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# Oxidative Addition to Platinum Atoms

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Oxidative addition of alkyl and aryl halides (RX and ArX) to Co, Ni, and Pd atoms yields the interesting structures RMX and $R_2M$ (plus $MX_2$ by disproportionation of RMX).[1,2] Coordinative unsaturation of these species allows the formation of unusual adducts such as ($\eta^6$-arene)$MR_2$ and $L_2MR_2$.[3-6] The success of these experiments with Co, Ni, and Pd prompted us to investigate Pt.[7]

A higher temperature is required to vaporize Pt; for example, the vapor pressure of Pt is 10 mtorr at 2090 °C. Therefore, synthetic amounts of Pt (0.5–2 g/experiment) are most conveniently vaporized by using electron-beam techniques.[8,9]

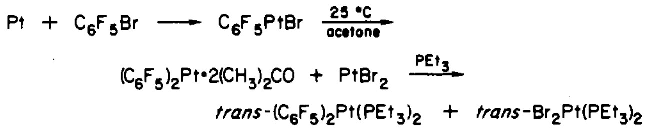
## Results and Discussion

In order to compare the chemistry of Pt atoms with that of Ni and Pd, a series of compounds has been studied: $C_6H_5Br$, $C_6F_5Cl$, $C_6F_5Br$, *n*-BuBr, $CF_3Br$, $CF_3I$, $CF_3COCl$, $C_6H_5CH_2Cl$, $HSiCl_3$, $SiCl_4$, $HSiCl(CH_3)_2$, and $Si_2(CH_3)_6$. Only $C_6F_5Br$, $C_6H_5Br$, $CF_3I$, $CF_3COCl$, and $C_6H_5CH_2Cl$ yielded isolable products.

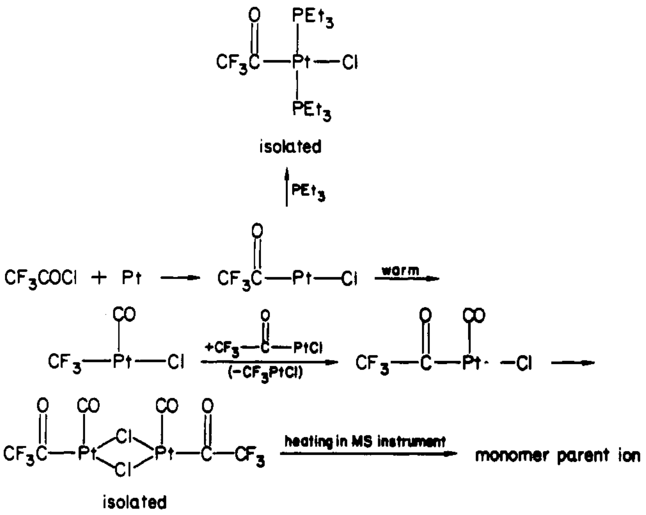
**Bromopentafluorobenzene.** The reactivity of $C_6F_5Br$ along with the ability of $C_6F_5$ to impart stability and solubility to organometallic derivatives has allowed the successful preparation of $C_6F_5NiBr$ (−80 °C stability with a strong tendency to disproportionate to $(C_6F_5)_2Ni)$)[3-5] and $C_6F_5PdBr$ (100 °C stability and no tendency to disproportionate).[5,10] In the case of $C_6F_5PtBr$, disproportionation took place below room temperature in acetone solution (Scheme I). The intermediate, $C_6F_5PtBr$, could be trapped at −78 °C with $PEt_3$ to yield the cis and trans isomers. This means that $C_6F_5PtBr$ was attacked by $PEt_3$ indiscriminately to yield both stable isomers. However, $C_6F_5PtBr{\cdot}2(CH_3)_2CO$ is quite labile and readily disproportionates to $(C_6F_5)_2Pt((CH_3)_2CO)_2$.[11] The lability of the acetone complex probably allows a trans geometry to be adopted, which is subsequently obtained when acetone is replaced by $PEt_3$.

**Bromobenzene.** Bromobenzene plus Pt yielded a very unstable intermediate (probably $C_6H_5PtBr$) that quickly disporportionated, and small amounts of $(C_6H_5)_2Pt(PEt_3)_2$ were obtained by addition of $PEt_3$ at low temperature. Similar results have been observed with $C_6H_5PdBr$, which is only stable to approximately −130 °C.[5,10]

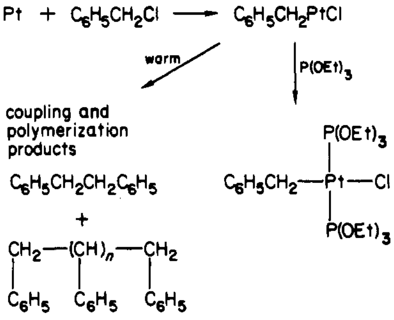
Scheme I



Scheme II



Scheme III



**Trifluoromethyl Iodide.** Codeposition of $CF_3Cl$, $CF_3Br$, or $CF_3I$ with Pt atoms at −196 °C followed by warming and solvent extraction of residues yielded no organometallic products. Only Pt metal powder remained, with little $PtX_2$. This interesting unreactivity of Pt atoms is different from that of the other metals and suggests that a prior complex $(CF_3I)_x$- - -Pt is more favorable for Pt than for Ni or Pd, which serves to inhibit the oxidative-addition process. On being warmed, the complex apparently releases $CF_3I$ at a temperature where it vaporizes into the vacuum chamber. This must be a temperature colder than that needed to favor the oxidative-addition reaction

$$\mathrm{Pt} + \mathrm{CF_3I} \xrightarrow{-196\ ^\circ\mathrm{C}} \mathrm{CF_3I{-}{-}{-}Pt} \xrightarrow{\text{warm}} \mathrm{CF_3I(g)} + \mathrm{Pt}_n$$

In order to lower the matrix volatility, $CF_3I$ was deposited mixed with an excess of pentane. Upon warm-up and vacuum removal of $CF_3I$/pentane, after washing of the residue with toluene at 25 °C, a light yellow solution was obtained that turned brown upon vacuum removal of toluene. Addition of $PEt_3$ yielded $(PEt_3)_2PtI_2$. A subsequent experiment where the toluene wash was added immediately to a $PEt_3$/toluene solution did yield the expected product $(PEt_3)_2Pt(CF_3)I$. These results indicate that $CF_3PtI$ is formed upon warm-up of the $CF_3I$/pentane/Pt matrix and is stable for only short periods of time in toluene at 25 °C. This is similar to our earlier findings with Pd except again we observed *less* stability for the Pt analogue under similar conditions.

**Trifluoroacetyl Chloride.** Codeposition of $CF_3COCl$ with Pt followed by vacuum removal of excess $CF_3COCl$ and washing of the residue at 25 °C with acetone yielded a brown solution. Vacuum removal of acetone yielded a brown solid that exhibited two carbonyl stretching frequencies at 2100 and 1685 cm$^{-1}$, the former indicative of a terminal Pt–CO and the latter of $CF_3$–CO. After prolonged heating of the solid at 120 °C under vacuum, the two bands did not change. UV irradiation also caused no

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**Table I.** Physical and Spectral Properties of Pertinent Compounds Prepared by Pt Atom Reactions

| substrate (amt used in expt) | ligand (amt used in expt) | product | % yield | mp, °C | color | NMR ($CDCl_3/Me_4Si$), δ | IR, $cm^{-1}$ | MS (rel intens)[a] |
|---|---|---|---|---|---|---|---|---|
| $C_6F_5Br$ (160 g) | $PEt_3$ (2 mL) | $(C_6F_5)_2(PEt_3)_2Pt$ | 66 | 227–229 (228–229)[16] | white | | | |
| | | $(PEt_3)_2PtBr_2$ | 23 | 130–134 (134–135)[17] | white | | | |
| $C_6H_5Br$ (120 g) | $PEt_3$ (2 mL) | $(C_6H_5)_2(PEt_3)_2Pt$ | ~3 | 180–181 (176–180)[18] | white | | | |
| $CF_3I$ (18.0 g) | | $(PEt_3)_2PtI_2$ [b] | 12 | 133–135 (136)[19] | | | | CI: M − I (2.6), M − I − 2Et (23.6), Pt (100), $PEt_3$ (41.0) |
| | $PEt_3$ (1 mL) | $(PEt_3)_2(CF_3)PtI$ | 26 | 115–117 (115–118)[20] | white | | | EI (70 eV): M (0.2), M − $CF_3$ (1.5), M − I (5.4), M − $CF_3I$ (9.0), M − $CF_3$ − $C_2H_5$ (2.5), M − $CF_3$ − $PEt_2$ (17.5), $Pt(PEt_3)_2$ (2.2), $Pt(PEt_3)PEt_2$ (5.1), Pt (7.6), $PEt_3$ (100), I (5.5), $CF_3$ (4.4) |
| $CF_3COCl$ | | $(CF_3CO)Pt(CO)Cl$ | 27 | 93–96 | dark brown | | 2105 (s), 1695 (s), 1492 (m), 1254 (m), 1195 (m), 1147 (s), 1108 (w), 1072 (w), 1030 (w), 899 (s), 605 (w), 568 (w), 465 (w) | EI (30 eV): M (1.4), M − $CF_3$ (14.8), M − $CF_3CO$ (30.7), Pt (22.9), $CF_3CO$ (27.4), $CF_3$ (100) |
| | $PEt_3$ (1.0 mL) | $(CF_3CO)(PEt_3)_2PtCl$ | 51 | oil | orange | 1.23 (q, 3 H, $J_{H-H}$ = 9 Hz), 1.89 (br quintet, 2 H, $J_{H-H}$ = 9 Hz) | 2975 (m), 2940 (m), 2910 (m), 2885 (w, sh), 1770 (s), 1469 (m), 1419 (m), 1375 (w), 1275 (w), 1175 (s, br), 1106 (w), 1047 (m), 819 (w, sh), 791 (s), 714 (s), 607 (m), 450 (w), 425 (w), 418 (w) | EI (50 eV): M − CO (7.3), M − $CF_3$ (100), M − $CF_3CO$ (4.0), $Pt(PEt_3)_2$ (12.9), $Pt(PEt_3)(PEt_2)$ (14.4), $Pt(PEt_3)(PEt)$ (4.2), $PtP_2Et_3$ (4.3), $PtPEt_3$ (8.6)[c] |
| $C_6H_5CH_2Cl$ (88 g) | | $C_6H_5CH_2CH_2C_6H_5$ | 36 | 71 (71)[21] | white | | | |
| | $P(OEt)_3$ (2 mL) | $(C_6H_5CH_2)[P(OEt)_3]_2PtCl$ | 45 | oil | brown | 1.21 (t, 18 H, $J_{H-H}$ = 7 Hz), 2.08 (m, 2 H), 4.02 (q, 12 H, $J_{H-H}$ = 7 Hz), 7.04 (s, 5 H) | 3038 (w), 3005 (w), 2950 (m), 2915 (w), 2895 (w), 2860 (w), 1588 (m), 1545 (w), 1483 (w), 1440 (m), 1395 (s), 1250 (m), 1075 (s, br), 930 (m), 763 (m), 720 (m), 690 (w, sh), 580 (m), 460 (w), 370 (w) | EI (70 eV): M (2), M − Cl (21.0), M − $C_6H_5$ (4.0), M − $C_6H_5CH_2$ (42.0), $Pt(P(OEt)_3)_2$ (8.5), M − $C_7H_8$ − $C_2H_5$ (9.3), M − $C_7H_8$ − $OC_2H_5$ (10.7), $Pt(P(OC_2H_5)_2)PO(OC_2H_5)_2$ (22.4), $Pt(P(OC_2H_5)_3)P(OC_2H_5)_2$ (11.5), $Pt(P(OC_2H_5)_3P(OH)_2)$ (12.7), $Pt(P(OC_2H_5)_3PO)$ (9.7), $Pt(P(OC_2H_5)_3)$ (13.5), $H_2Pt(P(OC_2H_5)_3$ (100), $H_2PtP(OEt)_2$ (12.5), $H_2PtPOEt$ (81.9), $H_2Pt-OH$ (33.6) |

[a] Monoisotopic *m/z* values based on $^{35}Cl$ (75.8%) and $^{194}Pt$ (32.9%). [b] $PEt_3$ was added after decomposition of $CF_3$-Pt-I. [c] The characteristic isotopic distribution for Pt/Cl was exactly as theory predicts (see footnote *a*).

change. These results imply that the two CO species are contained in the same molecule.

Electron-impact MS showed $CF_3CO(CO)PtCl$ as a molecular ion. However, the probable intermediate $CF_3COPtCl$ could be trapped by $PEt_3$ addition at 25 °C, suggesting the sequence shown in Scheme II.

**Benzyl Chloride.** The benzyl ligand is one of the most interesting in metal atom chemistry. With $Pd/C_6H_5CH_2Cl$ unique $\eta^3$-benzyl systems, without other stabilizing ligands, have been isolated.[6] However, $Ni/C_6H_5CH_2Cl$ yielded only unstable organometallics that gave bibenzyl, polybenzyl, and $NiCl_2$ as the final products,[6,12] although in the presence of allyl chloride the $Ni/C_6H_5CH_2Cl$ reaction did yield a $\eta^3$-benzyl derivative of Ni.[13]

Platinum atoms with $C_6H_5CH_2Cl$ yielded unstable organometallic intermediates that, similar to those of Ni, gave bibenzyl, polybenzyl, and $PtCl_2$ as the major products. The unstable $C_6H_5CH_2PtCl$ intermediate (probably $\eta^3$-benzyl) could be trapped at 25 °C by $P(OEt)_3$[14] addition to yield $C_6H_5CH_2PtCl[P(OEt)_3]_2$, suggesting the sequence shown in Scheme III.

## Conclusions

In general Pt atoms react less efficiently than Ni or Pd atoms in organohalide oxidative-addition reactions. Also, the stabilities of the resultant RMX species are in the order $Pd > Pt \sim Ni$. In the case of $CF_3COCl$ a very stable $CF_3COPt(CO)Cl$ derivative was obtained.

## Experimental Section

**Reagents and Solvents.** Manipulations of solids and some solutions were carried out either in a Vacuum Atmospheres Dri Lab Model H-493 Dri Train employing prepurified nitrogen (99.998%) or in airless glassware employing prepurified nitrogen passed over Chemical Dynamics Catalyst R3-11 deoxygenation catalyst at 110 °C just prior to use. Ligands were degassed by freeze–thaw procedures. Solvents were continuously refluxed over sodium/benzophenone (toluene, pentane) under nitrogen or refluxed over calcium oxide (acetone), and fresh aliquots were used. Bromobenzene, benzyl chloride, and hexamethyldisilane were purchased from Aldrich, trifluoromethyl halides and trifluoroacetyl chloride were from PCR, trichlorosilane, tetrachlorosilane, and dimethylchlorosilane were from Petrarch Systems, and bromopentafluorobenzene was purchased from Fairfield; these reagents were used as received. Triethylphosphine and triethyl phosphite were purchased from Organomet, Inc., and platinum was obtained on loan from Johnson-Matthey, Inc.

**Physical Measurements.** Melting points were taken in sealed capillaries and are uncorrected. $^1H$ NMR spectra were obtained on a Varian T-60 instrument using $Me_4Si$ as standard. IR spectra were recorded with a Perkin-Elmer 1330 instrument using KBr pellets or Nujol mulls. Low-resolution MS spectra were obtained with a Finnigan 4021 quadrupole GC/MS and INCOS data system.

**General Metal Atom Procedure.** A general description of metal atom reactors has been reported before.[15] Detailed information concerning the Planer electron-beam reactor has been described by Green.[8] Our electron-beam reactor was purchased from Planer Instruments, Ltd. (Type VSF/500). A 50-L stainless-steel double-jacket bell jar was used as the reaction vessel, which was evacuated by a 160-mm oil diffusion pump (700 L/s rating), backed by a two-stage rotary pump. The diffusion pump was protected from chemical vapors by a −196 °C stainless-steel trap placed between the reaction vessel and the diffusion pump.

The metal sample ($\sim$7 g) was placed on the hearth, the system pumped down to $1 \times 10^{-4}$ torr, and the sample heated until meltdown and thereby degassed (the liquid nitrogen trap was filled, but the vessel was not cooled during the degassing step). The resultant ingot could be used for several reactions without further degassing.

To carry out a reaction, the reaction vessel was cooled and the degassed organohalide vapors passed through a needle value leading to the inlet "gas-ring". Heat could be applied to the gas-ring if necessary. The filament current was set at 38 A and the accelerating potential adjusted (3.5–5.5 kV) to yield a 0.4–0.5-mA beam current. During evaporation of Pt the rate of substrate inlet was controlled to maintain a system pressure of not higher than $(1–2.5) \times 10^{-4}$ torr. During deposition about 0.5 g of Pt ($2.56 \times 10^{-3}$ mol) was vaporized while about 80 mL of substrate was inlet. After the codeposition process, the Styrofoam-brand vessel insulator was lifted off and the reaction vessel allowed to slowly warm. During this time excess substrate was removed by cryogenic pumping. The vessel was vented to nitrogen, the residue was washed with three 50-mL portions of solvent (toluene or acetone), and the washings were collected from the gutter collection ring through a tube leading to airless glassware (which could contain trapping reagents if necessary). Products were isolated by using normal airless glassware techniques (filtering, solvent reduction, solvent precipitation, crystallization). Table I summarizes the results.

**Acknowledgment.** The support of the National Science Foundation for program support and purchase of the electron-beam reactor is acknowledged with gratitude.

**Registry No.** $(C_6F_5)_2(PEt_3)_2Pt$, 14840-51-8; *trans*-$(PEt_3)_2PtBr_2$, 13985-90-5; *cis*-$(PEt_3)_2PtBr_2$, 15636-78-9; $(C_6H_5)_2(PEt_3)_2Pt$, 16787-10-3; $(PEt_3)_2PtI_2$, 15692-97-4; $(PEt_3)_2(CF_3)PtI$, 95977-52-9; $(CF_3CO)Pt(CO)Cl$, 95912-50-8; $(CF_3CO)(PEt_3)_2PtCl$, 95912-51-9; $(C_6H_5CH_2)[P(OEt)_3]_2PtCl$, 95912-52-0; $C_6F_5PtBr$, 95912-47-3; $PtBr_2$, 13455-12-4; $C_6F_5PtBr((CH_3)_2CO)_2$, 95912-53-1; $(C_6F_5)_2Pt((CH_3)_2CO)_2$, 95912-54-2; $PtCl_2$, 10025-65-7; $PtI_2$, 7790-39-8; $CF_3PtI$, 95912-48-4; $CF_3CO(CO)PtCl$ dimer, 95912-55-3; $NiCl_2$, 95912-49-5; $C_6F_5Br$, 344-04-7; $C_6H_5Br$, 108-86-1; $CF_3I$, 2314-97-8; $CF_3COCl$, 354-32-5; $C_6H_5CH_2Cl$, 100-44-7; $PEt_3$, 554-70-1; $P(OEt)_3$, 122-5-1; $CF_3Cl$, 75-72-9; $CF_3Br$, 75-63-8; $C_6H_5Cl$, 344-07-0; *n*-BuBr, 109-65-9; $HSiCl_3$, 10025-78-2; $SiCl_4$, 10026-04-7; $HSiCl(CH_3)_2$, 1066-35-9; $Si_2(CH_3)_6$, 1450-14-2; $C_6H_5CH_2CH_2C_6H_5$, 103-29-7; Pt, 7440-06-4; Ni, 7440-02-0; polybenzyl, 31830-66-7.

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