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# PERFLUORO-N-OCTYLPALLADIUM AND -ZINC BROMIDES
## REMARKABLY STABLE COORDINATIVELY UNSATURATED ORGANOMETALLICS

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## SUMMARY

The novel compounds perfluoro-n-octyl palladium bromide and perfluoro-n-octylzinc bromide have been synthesized through the oxidative insertion reaction of palladium or zinc metal atoms into the alkyl carbon-bromine bond, using the metal atom (vapor) technique These intermediates, $R_FMBr$ (M=Pd,Zn), are formally coordinatively unsaturated and thus extremely reactive with acetonitrile, tertiary-phosphines, -arsine or CO to form tetra- coordinated adducts Although these $C_8F_{17}MBr$ species were expected to be rather unstable due to their extreme coordinative unsaturation, the long perfluoroalkyl chain bound to the metal atom imparts a remarkable stability to them Both electronic and steric effects appear to play a role in this stabilization

## INTRODUCTION

Earlier we have reported the syntheses of several alkyl-, aryl-metal halides, RMX, utilizing metal vapor synthesis techniques [2-4]. This method, in fact provides an ideal way to generate and study the products of

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** See [1].

the oxidative insertion of many transition metal atoms into the carbon-halogen bond of organic substrates These RMX species are formed in the absence of normal stabilizing ligands and their stabilities vary greatly depending on the metal and the organic group attached From these previous studies it was determined that perfluoroaryl and perfluoroalkyl groups impart stability to these coordinatively unsaturated species that normal aryl and alkyl groups do not The differences in decomposition temperatures between $CF_3PdI$ and $CH_3PdI$ ($85^oC$ and $<-100^oC$ respectively), $C_6F_5PdBr$ and $C_6H_5PdBr$ ($130^oC$ and $<-100^oC$ respectively) are really quite remarkable [5] In spite of long standing general knowledge that perfluoroalkyl groups ($R_f$) bound to transition metals are more stable systems than the hydrocarbon analogs, [6] explanations as to why this is so have not been conclusive Basically two ideas persist (1) $d\pi \rightarrow \sigma^*$ (metal d orbitals donate to C-F antibonding $\sigma$ orbitals) is important in strengthening the $R_f$-M bond, and (2) ionic-covalent resonance (a hyperconjugative effect) is important where $R_f\text{-}M \leftrightarrow R_f^- M^+$ gives an ionic bonding component as well as a covalent component, and tends to strengthen the $R_f$-M bond [7] This may be due to the (+) charge on M contracting the metal $\sigma$ orbitals which could improve overlap with the small carbon $\sigma$-orbitals Furthermore the presence of electronegative fluorines may increase the s-character of the carbon $\sigma$-orbital, resulting in improving overlap with the metal $\sigma$-orbital [7a, g] It must also be considered that decomposition may not involve homolysis of the $R_f$-M bond, but instead $F^-$ elimination by an allowed pathway to yield FMX and $F_2C{=}M$ (if $R_f{=}CF_3$).

With these considerations in mind we decided to investigate the effects of placing a very large $R_f$ group on a transition element and to compare thermal and chemical stabilities with $CF_3$ and $C_6F_5$ analogs Some striking findings resulted

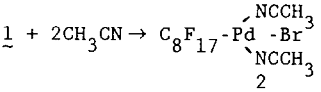
## SYNTHESES AND SPECTRA

### Palladium

Palladium is an ideal metal in these studies  It can be evaporated as atoms at a convenient temperature (~ 1400°C) and the atoms possess high reactivity  When Pd atoms were cocondensed with excess 1-bromoheptadecafluoro-n-octane ($C_8F_{17}Br$) at -196°C followed by warming and removal of excess $C_8F_{17}Br$, a thick yellow oil resulted  This material, shown to be $C_8F_{17}PdBr$ was moderately soluble in organic solvents such as diethyl ether, methylene chloride, and slightly in alkanes  It was highly soluble in acetone and acetonitrile

$$n\text{-}C_8F_{17}Br + Pd \xrightarrow{-196^\circ C} \xrightarrow[\text{to R T}]{\text{warm}} \underset{\underset{\sim}{1}}{n\text{-}C_8F_{17}Pd\ Br.}$$

Many attempts to solidify $\underset{\sim}{1}$ (in hopes of crystallizing this oil) met with only limited success  The long $R_f$ chain imparts a long liquid range to this compound.  Some success was achieved by dissolving $\underset{\sim}{1}$ in acetonitrile followed by solvent removal, thereby giving $\underset{\sim}{2}$, the solid acetonitrile adduct



$$\underset{\sim}{1} + 2CH_3CN \rightarrow C_8F_{17}\text{-}Pd(NCCH_3)_2\text{-}Br$$

$\underset{\sim}{2}$

Spectra of $\underset{\sim}{1}$ and $\underset{\sim}{2}$ showed the expected IR absorptions [8] and the mass spectrum of $\underset{\sim}{2}$ (heated solid probe) showed all the ions from $C_1$ to $C_8$ obtained from the fragmentation of the perfluoroalkyl chain  In addition some ions were observed where $R_f$-Pd bonds were intact  $^{19}F$ NMR studies on $\underset{\sim}{1}$ confirmed the presence of the $R_f$ chain, and each $CF_2$ group and the $CF_3$ could be resolved

### Zinc

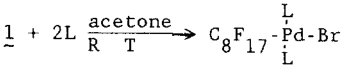
Zinc atoms are very readily formed by evaporation and were found to be quite reactive with $C_8F_{17}Br$.  The insertion

$$C_8F_{17}Br + Zn \xrightarrow{-196^oC} \xrightarrow[\text{to R T}]{\text{warm}} \underset{3}{C_8F_{17}\text{-}Zn\text{-}Br}$$

product 3 was obtained as a white solid Dissolving in acetonitrile followed by evaporating to dryness yielded the adduct $C_8F_{17}ZnBr(CH_3CN)_2$ (4) Solid 3 was extremely hygroscopic but very stable at room temperature The IR spectrum, recorded in $CH_2Cl_2$, showed $\nu_{C≡N}$, $\nu_{C-F}$, and $\nu_{C-C}$ bands as expected. The mass spectrum (heated solids probe) showed only ions obtained from the fragmentation of the $R_f$ group $^{19}F$ NMR confirmed the presence of the $R_f$ group.

REACTIVITY STUDIES

Tertiary phosphines or arsines reacted with a solution of 1 to readily form the trans-bis-coordinated adducts (5)



$$1 + 2L \xrightarrow[\text{R T}]{\text{acetone}} C_8F_{17}\text{-}\overset{L}{\underset{L}{Pd}}\text{-}Br$$

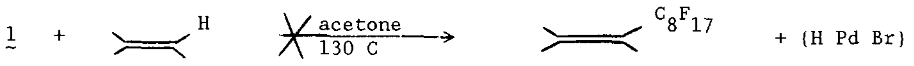
5

L = $PPh_3$, $PEt_3$, $AsPh_3$

the rapidity of these phosphine reactions was expected considering the high coordinative unsaturation of 1 The adducts 5 (L=$PPh_3$, $AsPh_3$) were slightly yellow microcrystalline solids They were insoluble in alkanes but soluble in chlorinated and oxygenated solvents NMR and IR studies showed that they were the trans-adducts

Both 1 and 2 showed unexpectedly high thermal stability and high resistance to hydrolysis Solutions of 1 or 1 as a pure oil could be stored for months at room temperature with no decomposition Heating 1 to 120°C for 2h yielded only slight decomposition In a separate experiment 2 ml of conc $H_2SO_4$ were added to an ethereal solution of 1 and refluxed for 4h No reaction occurred.

Several attempts to react 1 with alkenes, similar to the Heck reactions [9] were carried out without success For example,



acetone solutions of 1 were saturated with ethylene (about 20 atm), and heated at 130°C for 1 day in an autoclave The oil obtained by evaporating the volatiles proved to be unreacted starting material

Other attempts to react 1 with $CO_2$ to eventually yield perfluorocarboxylic acid (as obtained from $C_8F_{17}MgBr$ [10]), also failed. Thus, degassed acetone solutions of 1 were saturated with $CO_2$ and heated to 130°C for 1 day in an autoclave Treating these solutions at room temperature with water and $H_2SO_4$, in order to hydrolyze them, and extracting the mixtures with diethyl ether, only yielded starting 1

Reactions of 1 with CO yielded a red-orange oil Its IR spectrum showed intense bands for $\nu c{=}o$ Thus, weak coordination to CO by Pd is evident [11]

## DISCUSSION

Bennett and coworkers [7a,b] have presented evidence that the presence of a $CF_3CF_2$ group can cause a further shortening of a $CF_3CF_2$-Pt bond over $CH_3$, but also $CF_3$. Likewise, Tamborski and coworkers [10a,c] have found that long chain $R_f$ groups provide more stable $R_fMgX$ reagents than $CF_3$ Our work with coordinatively unsaturated $R_f$-M [12] and $R_fMX$ [13] species has shown that larger $R_f$ groups sometimes yield more thermally stable species

The various $R_fPdX$ species we have prepared all show some similarities Thus, all such species are readily ligated even by solvents such as diethylether, acetone, and acetonitrile Apparently such weak Lewis bases are capable of breaking up metal-halide bridging that probably exists in non-ligated RPdX [2,3] However, $C_8F_{17}PdBr$ (1) is unusual in its own right Thermal stability of 1 is remarkably high, better than with $CF_3PdI$ Furthermore, 1 is more resistant to hydrolysis or thermal degradation than $C_6F_5PdBr$ [3-5] And $C_8F_{17}ZnBr$ exhibits unprecedented stability compared with other non-ligand stabilized $CF_3ZnI$ or $(CF_3)_2CFZnI$ [13]

In explaining these unusual properties we suggest that (1) the ionic-covalent resonance effect is even more favorable when an $R_f$ is involved (compared with $CF_3$). An $R_f$ group attached to $CF_2$ (in this case $R_f$=n-$C_7F_{15}$) should be even more effective at encouraging such resonance and changes in S-character of the bonding $\sigma$-orbitals than fluorine itself,

(2) the long n-$C_8F_{17}$ chain must afford an unusual steric protection of the C-M bond towards hydrolysis The sweeping action of a long negatively polarized chain could effectively repell incoming reagents,

(3) fluoride ion elimination is not facile in the $C_8F_{17}Pd$ Br system (to give perfluorolefin and FPd Br) It would appear that the presence of a long, rapidly moving chain inhibits access to a conformation that allows such an elimination reaction

Finally, we point out that $C_8F_{17}Br$ itself is a very 'inert' fluorocarbon by most standards However, its reactions with metal atoms do proceed well, although product yields are lower than with $R_fI$ systems

## EXPERIMENTAL

### Analytical Methods

Quantitative elemental analyses were performed by Galbraith Laboratories, Inc , Knoxville, Tennessee. Infrared spectra were recorded on a Perkin-Elmer 1330 using CsI or KBr cells. Nuclear magnetic resonance spectra ($^{1}H$, $^{13}C$, $^{19}F$) were recorded by using a Bruker 400 MHz nuclear magnetic resonance spectrometer The mass spectral analyses were performed on a Finnigan 4000 mass spectrometer.

### Yields

The per cent yields are based on the metal vaporized and are uncorrected for some metal loss (20-40%) to electrode supports or wide spread deposition

### Metal Atom Vapor Apparatus

Our metal atom reactor has been described in detail in a previous publication [14] In these experiments palladium or zinc vapors were generated by electrical heating of aluminum oxide coated tungsten crucibles (Sylvania Emmissive Products, CS-1002A) Power input was about 5V, 60A.

### Reaction Procedures

Synthesis of n-heptadecafluorooctylpalladium bromide (1). n-$C_8F_{17}Br$ (about) 0.2 mol.) and palladium vapor (about 5 mmol) were cocondensed at -196°C in approximately 2 hours. Then the reactor was allowed to warm slowly to room temperature The melted matrix was stirred for 30 min and then the excess substrate was pumped off and the reactor chamber vented to a nitrogen atmosphere. The $R_fPdBr$ species was washed out with distilled acetone The resultant black suspension was filtered to yield a yellow clear solution These solutions were used for carrying out subsequent reactions or evaporated under vacuum to give a yellow oil, usually in 10-15% yield IR($CH_2Cl_2$ solution KBr, 0.5 mm cells) $\nu$(C-F)1210 vs, 1150 vs, 1060 s, cm$^{-1}$, $\nu$(C-C) 810 w, cm$^{-1}$ $^{19}$F NMR (d$_6$-Acetone, CFCl$_3$); -80 8 ppm s (i 3), CF$_3$-, -125 2 ppm s (i 2), CF$_3$-$\underline{CF_2}$-(CF$_2$)$_n$-, -122 3, -121 5, -121 3, -120 8, -120 3 ppm five s (each i 2), CF$_3$-CF$_2$-(CF$_{\underline{2}}$)$_5$CF$_2$-Pd Br, -113 29 ppm m. broad (i 2), -CF$_2$-Pd Br

Synthesis of n-C$_8$F$_{17}$PdBr(CH$_3$CN)$_2$, 2 Compound 1 was treated with excess acetonitrile followed by stirring and removal of volatiles in vacuo The yield of 2 was essentially quantitative Pale yellow solid, melting point 122°C Mass spectrum (E I 22 ev, 90 °C) CF$_3$, (10%), C$_3$F$_5$, (4), C$_3$F$_7$, (2); Pd(CH$_3$CN)$_2$, (1), C$_4$F$_9$, (1), C$_5$F$_{11}$, (0 2), C$_6$F$_{11}$, (0.4), C$_7$F$_{13}$, (0 2), C$_3$F$_{17}$Pd, (1), C$_8$F$_{17}$Pd(CH$_3$CN), (0 3), C$_8$F$_{17}$Pd(CH$_3$CN)$_2$, (0 1) Analysis found: C, 21 30%, H, 0 73, F, 49 71, Pd, 14 02 C$_8$F$_{17}$PdBr(CH$_3$CN)$_2$ requires, C, 20 96%, H, 0 88, F, 46 98, Pd, 15 48% IR(CH$_2$Cl$_2$ solution, KBr 0 5mm cells): 2860-2840cm$^{-1}$ vs, 2320 w, 2300w, 1460s, 1370s; 1360w, 1240vs, 1210vs, 1150vs, 1110m, 1070s, 990m, 920m, 740m, 640s, 555m, 530m

### Preparation of Bromoheptadecafluoro-n-octylbis(triphenyl phosphine) palladium (II)(5)

To an acetone solution (about 40ml) of 1 (about 0 5mmol) an acetone solution of triphenylphosphine (2 mmol) was slowly added at 0 °C working under inert atmosphere The resulting solution was stirred for 12h and allowed to warm to room temperature It was concentrated under vacuum and after the addition of pentane a pale yellow solid was obtained which was recrystallized from CH$_2$Cl$_2$/pentane Yield 5% (respect to metal vaporized) Melting point: 148°C with decomposition Analysis found, C, 46 54%, H, 2 94; P, 5.57, C$_8$F$_{17}$Pd(Br)(PPh$_3$)$_2$ requires, C, 46 77%, H, 2 67, P, 5 48,. $^1$H NMR (in CDCl$_3$, TMS) 7 75 ppm m.(i 2), 7 34 ppm m (i 3) Mass spectrum (E I 25ev, 280 °C) CF$_3$, (10%), C$_3$F$_7$, (10); C$_4$F$_9$, (5), PPh$_3$, (100), C$_8$F$_{17}$, (4); BrPdPPh$_3$, (1). IR (mineral oil, CsI cells): 3060cm$^{-1}$ w;

2980÷2840vs; 1480m, 1460s; 1430s, 1370m; 1240vs, 1210vs; 1140m, 1100m, 1050m, 1020m, 740vs, 700vs, 630vs, 520vs, 510vs, 460w, 420vw

### Preparation of Bromoheptadecafluoro-n-octylbis(triphenylarsine) palladium (II)

To a $CH_2Cl_2$/acetone 5 1 (vol ) solution (about 50ml) of 1 (about 0.5 mmol) a methylene chloride solution of triphenylarsine (2mmol) was slowly added at room temperature working under inert atmosphere The solution was stirred for 12h at 35°C. Then it was concentrated under vacuum, and after the addition of pentane a pale yellow solid was obtained which was recrystallized from $CH_2Cl_2$/pentane Yield 8% (respect to metal vaporized) Melting point 162°C with decomposition Analysis found, C, 40 88%, H, 2 38, As, 11 90; Br, 5 78 $C_8F_{17}Pd(Br)(AsPh_3)_2$ requires, C, 43 38, H, 2 48, As, 12 30, Br, 6 56

$^1H$ NMR (in $CDCl_3$, TMS) 7 70ppm m(i.2); 7.39 ppm m (i.3).

Mass spectrum (E.I. 15 ev, 281 °C) some of the most interesting ions observed are the following AsPh, $AsPh_2$, $AsPh_3$, $C_8F_{17}$, IR (mineral oil, CsI cells) 3060cm$^{-1}$w, 2980-2860vs. 1480 m; 1460s, 1440vs, 1370m; 1240vs, 1200vs, 1140s, 1060s, 1000m, 810w, 770w, 740vs, 690vs, 480s; 470m, 350w, 240vw.

### Reaction of 1 with CO

An acetone solution of 1 (about 1 mmol) was cooled to -10 °C and degassed A rubber balloon of CO was connected The reagent mixture was allowed to warm up to room temperature in about 4h, and stirred for 1 day After the solution was saturated with CO for a few minutes, a change in color from yellow to green was observed The solution was evaporated to give a red-orange oil. Attempts to solidify it were carried out without success IR (neat, CsI cells) $\nu(C{=}O)$ 2130s; $\nu(C-F)$1360m, 1240vs, 1205vs, 1150vs, 1060s cm$^{-1}$ Mass spectrum (E I 20eV, 72 °C) Some of the most interesting ions observed are the following n-$C_8F_{17}$, $C_8F_{17}$PdBr, $C_8F_{17}$PdBr(CO)

Synthesis of n-heptadecafluoroctylzinc bromide. (3) n-$C_8F_{17}$Br (about 0 2 mol) and zinc vapor (about 5 mmol) were cocondensed at -196 °C in approximately 1 hour The reactor was allowed to warm slowly to room temperature The melted matrix was stirred for 30 min. and the excess substrate was pumped off The $R_f$ZnBr species was washed out with distilled acetone. The dark suspension was filtered to give a white solution, which after evaporation under vacuum yielded a white low melting solid or oil, yield 19% $^{19}F$ NMR ($d_6$-Acetone, $CFCl_3$) -80 5 ppm s (i 3), -$CF_3$, -125 6 ppm s (i 2), $CF_3CF_2$-$(CF_2)_n$-, -122 2, -122 0, -121 3, three s (each i 2) and 121 5 ppm s (i.4), $CF_3$-$CF_2$-$(CF_2)_5CF_2$-ZnBr, -116 3 ppm s (i 2), -$CF_2$-ZnBr Mass spectrum (E I. 21 eV , 100 °C) $C_3F_5$, (21%), $C_3F_7$, (37), $C_4F_7$, (25); $C_4F_9$,(24), $C_5F_9$, (14), $C_5F_{11}$, (11), $C_6F_{11}$, (14), $C_7F_{13}$, (12), $C_7F_{15}$, (11); $C_8F_{15}$, (7), $C_8F_{17}$, (16)

Synthesis of (n-$C_8F_{17}$ZnBr$(CH_3CN)_2$) (4)

Addition of excess acetonitrile to 3 resulted in the quantitative production of 4, mp = 93 - 95°C, with color change/some decomposition, IR ($CH_2Cl_2$ solution, KBr 0 5 mm cells) ν(CN) 2310cm$^{-1}$m , 2290m , ν(C-H) 2930 cm$^{-1}$m , ν(C-F) 1360 cm$^{-1}$m , 1210 vs, 1150 vs, 1070m, 990m

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