A in quantities detectable by ^{31}P spectroscopy or TLC implies that no racemization of **8** occurs under these conditions.

Conversion of one of the purified diastereomers of *cis*-$Cl_2Pt(\mathbf{8})_2$ (^{31}P 74.1 ppm, $^1J_{PPt}$ = 5190 Hz) to the corresponding *cis*-diiodo complex in the usual way[48] showed that according to the ^{31}P NMR spectrum, the latter complex was the meso diastereomer (73.6 ppm, $^1J_{PPt}$ = 4989 Hz). Thus the *cis*-dichloro precursor must also be a meso diastereomer.

Acknowledgment. J.G.V. is grateful to the National Cancer Institute of the National Institutes of Health and the National Science Foundation for grants supporting this research.

Registry No. (–)-**2**, 66849-33-0; (+)-**2**, 66849-34-1; (–)-**3**, 72282-84-9; (+)-**3**, 72282-85-0; (+)-**7**, 75045-93-1; *cis*-Cl_2Pt[(*S*)-(+)-**7**]$_2$, 72316-66-6; *cis*-I_2Pt[(*S*)-(+)-**7**]$_2$, 72316-69-9; *meso-cis*-$I_2Pt(\mathbf{7})_2$, 75082-09-6; *dl-cis*-$I_2Pt(\mathbf{7})_2$, 75082-10-9; *meso-cis*-$Cl_2Pt(\mathbf{7})_2$, 75082-11-0; *cis*-$I_2Pt(\mathbf{8})$[(*S*)-(+)-**7**] (isomer 1), 72316-68-8; *cis*-$I_2Pt(\mathbf{8})$[(*S*)-(+)-**7**] (isomer 2), 72376-60-4; *cis*-$Cl_2Pt(\mathbf{7})(\mathbf{8})$ (isomer 1), 75045-95-3; *cis*-$Cl_2Pt(\mathbf{7})(\mathbf{8})$ (isomer 2), 75082-12-1; *cis*-$I_2Pt(\mathbf{9})$[(*S*)-(+)-**7**] (isomer 1), 75045-96-4; *cis*-$I_2Pt(\mathbf{9})$[(*S*)-(+)-**7**] (isomer 2), 75109-25-0; *dl-cis*-$I_2Pt(\mathbf{9})_2$, 72316-67-7; *meso-cis*-$I_2Pt(\mathbf{8})_2$, 72346-74-8; *l-cis*-$I_2Pt(\mathbf{8})_2$, 75109-26-1; *meso-cis*-$Cl_2Pt(\mathbf{8})_2$, 74858-59-6; *dl-cis*-$Cl_2Pt(\mathbf{8})_2$, 75082-13-2; *trans*-$Cl_2Pt(\mathbf{8})_2$, 75082-14-3; *trans*-$Cl_2Pt(\mathbf{8})$[(+)-PhCH(CH$_3$)NH$_2$], 75045-97-5; *trans*-$Cl_2Pt(\mathbf{8})$[(–)-PhCH$_2$CH(CH$_3$)NH$_2$], 75045-98-6; *trans*-$I_2Pt(\mathbf{8})$[(–)-PhCH$_2$CH(CH$_3$)NH$_2$], 75045-99-7; *cis*-$Cl_2Pt(\mathbf{8})$(MeOPOCHMeCH$_2$CH$_2$O) (isomer 1), 75046-00-3; *cis*-$Cl_2Pt(\mathbf{8})$(MeOPOCHMeCH$_2$CH$_2$B) (isomer 2), 75082-15-4; *cis*-$Cl_2Pt(\mathbf{8})$[(+)-PhMeCHNHP(OMe)$_2$], 75059-71-1; *cis*-$I_2Pt(\mathbf{8})$(MeOPOCHMeCH$_2$CH$_2$O) (isomer 1), 75046-01-4; *cis*-$I_2Pt(\mathbf{8})$(MeOPCHMeCH$_2$CH$_2$O) (isomer 2), 75082-16-5; *meso-cis*-$I_2Pt(\mathbf{9})_2$, 75046-02-5; *meso-cis*-$Cl_2Pt(\mathbf{9})_2$, 74858-58-5; *dl-cis*-$I_2Pt(\mathbf{9})_2$, 75109-27-2; *dl-cis*-$Cl_2Pt(\mathbf{9})_2$, 74892-36-7; $Cl_2Pt(CH_2{=}CH_2)$[(+)-PhCH(CH$_3$)N(CH$_3$)$_2$], 75046-03-6; $Cl_2Pt(CH_2{=}CH_2)$[(+)-PhCH(CH$_3$)NH$_2$], 53274-62-7; $Cl_2Pt(CH_2{=}CH_2)$[(–)-PhCH$_2$CH(CH$_3$)NH$_2$], 75082-17-6; $Cl_2Pt(CH_2{=}CH_2)$[(+)-PhCH$_2$CH(CH$_3$)NH(CH$_3$)], 75082-18-7; *cis*-Cl_2Pt(MeOPOCHMeCH$_2$CH$_2$O)$_2$, 75046-04-7; *trans*-Cl_2Pt([(–)-menO]$_2$PPh)$_2$, 75046-07-0; *trans*-Cl_2Pt([(–)-menO]$_3$P)$_2$, 75046-08-1; *cis*-Cl_2Pt[(+)-PhMeCHNHP(OMe)$_2$]$_2$, 75046-05-8; *cis*-I_2Pt(MeOPOCHMeCH$_2$CH$_2$O)$_2$, 75046-06-9; di-(–)-menthyl phenylphosphonite, 58359-50-5; methyl mandelate, 21210-43-5; 2-chloro-1,3,2-dioxaphosphorinane, 6362-89-6; $Cl_2Pt(C_6H_5CN)_2$, 15617-19-3; $(MeO)_2PCl$, 3743-07-5; (R)-(+)-PhMeCHNH$_2$, 3886-69-9; (+)-PhMeCHNHP(OMe)$_2$, 75045-94-2.

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Metal Atom Reactions with Fluorocarbons. 9. Preparation and Spectral Analyses of (Perfluoroalkyl)- and (Perfluoroaryl)palladium Halides

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Received January 14, 1980

Oxidative insertion of palladium atoms into pefluoroalkyl and -aryl halide C–X bonds has yielded stable C_6F_5PdBr and CF_3PdI. These formally two-coordinate nonligand-stabilized organometallics have been isolated and characterized. Their tendency to form bridging telomers in solution in order to fill open coordination sites and their unusual bonding and thermal stabilities are discussed. Their chemistry with a host of added ligands, including dienes, sulfides, amines, and phosphines, has yielded a number of new Ar_f and $R_fPdX(L)_2$ complexes. Spectra of these complexes are reported and compared. For the CF_3PdI and $CF_3PdI(L)_2$ systems a $d_\pi \rightarrow \sigma^*$ back-bonding scheme to explain the robust character of the C–Pd bond is *not* supported by the spectroscopic data. An ionic–covalent resonance interaction appears more appropriate and is encouraged by the presence of PEt_3 and C_5H_5N ligands.

Introduction

Formal two-coordinate organopalladium complexes RPdX, ArPdX, and RCOPdX have been proposed as intermediates in a variety of important catalysis schemes.[2-7] Generally, it had been assumed that coordinatively unsaturated species such as these were too short-lived to detect or isolate and that it would be necessary to trap them with stabilizing ligands to yield $RPdX(L)_2$. However, there are now several examples in palladium chemistry where RPdX or R_2Pd species possessing very unusual R groups (or Ar groups) have been isolated.[8] Pracejus and co-workers[9] have prepared $Pd(CH_2CN)_2$ which is stable in air and decomposes thermally at 220 °C.

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(2) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518, 5526, 5531, 5535, 5538, 5546 (1968).
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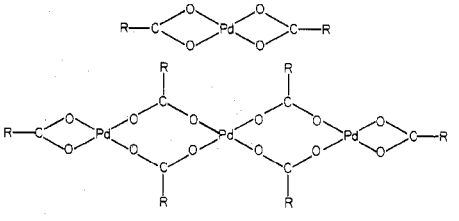
(8) We are only referring to σ-bonded C–Pd species here. Of course it should be noted that palladium dihalides (PdX_2) are well-known two-coordinate palladium compounds that fill open coordination sites through extensive halide bridging and are actually best described as polymers in the solid state. Also, the work of Wilkinson and co-workers on the preparation of carboxylates of palladium [$Pd(OCOR)_2$ where R = CH_3, CH_3CH_2, C_6H_5, CF_3, and C_6F_5] are examples of formally two-coordinate Pd–O bonded species. Extensive bridging also occurs in these cases:



T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

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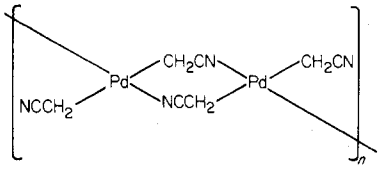
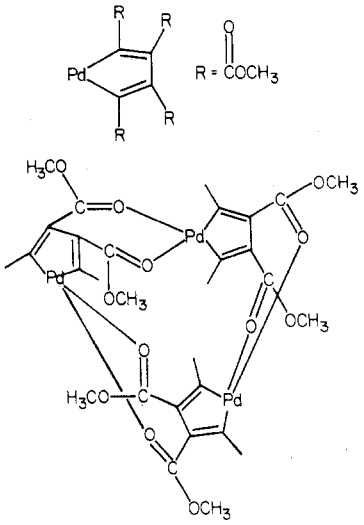
This compound is also stable to light. A coordination polymer



was proposed as a logical structure. Related studies by Moseley and Maitlis[10] showed that metallacyclopentadiene complexes of Pd are stable, and in this case open sites are apparently filled by trimerization through oxygen bridging:

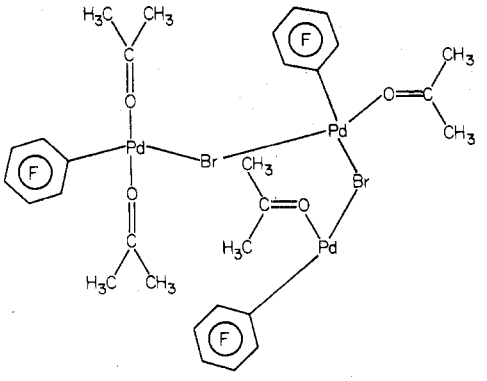


In 1973–1974 we reported that by employing Pd atom–RX and –RCOX reactions we were able to generate RPdX and RCOPdX species at low temperature.[11,12] By investigating a series of organohalides we were able to clarify stability trends for these species[12] as well as derive mechanistic information regarding their formation.[13] Normal perhydroalkyl and -aryl derivatives were found to be very unstable. However, perfluoro derivatives[12,14] and benzyl derivatives[15] exhibited surprisingly good stability, and the benzyl derivatives (e.g., $C_6H_5CH_2PdCl$) were subsequently isolated and characterized, and bonding and chemical properties were elucidated.[16] However, for some time the high reactivity and lability of the perfluoro derivatives have caused their detailed characterizations to elude us. We now report these details for C_6F_5PdBr and CF_3PdI and show how they can be used as intermediates for the preparation of a series of new $C_6F_5PdBr(L)_2$ and $CF_3PdI(L)_2$ compounds. We also briefly discuss the spectra and bonding aspects for these materials.

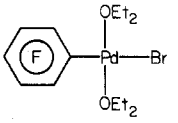
Results and Discussion

C_6F_5PdBr. The isolation of this material, prepared by the codeposition of Pd vapor and C_6F_5Br, was quite difficult. It took some time to learn that solvent purity was critically important and that a series of decreasingly polar solvents worked best. Thus, acetone solutions of C_6F_5PdBr were readily prepared in a reproducible fashion. After vacuum removal of the acetone, benzene (or toluene) was employed to dissolve the oily C_6F_5PdBr, and the complex was precipitated by slow addition of carefully purified pentane (or hexane) to yield a light orange-brown powder. These manipulations had to be done fairly rapidly since C_6F_5PdBr decomposes to Pd, $PdBr_2$, and $C_6F_5C_6F_5$ in arene solvents (over several hours).[12]

It is assumed that the open coordination sites on C_6F_5PdBr are filled (or nearly so) in the solid state by bridging through Br and/or the π bonds of C_6F_5. We were unable to clarify this situation through crystallographic studies due to the low quality of crystals obtained, and so attempts were made to gain some understanding through solution studies. Polar aprotic solvents serve to stabilize C_6F_5PdBr with acetone being very effective in this regard. In acetone, molecular weight determinations would suggest a trimeric structure, probably with acetone serving as a weakly bonding ligand, perhaps as



In Et_2O however, a monomeric structure



is suggested by molecular weight studies.[12] Upon vacuum removal of acetone, diethyl ether, or toluene, complete removal of solvent is possible. As the last molecules of solvent are removed, Br and/or C_6F_5 bridges must form. However, almost any ligand or polar, basic solvent is capable of cleaving these bridges, whereas acetone, a polar nonbasic solvent, only partially does so, and a trimer results. It seems quite likely that by proper choice of solvents, a variety of bridged Pd cluster species could be prepared.

A variety of ligands react rapidly with C_6F_5PdBr to yield stable $C_6F_5PdBr(L)_2$ complexes. Table I summarizes the compounds prepared and their characteristic properties. Note that a wide range of ligands, including amines, phosphines, sulfides, and dienes, can be added, including mono- and bidentate ligands yielding trans and cis complexes, respectively. *Consequently, this synthetic procedure is a useful preparative method for $C_6F_5PdBr(L)_2$ complexes that are not available by classical synthetic means.*

Spectra and Bonding. Since this study presented a rare opportunity to examine spectroscopically an organometallic complex (C_6F_5PdBr) in the absence of ligands as well as bearing a variety of quite different ligands, we anticipated, through spectroscopy, learning something about the nature of this unusual Pd–C bond. However, to our disappointment, the IR and ^{19}F NMR data were devoid of clear trends. Random patterns resulted when plots were made of ^{19}F chemical shifts (ortho F or para/meta) vs. π-acid strength of the ligands or σ-donor strength of the ligands.

The ortho ^{19}F resonances range from 115.3 ppm upfield from $CFCl_3$ in the NH_3 complex to 122.3 ppm in the pyridine complex. It is interesting that considering the range of complexing atoms, N, P, As, S, and O (acetone), the extremes are represented by two nitrogen ligands. On the assumption that

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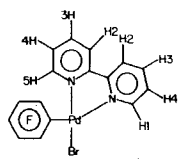
Table I. Properties and Spectra for C_6F_5PdBr, $C_6F_5PdBr(L)_2$, CF_3PdI, and $CF_3PdI(L)_2$

compd	color	mp, °C	%C found (calcd)	%H found (calcd)	%F found (calcd)	%Br found (calcd)	%S found (calcd)	%N found (calcd)	mol wt (osm) found	mol wt (osm) calcd	^{1}H NMR[1] (δ)	^{19}F NMR upfield from $CFCl_3$,[i] ppm	characteristic IR for C_6F_5, CF_3,[k,n] cm^{-1}
$(C_6F_5PdBr)_n$	orange-brown	105 dec	20.37 (20.39)	0.40 (0.0)	26.37 (26.88)	22.37 (22.63)			400 (ether) 1050 (acetone)	353 353		119.2 (ortho), 161.5 (para), 165.3 (meta)	1505, 1060, 955
$C_6F_5PdBr(SPh_2)_2$	light yellow	166–181 dec									7.62[a] (m, 2 H) (ortho), 7.42 (m, 3 H) (meta and para)	121.4 (ortho), 160.9 (para), 163.9 (meta)	1510, 1065, 960
$C_6F_5PdBr(SEt_2)_2$	yellow	50–51	31.42 (31.50)	3.51 (3.78)	17.61 (17.80)		12.08 (12.01)		483 (benzene)	533	2.91[b] (q, 2 H), 1.40 (t, 3 H)	118.5 (ortho), 159.8 (para), 162.4 (meta)	1502, 1059, 954
$C_6F_5PdBr(SMe_2)_2$	yellow	115–120									2.38[c] (s)	121.4 (ortho), 159.6 (para), 162.0 (meta)	1505, 1055, 960, 950
$C_6F_5PdBr(NHEt_2)_2$	yellow	133–134	33.78 (33.65)	4.30 (4.43)				5.64 (5.60)	460 (benzene)	499	3.8 (br, 1 H), 2.67 (m, 2 H), 1.54 (t, 3 H)[d]	119.2 (ortho), 162.7 (para), 164.7 (meta)	1505, 1070, 1060, 958
$C_6F_5PdBr(NH_2Et)_2$	light yellow	175–180									3.58, 3.34, 3.10, 2.75, 2.54, 2.28, 1.52, 1.30 (all m)[e]		1504, 1059, 956
$C_6F_5PdBr(NMe_3)_2$	light yellow	64–70 dec									1.80 (s), 1.74 (s)		1500, 1055, 950
$C_6F_5PdBr(NH_3)_2$	white	222–223									3.18 (s)[f]	115.3 (ortho), 163.3 (para), 165.3 (meta)	1504, 1064, 960, 952
$C_6F_5PdBr(C_5H_5N)_2$	yellow	126–127	36.69 (37.56)	2.06 (1.97)				5.42 (5.47)	493 (benzene)	511	8.79 (d, 2 H) (ortho),[g] 7.69 (m, 1 H) (para), 7.39 (t, 2 H) (meta)	124.3 (ortho), 162.0 (para), 164.3 (meta)	1505, 1075, 1060, 958
$C_6F_5PdBr(PEt_3)_2$[12]	white	124–125										116.1 (ortho), 163.3 (para), 164.4 (meta)	1505, 1058, 955
$C_6F_5PdBr(bpy)$[p]	light yellow	285–299	37.63 (37.72)	1.67 (1.58)				5.46 (5.50)			9.40 (d, 1 H), 8.58 (d, 2 H), 8.32 (t, 2 H), 7.72 (m, 2 H), 5.52 (s, 1 H)[h]	118.7 (ortho), 163.2 (para), 165.9 (meta)	1510, 1065, 960
$C_6F_5PdBr(AsPh_3)_2$	yellow-brown	235 dec										119.2 (ortho), 160.1 (para), 162.6 (meta)	1505, 1062, 958
$C_6F_5PdBr(COD)$[q]	yellow-white	75 dec									6.20 (d, 8 H), 5.82 (s, 4 H)		1508, 1062, 958
$CF_3PdI\cdot(tol)_x$	amber	83–90 dec	17.21 8.23 (3.97[j])	2.84 2.84 (0.0)								23.9 (s)	1100, 1075, 1055
$CF_3PdI(C_5H_5N)_2$	light yellow	185 dec	29.00 (28.66)	2.14 (2.18)				6.05 (6.08)			8.90 (d, 2 H) (ortho), 7.93 (m, 1 H) (para), 7.52 (m, 2 H) (meta)	30.1 (s)	1095, 1030, 1000
$CF_3PdI(PEt_3)_2$[12]	white											10.1 (t, J_{F-P} = 32 Hz)	1075, 1035, 1010,[o] 994, 982, 1083, 1042, 1017

[a] Upon complexation the shift is from δ 7.26 (free SPh_2) to 7.62 and 7.42. [b] Upon complexation the shift is from δ 2.47 (free SEt_2) to 2.91 and from 1.23 to 1.40. [c] Upon complexation the shift is from δ 2.06 (free SMe_2) to 2.38. [d] In acetone-d_6; δ 3.8 (N–H), 2.67 (CH_2), 1.54 (CH_3); D_2O addition causes shift from δ 3.80 to 3.86. Also, the shifts upon complexation are from δ 1.98 to 3.80, 2.58 to 2.67, and 1.02 to 1.54. [e] Unexplained complex spectrum. [f] In Me_2SO-d_6; upon addition of D_2O, the resonance shifted to δ 3.92. [g] Free ligand to complexed: δ 8.54 to 8.79; 7.60 to 7.69; 7.25 to 7.30 (ortho protons affected most). [h] In acetone-d_6 the following assignments are reasonable for



δ 9.40 (H-1), 8.58 (H-2), 8.32 (H-3), 7.72 (H-4), 5.52 (H-5). [i] All ^{19}F spectra taken in acetone except NH_3 complex taken in $CDCl_3$. [j] Solvent incorporation complicated these analyses. See text for discussion. Repeated recrystallization from pentane yielded the sample with less solvent (toluene) incorporation. (The expected analysis for a $CF_3PdI\cdot(tol)$ complex is 24.4% C and 2.05% H.) [k] Complete tabulations of IR bands are listed in the Experimental Section as each compound is described. [l] All pentafluorophenyl ^{1}H spectra in acetone-d_6 except NMe_3 complex in C_6D_6 and NH_3 complex in Me_2SO-d_6. [m] In $CDCl_3$. [n] M. D. Rausch and F. E. Tibbetts, *J. Organomet. Chem.*, 21, 487 (1970); *Inorg. Chem.*, 8, 1355 (1969); R. D. Chambers and T. Chivers, *Organomet. Chem. Rev.*, 1, 279 (1966). [o] This work. [p] bpy = 2,2'-bipyridine. [q] COD = 1,5-cyclooctadiene.

Table II. ^{19}F NMR Shifts for $C_6F_5PdBr(L)_2$ Complexes[a,b]

complex	ortho F	para F	meta F	meta − para
Ph_fPdBr	119.2	161.5	165.3	3.8
$Ph_fPdBr(SPh_2)_2$	121.4	160.9	163.9	3.0
$Ph_fPdBr(SEt_2)_2$	118.5	159.8	162.4	2.6
$Ph_fPdBr(AsPh_3)_2$	119.2	160.1	162.6	2.5
$Ph_fPdBr(SMe_2)_2$	121.4	159.6	162.0	2.4
$Ph_fPdBr(py)_2$	124.3	162.0	164.3	2.3
$Ph_fPdBr(NHEt_2)_2$	119.2	162.7	164.7	2.0
$Ph_fPdBr(NH_3)_2$	115.3	163.3	165.3	2.0
$Ph_fPdBr(PEt_3)_2$	116.1	163.3	164.9	1.6
$Ph_fPdBr(bpy)$	118.7	163.2	165.9	2.7

[a] Values are in ppm upfield from $CFCl_3$. [b] All spectra were obtained in acetone solvent except for the NH_3 complex which was in $CDCl_3$.

C_6F_5PdBr is acetone solvated (NMR solvent used), these ligands can be ranked according to their influence on the downfield ^{19}F ortho shift as $NH_3 < PEt_3 < SEt_2 <$ bpy $< AsPh_3 \approx NHEt_2 \approx$ acetone $< SMe_2 \approx SPh_2 <$ py. It should be noted, however, that the spectrum of the NH_3 complex was obtained in $CDCl_3$ while the others were obtained in acetone and that the only cis complex in this list is the bpy complex, which is not directly comparable.

Some discussion of related prior literature may be relevant. Rosevear, Stone, and co-workers[17] examined the ^{19}F spectra of a series of *trans*-$[C_6F_5PtX(PEt_3)_2]$ complexes, where X = CH_3, CN, NO_2, I, NCS, Br, Cl and ONO_2. The ortho ^{19}F values ranged from 116.4 to 117.9 ppm, a rather small variation (note that they were examining the effect of trans X on C_6F_5 with L = PEt_3 constant). Their meta–para differences correlated roughly with the π-bonding ability of X; that is, the difference became greater as the π-bonding ability increased, which would be predicted if electron density were being drained away from C_6F_5 by resonance effects as X π bonds more strongly. Furthermore, variations in the Pt–F coupling constants were found to correlate with the Pt–C bond order as affected by the trans ligand X. Additional studies of trans effects were carried out by Chatt and co-workers[18a] by employing a series of *cis*- and *trans*-PtX_2L_2 complexes, where X = Br and Cl and L = SEt_2, py, NH_3, $AsEt_3$, As(*n*-Pr_3), PPr_3, and PEt_3. The strength of the Pt–X bond as indicated by ν_{Pt-X} in the far-IR region was found to depend upon ligands trans to X (i.e., *cis*-PtX_2L_2). This effect was not observed for the *trans*-PtX_2L_2 complexes. Additional work by Chatt and Westland[18b] on proton NMR studies of *trans*-$PtCl_2(C_5H_5N)(X)$ were intended to differentiate inductive and mesomeric (resonance) effects, in order to clarify d_π–d_π bonding. Thus, it was stated that "the use of pyridine as a detector could afford an opportunity to observe mesomeric effects bacause the π-electron system of the ring can interact with the d orbitals of the metal atom which may be engaged in π bonding to the ligand (X) in the trans position". However, variations in X caused only small differences in resonance energies of the pyridine protons. It was concluded that inductive and mesomeric effects are somewhat balanced (at least at the β position of pyridine) and that the small shift differences would allow no conclusions about the quantitative significance of mesomeric effects and/or d_π–d_π bonding.

Thus, spectroscopic probes seem to be more sensitive to investigation of trans effects as opposed to cis effects. In the present study, L in $C_6F_5PdBr(L)_2$ is always cis to C_6F_5 except in the case of bpy. Indeed, of all the ligands studied the bpy system yielded the largest δ(meta) − δ(para) value of 2.7, which reflects the ability of the trans pyridine ring to interact in a resonance fashion with C_6F_5. The rough order observed for the δ(meta) − δ(para) value (amount of resonance-like interaction) is "acetone solvated" > bpy (cis complex) ≈ sulfides > $AsPh_3$ > amines > PEt_3. Although the differences are relatively small, it does seem clear that a trans position to the C_6F_5 group has a significant effect and that PEt_3 is a unique ligand in the set. It seems futile to attempt further interpretations of these values, however, considering the variety of electronic and magnetic effects that can operate and the relatively small chemical shift differences in these complexes.

CF_3PdI. Isolation of this compound was complicated by its ability to bond solvents in a quasi-reversible fashion. In acetone solution CF_3PdI is reasonably long-lived, but complete removal of the acetone was not possible. Also, PdI_2 contaminated the CF_3PdI solution. Therefore, toluene was employed to extract the CF_3PdI complex directly from the metal atom reactor (very pure toluene was necessary). Removal of the toluene under vacuum was partially accomplished, and the resultant red oil was repeatedly extracted with pentane, and the pentane extracts combined and cooled, yielding a precipitate of CF_3PdI still partially toluene solvated. Thus, the theoretical value for carbon in CF_3PdI is 3.97% and in $CF_3PdI{\cdot}C_6H_5CH_3$ is 24.4%. The observed values were 17.21% (first crop of fine crystals) and 8.23% (after redissolving in pentane, crystallizing and drying).

Direct reaction of the "first crop" solid product with PEt_3 gave $CF_3PdI(PEt_3)_2$ in 84% yield (isolated). Similarly, acetone solutions of CF_3PdI were allowed to react with pyridine to yield $CF_3PdI(C_5H_5N)_2$. Other ligands behave similarly such as SMe_2 and PPh_3. Again, it should be noted that this procedure allows the synthesis of $CF_3PdI(L)_2$ species that are not available by other means.

Spectra and Bonding. There are surprisingly large ^{19}F NMR shift differences for $CF_3PdI(L)_2$ where the order of upfield shift is L = pyridine > acetone (NMR solvent employed for CF_3PdI) > PEt_3. Since this cannot be explained by donor strength alone, this chemical shift order would support a strong π-back-bonding scheme for PEt_3, thereby lowering electron density on Pd and thus on CF_3.[19] The large upfield shift for C_5H_5N would support a strong σ-donation scheme without much π back-bonding to compensate. Examination of the IR spectra reveals that the ν_{C-F} absorption regions are shifted significantly and the ν_{C-F} values are in the order CF_3PdI > $CF_3PdI(C_5H_5N)_2$ > $CF_3PdI(PEt_3)_2$ (cf. Table I; note that acetone solvation of CF_3PdI is no longer present). These data would mitigate against a $d_\pi \rightarrow \sigma^*$ back-bonding scheme[20] for the CF_3–Pd system, as it would be expected that better back-bonding ligands $PEt_3 > C_5H_5N >$ "no ligand or partially toluene solvated" would cause the $d_\pi \rightarrow \sigma^*$ interaction to change in the opposite direction. That is, for $CF_3PdI(PEt_3)_2$ it would be expected that the C–F bond would be strongest (ν_{C-F} highest in energy) since because of the presence of

(17) F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc. A*, 1326 (1966).
(18) (a) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964); (b) J. Chatt and A. D. Westland, *J. Chem. Soc. A*, 88 (1968).
(19) Donor strength order would be pyridine > $PEt_3 \gg$ acetone. This order is taken from the known order of $R_3N > R_3P > R_2O$, and since ethers are stronger bases than ketones, phosphines are also stronger than ketones. Furthermore, pK_a data for conjugate acids indicate the base strength order PEt_3 > pyridine > acetone. See: K. F. Purcell and J. C. Kotz, "Inorganic Chemistry", Saunders, Philadelphia, 1977, p 912; R. S. Drago and N. A. Matwiyoff, "Acids and Bases", Heath, Lexington, MA, 1968, p 51; J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry", McGraw-Hill, New York, 1970, p 304; B. I. Stepanov, A. I. Bkoanov, and B. A. Korolev, *Teor. Eksp. Khim.*, **4**, 354 (1968).
(20) For a brief review and a discussion of $d_\pi \rightarrow \sigma^*$ effects in R_f–Pt systems cf.: (a) M. A. Bennett, H. K. Chee, and G. B. Robertson, *Inorg. Chem.*, **18**, 1061 (1979); (b) M. A. Bennett, H. K. Chee, J. C. Jeffrey, and G. B. Robertson, *ibid.*, **18**, 1071 (1979); (c) F. A. Cotton and J. A. McCleverty, *J. Organomet. Chem.*, **4**, 490 (1965); (d) F. A. Cotton and R. M. Wing, *ibid.*, **9**, 511 (1967); (e) R. B. King and M. B. Bisnette, *ibid.*, **2**, 15 (1964); (f) H. C. Clark and J. H. Tsai, *ibid.*, **7**, 515 (1967); (g) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972).

back-bonding PEt_3 there would be less tendency for back-bonding into CF_3. The opposite trend being observed would tend to support a different mechanism for this R_f stabilization. An ionic–covalent resonance interaction[20] would seem more appropriate since it would seem logical that the $Pd(PEt_3)_2I$ system would be more able to participate in such a scheme as compared to PdI alone (C–Pd ↔ C^-Pd^+) due to the presence of the σ electrons of :PEt_3 (and C_5H_5N:). This increased resonance interaction then could cause the C–F bonds to lengthen and lower ν_{C-F}. We might note at this stage, however, that these are cis effects (L cis to CF_3) being measured, and cis effects are more poorly understood than the more familiar trans effects in organometallic complexes.

Conclusions. The unusual formally two-coordinate complexes C_6F_5PdBr and CF_3PdI are available by metal atom oxidative insertion reactions. The C_6F_5 and CF_3 groups cause the stability of these complexes to be great enough to allow isolation. This is in contrast to analogous perhydroaryl and -alkyl complexes which are extremely thermally unstable. In a sense the C_6F_5 and CF_3 groups mimic halides such as Cl or Br. There is evidence that the C_6F_5PdBr species is telomeric in some solutions, and it is assumed that in the solid state open coordination sites are filled by bridging Br and/or C_6F_5 groups. Similarly, CF_3PdI must be stabilized by bridging. In solution such as in acetone, it appears that open sites are filled by solvation, and in this solvent stability and storability are enhanced for both systems.

Addition of many different ligands to C_6F_5PdBr and CF_3PdI immediately yields $R_fMX(L)_2$ complexes, many of which are not available by other synthetic means.

Spectroscopic studies of this wide series of complexes have not been extremely revealing but in the case of $CF_3PdI(L)_2$ tend to support an ionic–covalent resonance interaction rather than a $d_\pi \rightarrow \sigma^*$ interaction as a means of rationalizing the robust character of the CF_3–Pd bond, and this resonance interaction is encouraged by the presence of cis PEt_3 and C_5H_5N ligands.

Experimental Section

Analytical Methods. Quantitative elemental analyses and osmometric molecular weight determinations were performed by Spang Microanalytical Laboratory, Eagle River, MI, or Dornis and Kolbe, Mülheim, West Germany. Melting points are uncorrected. These data are summarized in Table I.

Metal Atom Apparatus and Techniques. A very detailed description has recently been published,[21] along with typical techniques.[22] Palladium was vaporized from W–Al_2O_3 crucibles (CS-1008) purchased from Sylvania Emissive Products, Exeter, NH. Yields are based on palladium vaporized and are uncorrected for some metal loss (20–40%) to electrode supports, widespread deposition, etc.

Spectra. NMR spectra (^1H and ^{19}F) were obtained by using a Varian EM-390 instrument. IR spectra were obtained by using a Beckman IR-12 unit, and mass spectra were obtained at 70 eV by using a Du Pont 491 unit.

Inert Atmosphere and Solvents. All manipulations were carried out under purified N_2 (passed through BASF deoxygenation catalyst R3-11 at 100 °C). Toluene, pentane, and hexane were purified by continuous reflux over benzophenone ketyl under N_2. However, it was necessary to pretreat the alkanes with $KMnO_4$ and concentrated H_2SO_4 (to remove olefins) before benzophenone–Na treatment. Acetone employed was Burdick and Jackson spectral grade and was degassed by freeze–thaw cycles before use.

Preparation and Isolation of C_6F_5PdBr. Palladium vapor (about 1 g, 10 mg-atom) and bromopentafluorobenzene (about 50 mL, 394 mol) were codeposited over a 2-h period. The reactor was warmed to room temperature and excess C_6F_5Br removed under vacuum. The reactor was pressurized with N_2, and the contents were washed[23] with three 20-mL portions of purified deoxygenated acetone by means of a syringe and long Teflon needle, with continuous N_2 flushing. The extracts were combined and filtered with N_2 through a 10–20 μm fritted filter. The acetone was removed under vacuum, leaving a thick orange oil. In a Vacuum Atmospheres N_2-filled inert-atmosphere box this oil was washed with 20 mL of dry, deoxygenated benzene (or toluene). The benzene solution was decanted and this same solution slowly added to a flask containing 400 mL of dry deoxygenated pentane with rapid magnetic stirring. The powdery precipitate was filtered to yield a light orange powder, C_6F_5PdBr, in a 10.5% overall yield. Table I lists analytical data and spectra. IR (cm^{-1}) (in KBr): 1632 m, sh, 1622 m, sh, 1614 m, 1525 m, sh, 1505 vs, 1466 vs, sh, 1462 vs, 1455 s, sh, 1445 m, sh, 1435 m, sh, 1425 w, sh, 1365 m, 1060 s, 955 vs, 795 s, 668 w.

Preparation and Isolation of CF_3PdI·(Sol)x. Palladium vapor (about 1 g, 10 mg-atom) was codeposited with CF_3I (about 25 mmol) as described by Low.[12] After reaction (about 1 h) the reactor was allowed to warm to room temperature with removal of excess CF_3I under vacuum. The reactor was pressurized with N_2, and N_2 flushing continued as the reactor contents were washed with three 25-mL portions of dry, deoxygenated toluene.[23] The combined extracts were filtered under N_2 through a 10–20 μm fritted filter, and the toluene was removed from the filtrate under vacuum, leaving a dark red oil. The oil was extracted with several portions of pentane until the pentane washes were almost colorless. The combined pentane washes were reduced in volume under vacuum to about 10 mL, and this concentrated solution was cooled at −78 °C overnight. A fine brown precipitate was formed, and the pentane was syringed off. The precipitate was washed with cold pentane and dried under vacuum. This powder was $CF_3PdI(solvent)_x$ with partial toluene solvation. Table I lists the analytical data and spectra. About a 2% overall yield was obtained.

General Procedure for Addition of Ligands to C_6F_5PdBr. A sample of pure, dry C_6F_5PdBr (~1.0 mmol) was placed in a small Schlenk tube and dissolved in 50 mL of purified acetone with magnetic stirring. The solution was attached to a vacuum system and freeze–thaw degassed. Then ~4 mL of ligand in 15 mL of acetone was distilled in while the sample was frozen. The sample was allowed to slowly warm to room temperature with stirring commenced upon meltdown. Color changes were generally evident at this stage, indicating reaction taking place. After about $^1/_2$ h stirring at room temperature the excess ligand and acetone were slowly (with stirring) removed under vacuum, and the resultant yield was redissolved in acetone and filtered. This solution was partially decolorized with activated carbon and filtered, and the colored (usually yellow-orange) solution was added to 10 g of Florisil. The acetone was evaporated, leaving the $C_6F_5PdBr(L)_2$ mounted on Florisil, and this was washed twice with 15-mL portions of pentane to remove any excess L still present. At this stage each $C_6F_5PdBr(L)_2$ system was treated slightly differently, as described separately as follows.

$C_6F_5PdBr(SR_2)_2$ (Sulfide Complexes). The Florisil was washed with 20-mL portions of hot hexane until the washes were colorless (about 200 mL total). These combined washes were reduced under vacuum to 25 mL, and this solution was refrigerated. Red orange crystals separated ($PdBr_2(SR)_2$) and were separated. The mother liquor was further reduced and refrigerated, and yellow crystals (desired product) separated. Recrystallization from hexane yielded light yellow $C_6F_5PdBr(SPh_2)_2$ (0.09 g, 10% overall) [IR (cm^{-1}) (in KBr): 3088 vs, 1510 vs, 1480 sh, s, 1472 s, 1450 m, 1442 m, 1405 vw, 1370 m, 1065 s, 1025 m, 1004 m, 960 vs, 800 s, 742 s], $C_6F_5PdBr(SEt_2)_2$ (0.18 g, 4.4%) [IR (cm^{-1}) (in KBr): 2970 m, 2935 m, 1502 vs, 1460 vs, 1445 sh, s, 1380 m, 1365 m, sh, 1358 m, 1270 m, sh, 1255 m, 1070 m, sh, 1059 s, 920 w, sh, 954 vs, 785 s] and $C_6F_5PdBr(SMe_2)_2$ (0.08 g, 3.2%) [IR (cm^{-1}) (in KBr): 1505 s, 1470 s, 1454 m, sh, 1442 m, sh, 1429 m, 1415 m, sh, 1405 w, sh, 1368 w, sh, 1062 m, sh, 1055 m, 1032 m, 985 m, sh, 978 m, 960 s, 950 s, 795 m.

$C_6F_5PdBr(NHEt_2)_2$. The Florisil was washed with hexane until the washes were colorless. The washes were combined and the volumes reduced under vacuum, and the resultant solution was refrigerated. The first crop of crystals contained both yellow and orange crystals. The mother liquor was further reduced and cooled, and yellow crystals of $C_6F_5PdBr(NHEt_2)_2$ precipitated (0.64 g, 12%). IR (cm^{-1}) (in KBr):

(21) K. J. Klabunde, P. L. Timms, P. S. Skell, and S. Ittel, *Inorg. Synth.*, **19**, 59 (1979).
(22) K. J. Klabunde, B. B. Anderson, and M. Bader, *Inorg. Synth.*, **19**, 72 (1979).
(23) Scrubbing of the inside reactor walls was accomplished with a small hand magnet outside manipulating a magnetic stirring bar inside. Solvent could also be splashed up on the walls in this way.

3222 s, 3212 s, 3192 s, 2975 vs, 2928 s, 2885 s, 1505 vs, 1495 vs, sh, 1480 vs, 1465 vs, 1455 vs, 1448 vs, 1440 vs, 1435 vs, 1428 vs, sh, 1400 m, sh, 1386 vs, 1360 s, 1350 vs, 1335 m, sh, 1154 s, 1070 vs, 1060 vs, 1044 vs, 1035 vs, sh, 958 vs, 828 vs, 778 vs.

$C_6F_5PdBr(NH_2Et)_2$. No Florisil mount was used. The grey-white crude product from $EtNH_2$ addition to C_6F_5PdBr in acetone was dissolved in acetone and filtered. The resultant yellow solution was reduced in volume and hexane added slowly to yield light yellow $C_6F_5PdBr(NHEt_2)_2$ (0.10 g, 3.5%). IR (cm^{-1}) (in KBr): 1512 s, sh, 1504 vs, 1500 vs, sh, 1496 s, sh, 1462 vs, 1458 vs, 1442 s, sh, 1438 s, sh, 1428 s, sh, 1424 m, sh, 1418 m, sh, 1059 s, 956 vs.

$C_6F_5PdBr(NMe_3)_2$. No Florisil mount was used. The C_6F_5PdBr–acetone–NMe_3 reaction yielded a dark orange residue, which was washed with hexane until the washes were almost colorless. The washes were combined, reduced, and refrigerated, yielding some crystals of decafluorobiphenyl which were removed. The solvent was removed, the residue was dissolved in acetone and filtered, and then the acetone was removed. The residue was washed with benzene until the washes were colorless. The washes were combined, decolorized with activated charcoal, filtered, and reduced. Hexane addition yielded a light yellow precipitate which was filtered and washed with hexane. The product was $C_6F_5PdBr(NMe_3)_2$ (0.52 g, 2%). IR (cm^{-1}) (in KBr): 1505 s, sh, 1500 vs, 1495 vs, sh, 1492 vs, sh, 1478 s, 1462 vs, sh, 1458 vs, 1450 vs, 1440 vs, 1430 s, sh, 1055 vs, 950 vs, 790 s.

$C_6F_5PdBr(C_5H_5N)_2$. The yellow-green C_6F_5PdBr–acetone–pyridine reaction residue was dissolved in acetone, filtered, and mounted on Florisil as described previously. A 4-in. Florisil–pentane column was used for column chromatography (Florisil mounted with product was placed on top of this column). Elution with pentane–toluene with increasing toluene concentrations yielded a yellow band which was finally collected with pure toluene elution. Pentane addition to the yellow toluene solution resulted in the precipitation of a fine yellow solid, which was filtered and collected and was $C_6F_5PdBr(C_5H_5N)_2$ (0.73 g, 13%). IR (cm^{-1}) (in KBr): 1610 s, 1505 vs, 1488 m, 1462 vs, sh, 1455 vs, 1442 s, sh, 1438 s, sh, 1358 m, 1214 m, 1158 m, 1154 m, 1705 s, 1060 s, 1054 s, sh, 1020 m, 958 vs, 790 m, 766 s, 690 vs.

$C_6F_5PdBr(2,2'\text{-bpy})$. An acetone solution of C_6F_5PdBr was added to a stirred solution of bipyridine. The acetone was removed and the resultant yellow solid washed with hexane. The residue was again dissolved in acetone, and the mixture was mounted on Florisil and this material placed on top of a 2-in. clean Florisil–hexane column. Elution with hexane and then pure benzene yielded a yellow product which was recrystallized from CH_2Cl_2 to yield $C_6F_5PdBr(bpy)$ (0.47 g, 9%). IR (cm^{-1}) (in KBr): 1640 m, 1608 s, 1525 s, sh, 1510 vs, 1475 vs, sh, 1465 vs, 1450 vs, 1440 s, sh, 1362 m, 1318 m, 1262 m, 1255 m, 1222 w, 1165 m, 1108 m, 1065 vs, 1035 s, 1022 m, 960 vs, 900 m, 798 s, 792 s, 768 vs, 730 m, 685 m.

$C_6F_5PdBr(NH_3)_2$. Ammonia was added to an acetone solution of C_6F_5PdBr, the resultant grey solution was filtered, and solvent was removed, leaving a yellow-brown residue. This residue was washed repeatedly with CH_2Cl_2, and the volume of the combined washings was reduced and refrigerated, yielding white crystals of $C_6F_5PdBr(NH_3)_2$ (0.045 g, 5.4%). IR (cm^{-1}) (in KBr): 3315 s, 3235 s, 1660 vs, 1654 s, sh, 1586 vs, 1510 s, 1504 vs, 1495 s, sh, 1468 vs, 1462 vs, 1452 vs, 1448 vs, 1435 vs, 1428 vs, sh, 1415 s, 1408 s, 1395 s, 1375 s, 1365 s, 1355 s, 1212 s, 1138 s, 1128 s, 1118 m, sh, 1075 vs, sh, 1064 vs, 1055 vs, sh, 1048 vs, 1030 s, 1014 vs, 995 s, 960 vs, 952 vs, 910 s.

$C_6F_5PdBr(AsPh_3)_2$. An acetone solution of C_6F_5PdBr was added to a stirred solution of $AsPh_3$. Upon removal of acetone a yellow-brown solid precipitated which was impure $C_6F_5PdBr(AsPh_3)_2$. IR (cm^{-1}) (in KBr): 1505 s, 1486 m, 1468 s, 1442 m, 1062 m, 958 s, 794 m, 740 m, 734 m, sh, 690 m.

$C_6F_5PdBr(1,5\text{-COD})$. An acetone solution of C_6F_5PdBr was slowly added to an acetone solution of 1,5-cyclooctadiene. Removal of acetone yielded a yellow solid which was taken up in pentane, the solution was filtered, and the pentane was reduced, yielding $C_6F_5PdBr(1,5\text{-COD})$ (0.23 g, 7%). IR (cm^{-1})(in KBr): 2980 m, 2940 m, 1638 m, 1560 m, 1508 vs, 1468 vs, 1450 s, sh, 1430 s, 1368 s, 1360 s, 1070 vs, sh, 1062 s, 1014 m, sh, 1008 m, 1000 m, 958 vs, 858 m, 845 m, 785 vs, 752 m.

General Procedure for the Additions of Ligands to $CF_3PdI\cdot x$solvent. The complex (~1.0 mmol) was dissolved in about 10 mL of acetone, and this solution was attached to a vacuum system and freeze–thaw degassed. The ligand (~50 mmol) was dissolved in acetone, and this degassed solution was distilled onto the frozen CF_3PdI sample, which was then slowly warmed with stirring commenced on meltdown. The resultant $CF_3PdI(L)_2$ complexes were isolated as described below. IR of $CF_3PdI\cdot x$tol (cm^{-1}) (in KBr): 1385 m, 1265 m, 1100 vs, 1075 vs, sh, 1055 vs, 1012 s, sh, 800 m, 730 m.

$CF_3PdI(C_5H_5N)_2$. Addition of C_5H_5N(pyridine) in acetone to CF_3PdI–acetone yielded a light yellow solution. Excess pyridine and acetone were removed under vacuum, and the resultant yellow-white solid was redissolved in acetone and decolorized with activated charcoal, the solution was filtered, and acetone was removed. The residue was dissolved in hot methanol followed by filtration and refrigeration, yielding light yellow $CF_3PdI(C_5H_5N)_2$ (0.17 g, 4%). IR (cm^{-1}) (in KBr): 1610 m, 1488 m, 1457 s, 1242 m, 1218 m, 1152 m, 1095 vs, 1050 s, sh, 1030 vs, 1000 vs, 950 m, 765 s, 696 s.

$CF_3PdI(PEt_3)_2$.[12] Further IR data (cm^{-1}) (in KBr): 2970 m, 2938 m, 2880 m, 1475 w, sh, 1462 m, sh, 1460 m, sh, 1455 m, 1424 m, 1384 m, 1244 m, 1075 vs, 1035 s, 1010 s, 994 vs, 982 vs, sh, 795 s, 724 s, 635 m.

Acknowledgment. The initial work on this project was done by Dr. J. Y. F. Low. We thank the National Science Foundation (Grant No. CHE-7402713) for generous support.

Registry No. C_6F_5PdBr, 48133-13-7; $C_6F_5PdBr(SPh_2)_2$, 74998-64-4; $C_6F_5PdBr(SEt_2)_2$, 74998-65-5; $C_6F_5PdBr(SMe_2)_2$, 74998-66-6; $C_6F_5PdBr(NHEt_2)_2$, 74998-67-7; $C_6F_5PdBr(NH_2Et)_2$, 74998-68-8; $C_6F_5PdBr(NMe_3)_2$, 74998-69-9; $C_6F_5PdBr(NH_3)_2$, 74998-70-2; $C_6F_5PdBr(C_5H_5N)_2$, 75044-11-0; $C_6F_5PdBr(PEt_3)_2$, 54071-54-4; $C_6F_5PdBr(bpy)$, 74998-71-3; $C_6F_5PdBr(AsPh_3)_2$, 75044-12-1; $C_6F_5PdBr(COD)$, 74998-72-4; CF_3PdI, 54056-39-2; $CF_3PdI(C_5H_5N)_2$, 74998-73-5; $CF_3PdI(PEt_3)_2$, 54122-37-1; Pd, 7440-05-3; CF_3I, 2314-97-8; C_6F_5Br, 344-04-7.