmol) was cocondensed with 6-bromo-1-hexene. The reactor was warmed to room temperature after the reaction was complete and the volatile contents were removed to a -196° trap. The -196° trap was fractionated through a -78° trap. The -196° trap did not contain any volatiles. Preparative GLC analysis of the -78° trap, using a 5' X 1/4", 25% SE-30, indicated that 67% of the original 6-bromo-1-hexene had been converted to 6-bromo-2-hexene. The presence of 6-bromo-2-hexene was determined by pmr spectroscopy: (6-bromo-1-

hexene) $^1$H NMR(δ)($H_2C$=CH, 5.27 multiplet, 3H; $CH_2Br$, 3.35 triplet, 2H; ($CH_2$), 1.83 multiplet, 6H); (6-bromo-2-hexene) (CH=CH, 5.43 multiplet, 2H; $CH_2Br$, 3.35 triplet, 2H; ($CH_2$) 2.03 multiplet, 4H; $CH_3$, 1.63 doublet, 3H). Triethylphosphine addition to the reactor residues yielded only a small amount of triethylphosphine oxide.

## Acknowledgements

Generous support of the National Science Foundation is gratefully acknowledged.

## References

1. L. Vaska, Accts. Chem. Res., 1, (1968) 335.
   J. P. Collman, Acct. Chem. Res., 1, (1968) 136.
2. R. F. Heck, J. Amer. Chem. Soc., 86, (1964) 2796.
3. J. K. Stille and K. S. Y. Lau, J. Amer. Chem. Soc., 98, (1976) 5841 and references therein.
4. A. U. Kramer and J. A. Osborn, J. Amer. Chem. Soc., (1974) 7832; A. U. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, J. Amer. Chem. Soc., 96, (1974) 7145.
5. K. J. Klabunde and J. Y. F. Low, J. Amer. Chem. Soc., 96, (1974) 7674.
6. K. J. Klabunde, Accts. Chem. Res., 8, (1975) 393; Angew. Chem., 87, (1975) 309; Angew. Chem. Int. Ed. Engl., 14, (1975) 287.
7. B. B. Anderson, K. Neuenschwander, and K. J. Klabunde, manuscript in preparation describing detailed preparation and chemistry of ($CF_3PdI$)n.
8. K. J. Klabunde, J. Y. F. Low, and H. F. Efner, J. Amer. Chem. Soc., 96, (1974) 1984; also W. J. Kennelly, unpublished results from this laboratory.
9. (a) A. S. Gordon and J. R. McNesby, J. Chem. Phys., 31, (1950) 853.
   (b) H. M. Frey and R. Walsh, Chem. Rev., 69, (1969) 103.

10. (a) C. W. Larson and B. S. Rabinovitch, J. Chem. Phys., 50, (1970) 871; and E. A. Hardwidge, C. W. Larson, and B. S. Rabinovitch, J. Amer. Chem. Soc., 92 (1970) 3278, and references therein.

(b) J. Kochi, Editor, "Free Radicals," Chapter by J. A. Kerr, (1973) pg. 29.

11. J. S. Roberts and K. J. Klabunde, J. Amer. Chem. Soc., 99, (1977) 2509. J. Organometal Chem., 85, (1975) C-13.

12. J. S. Roberts, Ph.D. thesis, University of North Dakota, (1975).

13. J. Y. F. Low, Ph.D. thesis, University of North Dakota, (1973).

14. K. J. Klabunde, J. Fluorine Chem., 7, (1976) 95.

15. A similar proposal was brought forth by Skell and Girand in their RX-Mg vapor publication: P. S. Skell and J. E. Girand, J. Amer. Chem. Soc., 94, (1972) 5518; also private communications with P. S. Skell and J. E. Girand.

16. Alkyl halides can be reduced in a similar way by $HPtBr(PEt_3)_2$; cf. A. V. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, J. Amer. Chem. Soc., 96, (1974) 7145; W. R. Moser, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, MA, April, 1972, ORGN-14.