

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.)

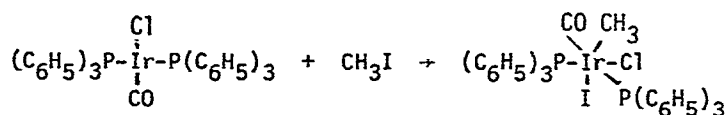
(Received April 15th, 1977)

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

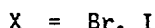
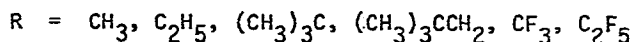
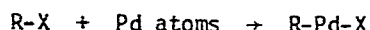
Some transition metal complexes exhibit interesting chemistry and catalytic activity because of their ability to undergo oxidative addition and reductive elimination reactions in a facile manner.¹ An example of oxidative addition to a transition metal complex by an alkyl iodide is shown below for Vaska's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



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.



Results

Isolable RPdX Species

Previous work in our laboratory showed the compounds $(\text{CF}_3\text{PdI})_n$, $(\text{C}_2\text{F}_5\text{PdI})_n$, and $(n\text{-C}_3\text{F}_7\text{PdI})_n$ 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 $(\text{CF}_3)_2\text{Pd}$ by nmr, and we believe CF_3 loss is due to polymer formation or decomposition and loss on the Pd-PdI₂ 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 $100^\circ C$. A study was made in which the composition and yields of products were determined upon matrix warmup ($-196^\circ C \rightarrow 25^\circ$; no CH_4 was formed during codeposition at $-196^\circ C$) 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 $\rightarrow 25^\circ C$	Released $\rightarrow 100^\circ$
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 pyrolysis 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 $\text{CH}_3\text{CH}_2\text{I}$ 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%, $\text{CH}_2 = \text{CH}_2$ 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 $\text{CH}_3\text{I-Pd}$ 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	$\text{C}_2\text{H}_6(\%)$	$\text{C}_2\text{H}_4(\%)$	$\text{PdX}_2(\%)$
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

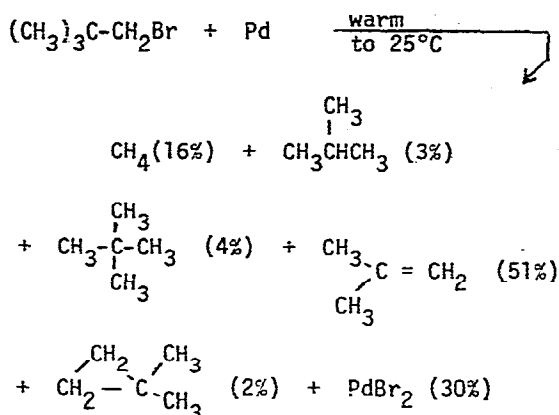
Table III. Yields of Gaseous Products
from the Cocondensation of *t*-Butyl
with Palladium Vapor

Reaction	2-methyl propane	2-methyl propene
Pd + (CH ₃) ₃ CBr	8.5	38
Pd + (CH ₃) ₃ CBr + HCl	16	40
Pd + HCl followed by (CH ₃) ₃ CBr	7.0	0.0

presence of HCl during the deposition of (CH₃)₃CBr did not affect the (CH₃)₂C = CH₂ 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.*

*In addition, an S_N2 process is probably not reasonable since a Pd atom (d¹⁰) 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 $(\text{CH}_3)_2\text{C}=\text{CH}_2$. 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 $(\text{Pd})_n$ residues. A study of product distribution changes when certain additives were incorporated was made. The additives used were NO (a good free radical scavenger), $\text{C}_6\text{H}_5\text{CH}_3$ (a good radical terminating agent since the $\text{CH}_2\text{-H}$ 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 $(\text{CH}_3)_2\text{C}=\text{CH}_2$ and a slight increase in $(\text{CH}_3)_3\text{CH}$ 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 $(\text{CH}_3)_2\text{C}=\text{CH}_2$ 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 $\text{CH}_3\text{PdBr}(\text{PET}_3)_2$ 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 radicals⁹ and on the generation of "hot" free radicals¹⁰ 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 η^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 π -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 π -complexation, followed by C-X insertion on warming, occurs in aryl halide systems as well,^{5,13} for example in the formation of $\text{C}_6\text{F}_5\text{PdBr}$.

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	$C_2H_6 + C_2H_4$	$n-C_4H_{10}$	CH_4	$(CH_3)_2C=CH_2$	$(CH_3)_3CH$	$(CH_3)_4C$	$\begin{array}{c} CH_2 \\ \diagup \\ CH_2-C(CH_3)_2 \end{array}$	$PdBr_2$
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:

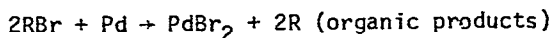
- (1) Coupling and disproportionation reactions of R radicals is a minor process and usually totally absent. Therefore, radicals, if formed are not free to migrate in the matrix.
- (2) Radical scavengers have no effect on products yields or distributions. Therefore a radical chain process is not important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

- (3) Photolysis by the crucible has no effect, at least in the case of a saturated alkyl halide such as 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 work¹⁴ showed that in the reaction $2\text{Ag} + \text{RX} \rightarrow \text{AgX} + \text{RAg}$ high RX/Ag ratios favored RAg formation, thus indicating prior RX-Ag complexation before slow reaction to form $\text{R}\cdot + \text{AgX}$ in warmup. The $\text{R}\cdot$ 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 $\text{R}\cdot$ portion possesses enough excess vibrational energy that decomposition processes may 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 $\text{RPdX}^* \ddagger$. 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 , some CH_2 appears to be formed, which reacts with CH_3I to form $\text{CH}_3\text{CH}_2\text{I}$. 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 $\text{CH}_3\text{Br} + \text{Pd}$ experiment when compared with the $(\text{CH}_3)_3\text{CCH}_2\text{Br} + \text{Pd}$ experiment (CH_4 9.4%, CH_3CH_3 1.8%, $\text{CH}_2 = \text{CH}_2$ 0.09%, PdBr_2 7.0% for CH_3Br experiment and CH_4 15%, CH_3CH_3 0.0%, $\text{CH}_2 = \text{CH}_2$ 0.0%, PdBr_2 33% for $(\text{CH}_3)_3\text{CCH}_2\text{Br}$ 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 $-\text{CH}_3$ by the Pd-PdX_2 residue, particularly in the case of Pd-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: $2\text{RI} + \text{Pd} \rightarrow \text{PdI}_2 + 2\text{R}$ (organic products). This further reinforces the idea that the Pd-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 iodide and CH_3 groups are complicating features. Note that for EtBr , $t\text{-BuBr}$, and $\text{Me}_3\text{CCH}_2\text{Br}$, the reaction stoichiometry is approximately correct, as shown in Table VI.



*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 implicate assumption is made that it did exist at least momentarily.

‡An alternative, which cannot be eliminated, is that some RPdX species, in particular $t\text{-butyl PdBr}$, were formed by direct front side attack (three centered).

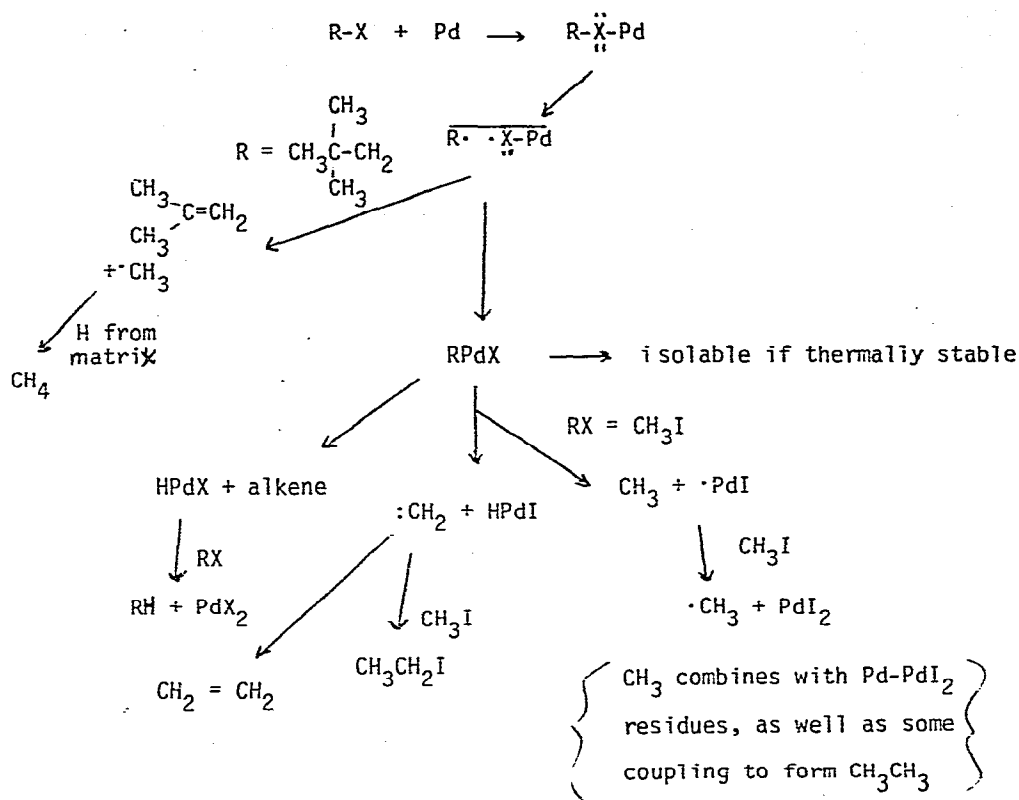


Table VI. Stoichiometry Comparisons for
R-X + Pd Reactions (% Yields)

	PdX ₂	Combined yield of organics
CH ₃ Br	7	12
CH ₃ CH ₂ Br	10	24
(CH ₃) ₃ CBr	29	55 ^a
(CH ₃) ₃ CCH ₂ Br	30	60 ^b
CH ₃ I	12	19 ^c
CH ₃ CH ₂ I	28	25

^aAverage value.

^bCH₄ not included since isobutylene and CH₄ come from same molecule.

^cHeating 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 nonvolatile 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 $(\text{CF}_3\text{PdI})_n$ 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 $\text{C}_2\text{F}_5\text{I}$ was cocondensed with palladium vapor (0.0811 g, 0.76 mmol). A red powder, $(\text{C}_2\text{F}_5\text{PdI})_n$ (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-condensable 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 $\sim 40^{\circ}$. 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% hexanediene column (no ethylene was found).

The traps (silica gel trap and first demountable trap) again were cooled to -196° and the reaction vessel was heated to $\sim 100^{\circ}$. 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 washes were combined, decolorized, and filtered. Upon blowing argon over the hexane solution, crystals of trans-(PEt_3)₂PdI₂ were isolated in 15% yield (0.576 g).

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

Reaction of Ethyl Iodide with Palladium Vapor. 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 x 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). Noncondensable 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 from 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-($P(C_2H_5)_3$)₂PdBr₂, 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-($P(C_2H_5)_3$)₂PdBr₂, 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-methylpropene, 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) ^1H NMR(δ)($\text{H}_2\text{C}=\text{CH}$, 5.27 multiplet, 3H; CH_2Br , 3.35 triplet, 2H; (CH_2) , 1.83 multiplet, 6H); (6-bromo-2-hexene) ($\text{CH}=\text{CH}$, 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 $(\text{CF}_3\text{PdI})_n$.
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 $\text{HPtBr}(\text{PET}_3)_2$; 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.