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Syntheses and Structures of the Complexes *cis*-[M(C_6F_5)$_2$(N$\frown$X)] (M = Pd, Pt; N$\frown$X = 2-Iodoaniline, 2-Benzoylpyridine) Containing N$\frown$X Acting as a Didentate Chelating Ligand and Displaying I→M or O→M Interactions

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Complexes *cis*-[M(C_6F_5)$_2$(THF)$_2$] (M = Pd, Pt) are weak Lewis acids and react with the halocarbon ligand 2-iodoaniline (R−I) yielding the corresponding *cis*-[M(C_6F_5)$_2$(R−I)] [M = Pd (**1**), Pt (**2**)]. In these complexes a (C−)I−M bond is present. The use of other 2-haloanilines (halogen = F, Cl, Br) does not yield the analogous complexes because of the lesser nucleophilic character of the halogen involved. The presence of the (C-)I-Pt bond in **2** has been confirmed by an X-ray structure determination, which also reveals an N−H···M hydrogen bond between two neutral molecules. Complex **2** crystallizes in the space group $P\bar{1}$: $Z = 4$; $a = 11.797(4)$ Å; $b = 13.735(4)$ Å; $c = 14.107(4)$ Å; $\alpha = 97.24(2)°$; $\beta = 90.91(2)°$; $\gamma = 99.44(2)°$; $V = 2235(2)$ Å^3. Similarly, complexes *cis*-[M(C_6X_5)$_2$(THF)$_2$] (M = Pd, Pt; X = F, Cl) react with the ligand 2-benzoylpyridine {R−C(O)-Ph}, in which the oxygen atom of the ketonic group can behave as a nucleophilic center, yielding the complexes *cis*-[M(C_6X_5)$_2${R−C(O)Ph}] [M = Pd, X = F (**3**); M = Pt, X = F (**4**), Cl (**5**)]. Complex **3** crystallizes in the space group $C2/c$: $Z = 16$; $a = 26.284(3)$ Å; $b = 10.623(1)$ Å; $c = 31.423(4)$ Å; $\beta = 93.15(1)°$; $V = 8760(2)$ Å^3. The I−M or O−M bonds in complexes **1**−**5** are weak and can be easily broken by the addition of neutral (CO, PPh_3, and CH_3CN) or anionic (Br^-) ligands.

Introduction

Some years ago we described the syntheses of complexes of stoichiometry *cis*-[M(C_6X_5)$_2$(THF)$_2$] (M = Pd, Pt; X = F, Cl; THF = tetrahydrofuran).[1] The study of their reactivity has shown that they are excellent precursors for the preparation of complexes not accessible by other routes since the two THF groups are easily replaced by other ligands.[2] In the "*cis*-M(C_6X_5)$_2$" fragment the metal atom has acid properties and is able to accept electron density from a ligand with a suitable nucleophilic center, forming a X→M dative bond. A judicious choice of the nucleophilic ligand can lead to the preparation of complexes containing interesting structural features. In this work we report the syntheses and structural characterization of complexes of the type *cis*-[M(C_6X_5)$_2$(N$\frown$X)], in which N$\frown$X is a bidentate N-donor ligand containing a substituent nucleophilic center such as halogen (halocarbon ligands) or oxygen atoms.

Halocarbons have the general formula RX in which R is an organic group and X is a halogen atom. This kind of compound is one of the more important and better represented organic substances.[3] However, the use of halocarbons as ligands forming RX−M complexes is relatively rare and recent.[4] Thus, only one palladium[4b] and two platinum complexes[5] have been reported prior to this work.

There are several reasons that explain the relatively small number of halocarbon complexes known. One is that the halocarbons are very weak bases so that the RX−M bonds formed are easily displaced by other donor ligands. In sharp contrast, complexes of the halide ions X^-, especially where X = Cl, Br, or I, constitute one of the largest classes of coordination compounds mainly because the anions X^- are much more basic than the halocarbons RX. Thus, among the halocarbons, iodocarbons should be the best candidates as ligands, being the best donors, especially toward soft Lewis acids such as the "*cis*-M(C_6X_5)$_2$" fragment.

Other common decomposition pathways for halocarbon complexes are nucleophilic attack at the α-carbon[3] and oxidative addition to the metal center to give an alkyl metal halide, R−M−X. Haloarenes have a greater C−X bond strength that helps to prevent this reaction. The chelate effect can be used to increase the binding tendency of ligands, and thus, chelating haloarenes are the largest class of halocarbon ligand found to date.

The oxygen atoms of ketonic groups are also nucleophiles able to donate electron density to the metal center in the "*cis*-M(C_6X_5)$_2$" fragment in a way similar to that of halogen atoms in halocarbon ligands. This capability has been used in the preparation of complexes possesing RO→M bonds.

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Experimental Section

C, H, and N analyses were done with a Perkin-Elmer 240B microanalyzer. The IR spectra were recorded on a Perkin-Elmer 883 or 1710 FTIR spectrophotometer (4000−200 cm^{-1}) using Nujol mulls between polyethylene sheets or CH_2Cl_2 solutions in NaCl windows. The ^{1}H and ^{19}F NMR spectra were recorded on a Varian XL-200 or a Unity-300 in CD_2Cl_2, $CDCl_3$, or HDA (acetone-d_6) solutions. *cis*-[M(C_6X_5)$_2$(THF)$_2$] (M = Pd, Pt; X = F, Cl) was prepared as described elsewhere.[1] 2-Fluoroaniline, 2-chloroaniline, 2-bromoaniline, 2-iodoaniline, and 2-benzoylpyridine were obtained from commercial sources and used as delivered.

***cis*-[M(C_6F_5)$_2$(R−I)] [R−I = 2-Iodoaniline; M = Pd (1), Pt (2)].** To a solution of 0.200 g of *cis*-[M(C_6F_5)$_2$(THF)$_2$] (M = Pd, 0.342 mmol; M = Pt, 0.297 mmol) in 20 mL of CH_2Cl_2 was added 2-iodoaniline in a 1:1 molar ratio (M = Pd, 0.074 g, 0.34 mmol; M = Pt, 0.065 g, 0.30 mmol). The resulting brown solution was stirred at room temperature for 15 min, and the solvent was evaporated to dryness. The residue was thrice treated with 3 mL of $CHCl_3$ and then evaporated to dryness, and finally, the residue was treated with ^{i}PrOH, rendering complexes **1** (96% yield) and **2** (90% yield).

Anal. Found (Calcd) for **1**: N, 2.29 (2.12); C, 33.95 (32.78); H, 1.25 (0.92). IR, cm^{-1}: C_6F_5 X-sensitive,[6] 797(s) and 783(s); others, 1638(m), 1600(m), 1501(vs), 1057(vs), and 960(vs); R−I, 3332(s), 3277(m), 1582(m), 1556(m), 1356(m), 1080(s), 814(m), 761(s), 647(m), and 429(m); in solution, ν(N−H) = 3307(m) and 3253(m). ^{1}H NMR ($CDCl_3$, room temperature), ppm: 4.64 (s, 2H); 7.19 (m, 1H); 7.28 (d, 1H); 7.44 (t, 1H); 7.77 (d, 1H). ^{19}F NMR ($CDCl_3$, room temperature), ppm: *o*-F, −117.04 (2F) and −119.09 (2F); *m*-F, −164.27 (2F) and −165.55 (2F); *p*-F, −160.76 (1F) and −161.93 (1F).

Anal. Found (Calcd) for **2**: N, 1.68 (1.87); C, 29.66 (28.89); H, 0.86 (0.81). IR, cm^{-1}: C_6F_5 X-sensitive,[6] 810(s) and 801(s); others, 1638(m), 1609(m), 1506(vs), 1064(vs), and 960(vs); R−I, 3315(m), 1557(m), and 757(s); in solution ν(N−H) = 3289(m) and 3240(m). ^{1}H NMR ($CDCl_3$, room temperature), ppm: 5.38 (s, 2H, $^2J_{Pt-H}$ = 37 Hz); 7.24 (d, 1H); 7.38 (t, 1H); 7.41 (t, 1H); 7.73 (d, 1H). ^{19}F NMR ($CDCl_3$, room temperature), ppm: *o*-F, −117.00 (2F, $^3J_{Pt-F}$ = 435.4 Hz) and −121.55 (2F, $^3J_{Pt-F}$ = 491.9 Hz); *m*-F, −163.03 (2F) and −164.57 (2F); *p*-F, −159.72 (1F) and −161.52 (1F).

Attempts To Prepare Similar Compounds with R−X (R−X = 2-Fluoroaniline, 2-Chloroaniline, or 2-Bromoaniline). The reactions between *cis*-[M(C_6F_5)$_2$(THF)$_2$] and R−X (R−X = 2-fluoroaniline, 2-chloroaniline, or 2-bromoaniline) under similar conditions only renders a mixture of unidentified compounds.

***cis*-[M(C_6X_5)$_2${R−C(O)Ph}] [R−C(O)Ph = 2-Benzoylpyridine; M = Pd, X = F (3); M = Pt, X = F (4); M = Pt, X = Cl (5)].** A typical preparation (**3**) was as follows. To a solution of 0.080 g (0.13 mmol) of *cis*-[Pd(C_6F_5)$_2$(THF)$_2$] in 20 mL of CH_2Cl_2 was added 0.025 g (0.13 mmol) of 2-benzoylpyridine. The yellow solution (red in the case of the platinum complexes) was stirred at room temperature for 5 min and then evaporated to dryness. In order to eliminate completely the THF, the residue was treated with 3 mL of $CHCl_3$ and evaporated to dryness. This operation was repeated 3 times, and finally, the residue was treated with *n*-hexane, rendering **3** as a yellow solid (red for **4** and **5**). Yields: **3**, 83%; **4**, 88%; **5**, 70%.

Anal. Found (Calcd) for **3**: N, 2.29 (2.25); C, 46.47 (46.22); H, 1.61 (1.45). IR, cm^{-1}: C_6F_5 X-sensitive,[6] 805(s) and 799(s); others, 1632(m), 1500(vs), 1057(vs), and 959(vs); R−C(O)Ph, 1608(m), 1598(m), 1589(m), 1577(m), 1566(s), 1334(s), 1267(s), 1185(m), 1177(m), 1168(m), 1023(m), 820(m), 789(s), 772(m), 754(s), 700(s), 685(m), 664(m), and 649(m). ^{1}H NMR ($CDCl_3$, room temperature), ppm: All the signals appear overlapped in the aromatic hydrogen region. ^{19}F NMR ($CDCl_3$, room temperature), ppm: *o*-F, −116.31 (2F) and −118.26 (2F); *m*-F, −163.05 (2F) and −164.15 (2F); *p*-F, −159.87 (1F) and −160.73 (1F).

Anal. Found (Calcd) for **4**: N, 1.77 (1.97); C, 39.88 (40.46); H, 1.18 (1.27). IR, cm^{-1}: C_6F_5 X-sensitive,[6] 819(s) and 814(s); others, 1636(m), 1503(vs), 1064(vs), and 959(vs); R−C(O)Ph, 1608(m), 1598(m), 1584(m), 1575(m), 1558(s), 1335(s), 1266(m), 1184(m), 1167(m), 1026(m), 806(s), 770(m), 754(s), 694(s), 683(m), 667(m), and 651(m). ^{1}H NMR ($CDCl_3$, room temperature), ppm: 8.56 (d, 1H, $^3J_{Pt-H}$ = 28 Hz); the rest of the signals appear overlapped in the aromatic hydrogen region. ^{19}F NMR ($CDCl_3$, room temperature), ppm: *o*-F, −120.42 (2F, $^3J_{Pt-F}$ = 516.7 Hz) and −121.76 (2F, $^3J_{Pt-F}$ = 428.5 Hz); *m*-F, −163.89 (2F) and −164.93 (2F); *p*-F, −161.02 (1F) and −161.62 (1F).

Anal. Found (Calcd) for **5**: N, 1.61 (1.60); C, 32.51 (32.87); H, 1.06 (1.03). IR, cm^{-1}: C_6Cl_5, 1335(s), 1319(s), 1294(s), 676(s), and 625(s); R−C(O)Ph, 598(m), 1584(m), 1575(m), 1551(s), 1268(m), 1026(m), 960(m), 814(m), 769(m), 751(s), 697(s), and 651(m). ^{1}H NMR ($CDCl_3$, room temperature), ppm: The signals appear overlapped in the zone of the aromatic hydrogens.

***cis*-[Pt(C_6F_5)$_2$(R−I)(CO)] (6).** Through a solution of 0.200 g (0.267 mmol) of *cis*-[Pt(C_6F_5)$_2$(R−I)], **2**, in CH_2Cl_2 (20 mL) at room temperature was bubbled CO for 5 min. After evaporation to dryness and addition of *n*-hexane (20 mL) a white solid, *cis*-[Pt(C_6F_5)$_2$(R−I)(CO)] (**6**), was isolated in 80% yield. *cis*-[Pd(C_6F_5)$_2$(R−I)], **1**, does not react with CO under similar conditions.

Anal. Found (Calcd) for **6**: N, 2.16 (1.80); C, 30.34 (29.39); H, 0.73 (0.78). IR, cm^{-1}: C_6F_5 X-sensitive,[6] 817(s) and 798(s); others, 1639(m), 1506(vs), 1064(s), and 964(vs); R−I, 3331(m), 3263(m), 1590(m), 1575(m), 1126(s), and 757(s); ν(CO) = 2123(vs). ^{1}H NMR (CD_2Cl_2, room temperature), ppm: 5.47 (s, 2H, $^2J_{Pt-H}$ = 35 Hz); 6.99 (t, 1H); 7.30 (d, 1H); 7.44 (t, 1H); 7.93 (d, 1H). ^{19}F NMR (CD_2Cl_2, room temperature), ppm: *o*-F, −118.22 (2F, $^3J_{Pt-F}$ = 413.4 Hz) and −118.77 (2F, $^3J_{Pt-F}$ = 359.6 Hz); *m*-F, −161.77 (2F) and −163.13 (2F); *p*-F, −156.93 (1F) and −159.28 (1F).

Reaction of 1 and 2 with CH_3CN. To a solution of *cis*-[M(C_6F_5)$_2$(R−I)] [M = Pd (**1**) or Pt (**2**)] in 20 mL of CH_2Cl_2, 5 mL of CH_3CN was added. The solution was stirred at room temperature for 5 min, and the solvent was evaporated to dryness. The residue was treated with *n*-hexane, rendering *cis*-[M(C_6F_5)$_2$(CH_3CN)$_2$].

Reaction of 2 with NBu_4Br. To a solution of 0.120 g (0.16 mmol) of *cis*-[Pt(C_6F_5)$_2$(R−I)] (**2**) in 20 mL of CH_2Cl_2 was added 0.052 g (0.16 mmol) of NBu_4Br. The solution was stirred at room temperature for 15 min, and the solvent was evaporated to dryness. The residue was treated with *n*-hexane, rendering [NBu_4]$_2$[Pt$_2$(μ-Br)$_2$(C_6F_5)$_4$].

***cis*-[Pt(C_6F_5)$_2${R−C(O)Ph}(CO)] (7).** CO was bubbled for 5 min through a solution of 0.200 g (0.281 mmol) of *cis*-[Pt(C_6F_5)$_2${R−C(O)Ph}] (**4**) in CH_2Cl_2 (20 mL) at room temperature. The red solution became colorless. After evaporation to dryness and addition of *n*-hexane (20 mL) a white solid *cis*-[Pt(C_6F_5)$_2${R−C(O)Ph}(CO)] (**7**) was isolated in 87% yield. *cis*-[Pd(C_6F_5)$_2${R−C(O)Ph}] (**3**) does not react with CO under similar conditions.

Anal. Found (Calcd) for **7**: N, 1.81 (1.89); C, 40.84 (40.55); H, 1.04 (1.23). IR, cm^{-1}: C_6F_5 X-sensitive,[6] 808(s) and 798(s); others, 1638(m), 1506(vs), 1064(vs), and 961(vs); R−C(O)Ph, 1681(s), 1600(m), 1573(m), 1558(m), 1321(m), 1304(f), 1278(m), 1184(m), 1175(m), 1160(m), 1108(m), 1026(m), 944(s), 931(m), 775(m), 759(m), 701(s), 649(s), 514(m), 460(m), and 368(m); ν(CO) = 2128(vs). ^{1}H NMR (HDA, room temperature), ppm: 7.58 (t, 2H); 7.75 (d, 2H), ≈7.8 (t, 1H); 7.96 (d, 1H); 8.05 (t, 1H); 8.40 (t, 1H); 9.50 (d, 1H, $^3J_{Pt-H}$ = 28 Hz). ^{19}F NMR (HDA, room temperature), ppm: *o*-F, −117.82 (2F, $^3J_{Pt-F}$ = 403.0 Hz) and −119.19 (2F, $^3J_{Pt-F}$ = 483.6 Hz); *m*-F, −163.00 (2F) and −165.43 (2F); *p*-F, −160.09 (1F) and −162.01 (1F). ^{19}F NMR (HDA, −90 °C), ppm: *o*-F, −118.40 (1F), −119.47 (1F), −119.97 (1F), and −121.37 (1F) (due to the poor resolution it is not possible to calculate the *o*-F−Pt coupling constants); *m*-F, −165.08 (4F); *p*-F, −160.62 (1F) and −161.43 (1F).

***cis*-[Pt(C_6F_5)$_2${R−C(O)Ph}(PPh$_3$)] (8).** To a solution of 0.150 g (0.211 mmol) of *cis*-[Pt(C_6F_5)$_2${R−C(O)Ph}], **4**, in CH_2Cl_2 (20 mL) 0.055 g (0.211 mmol), of PPh$_3$ was added. The red solution, which immediately changed to colorless, was stirred at room temperature for 2 min and then evaporated to dryness. The resulting white solid, *cis*-[Pt(C_6F_5)$_2${R−C(O)Ph}(PPh$_3$)] (**8**), was washed with *n*-hexane (20 mL) and was isolated in 85% yield.

Anal. Found (Calcd) for **8**: N, 1.58 (1.44); C, 51.73 (51.76); H, 2.52 (2.48). IR, cm^{-1}: C_6F_5 X-sensitive,[6] 787(s) and 775(s); others, 1638(m), 1503(vs), 1064(vs), and 956(vs); R−C(O)Ph, 1681(s), 1602(s), 1582(m), 1356(s), 1320(m), 1293(f), 1277(f), 1172(m), 1160(m), 1103(f), 1097(f), 1029(m), 940(f), 760(s), 698(s), 463(m), and 433(m); PPh$_3$, 807 (vs), 752(s), 740(s), 537(vs), 514(vs), and 494(s). ^{1}H NMR (HDA, room temperature), ppm: All signals except those corresponding to the pyridinic ring appear overlapped in the zone of the aromatic hydrogens; 8.82 (d, H$_\alpha$, $^3J_{Pt-H}$ = 26 Hz); 7.90 (t, H$_\beta$); 7.19 (t, H$_\gamma$);

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Table 1. Crystallographic Data for **2**·$^1/_4$CHCl$_3$ and **3**

complex	2	3
formula	$PtIF_{10}NC_{18}H_6 \cdot {}^1/_4CHCl_3$	$PdF_{10}NOC_{24}H_9$
molecular weight	778.078	623.729
space group	$P\bar{1}$	$C2/c$
crystal system	triclinic	monoclinic
a, Å	11.797(4)	26.284(3)
b, Å	13.735(4)	10.623(1)
c, Å	14.107(4)	31.423(4)
α, deg	97.24(2)	90
β, deg	90.91(2)	93.15(1)
γ, deg	99.44(2)	90
V, Å^3	2235(2)	8760(2)
Z	4	16
crystal size, mm	0.40 × 0.63 × 0.65	0.56 × 0.40 × 0.24
d_{calc}, g/cm^3	2.31	1.89
scan range, deg	$3 < 2\theta < 50.7$	$4 < 2\theta < 47$
scan mode	ω	$2\theta/\omega$
μ(Mo Kα), cm^{-1}	78.4	9.5
radiation	Mo Kα ($\lambda\alpha$ = 0.710 73 Å)	Mo Kα ($\lambda\alpha$ = 0.710 73 Å)
temp, °C	20 ± 2	20 ± 2
goodness of fit on F^2	1.312	1.190
R1[$I > 2\sigma(I)$]^a	0.056	0.060
wR2[$I > 2\sigma(I)$]^b	0.117	0.115
final diff. peak/hole, e/Å^3	1.56/−2.19	1.08/−1.55

^{a} $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^{b} $wR2 = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]^{1/2}$.

7.54 (d, H$_\delta$). ^{19}F NMR (HDA, room temperature), ppm: *o*-F, −114.23 (1F, $^3J_{Pt-F} = 373.4$), −116.02 (1F, $^3J_{Pt-F} = 351.4$ Hz), −116.84 (1F, $^3J_{Pt-F} = 460.2$ Hz), and −120.78 (1F, $^3J_{Pt-F} = 329.3$ Hz); *m*-F, −163.83 (1F), −165.83 (1F), −165.94 (1F), and −166.69 (1F); *p*-F, −163.04 (1F) and −165.00 (1F).

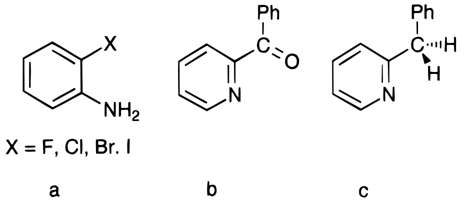
Preparation of Crystals of 2 for X-ray Structure Determination. Suitable crystals for X-ray purposes were obtained by slow diffusion of *n*-hexane into a solution of 0.03 g of **2** in CH$_2$Cl$_2$ (4 mL) at −30 °C.

Crystal Data for Complex 2. Table 1 summarizes the crystallographic data and least-squares residuals for the crystal structure of **2**. Diffraction data were measured by Crystalitics Company.[7] An empirical absorption correction was based on ψ-scan measurements. Six standard reflections, which were remeasured after every 300 data points, indicated that there was no decay. The structure was solved by direct methods and refined on $|F_o|^2$ using the SHELXL93 program.[8] All of the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions and refined as riding atoms [C−H, 0.96 Å and N−H, 0.90 Å] with their thermal parameters set up to 1.2 times the U_{eq} value for the parent atoms. The chlorine atoms of the solvent are disordered over two sites with a total occupancy of 0.25. The thermal parameters of each set of chlorine atoms have been constrained to be the same. Weights, *w*, were set equal to $[\sigma_c^2(F_o^2) + (gP)^2]^{-1}$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$ and $g = 0.0400$. A difference map following convergence showed 17 peaks higher than 1 e/Å^3 (1.56−1.01). These peaks lay very near the heavy atoms, and they are most likely due to series termination or residual absorption (minimum difference density of −2.19 e/Å^3).

Preparation of Crystals of 3 for X-ray Structure Determination. Suitable crystals for X-ray purposes were obtained by slow diffusion of n-hexane into a solution of 0.03 g of **3** in CH$_2$Cl$_2$ (4 mL) at −30 °C.

Crystal Data for Complex 3. Table 1 summarizes the crystallographic data and least-squares residuals for the crystal structure of **2**. Diffraction data for **3** were collected on a Siemens/STOE AED2 four-circle diffractometer. An absorption correction based on ψ-scans was applied. Three standard reflections were measured every 60 min showing no decay. The structure was solved by direct methods and refined on $|F_o|^2$ using the SHELXL93 program.[8] All of the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions and refined as riding atoms [C−H, 0.96 Å] with their thermal parameters set up to 1.2 times the U_{eq} value for the parent atoms. Weights, *w*, were set equal to $[\sigma_c^2(F_o^2) + (gP)^2]^{-1}$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$ and $g = 0.0400$. A difference map following convergence showed only one peak higher than 1 e/Å^3 (1.08) lying at 1.2 Å of the Pd(1) atom (minimum difference density of −0.55 e/Å^3).

Chart 1



Results and Discussion

Reactions of *cis*-[M(C$_6$F$_5$)$_2$(THF)$_2$] (M = Pd, Pt) with 2-Haloaniline (C$_6$H$_6$NX, X = F, Cl, Br, I). In our attempts to prepare complexes containing halocarbon ligands we have used the 2-haloaniline family, C$_6$H$_6$NX (X = F, Cl, Br, I; see Chart 1a). The nitrogen atom of these ligands must displace one of the THF groups of the starting material, leaving the halogen atom suitably disposed to replace the second THF group to establish a C−X→M bond. As mentioned above, the stability of the halocarbon complex formed should be favored by the chelating nature of the halocarbon ligand. Moreover, the higher strength of the X−C (arene) bond can prevent the cleavage of the C−X bond with oxidative addition to the metal center.

Thus, the reactions of complexes *cis*-[M(C$_6$F$_5$)$_2$(THF)$_2$] (M = Pd, Pt) with 2-haloaniline have been carried out in a 1:1 molar ratio using CH$_2$Cl$_2$ as a solvent. After 15 min of stirring, the solvent is evaporated to dryness yielding a solid. Spectroscopic and analytical data of the solids show that only for the 2-iodoaniline (R−I) the expected complexes, *cis*-[M(C$_6$F$_5$)$_2$(R−I)] [M = Pd (**1**), Pt (**2**)], have been formed. For the other 2-haloanilines a mixture of compounds is obtained. We have been unable to separate the components of this mixture in which, in addition to the starting materials, the complexes *cis*-[M(C$_6$F$_5$)$_2$(C$_6$H$_6$NX)$_2$] and *cis*-[M(C$_6$F$_5$)$_2$(C$_6$H$_6$NX)(THF)] probably are present. Attempts to prepare the complexes *cis*-[M(C$_6$F$_5$)$_2$(C$_6$H$_6$NX)], analogous to **1** and **2**, by changing conditions such as reaction time or solvent have proved unsuccessful.

These results confirm the higher basicity of the iodine which is able to compete successfully with the THF groups, leading to the formation of the R−I→M bond.[4c] Even for the complexes **1** and **2**, the presence in the NMR spectra of very small signals could suggest the presence of some other complex such as *cis*-[M(C$_6$F$_5$)$_2$(R−I)$_2$] (signals for THF are not observed) acting as an impurity and worsening slightly the analytical data (see Experimental Section).

The ^{1}H NMR spectra of **1** and **2** show only signals for the R−I ligand. The signal corresponding to the amminic protons is a singlet that, for complex **2**, has platinum satellites because of coupling with the ^{195}Pt nucleus ($^2J_{Pt-H} = 37$ Hz). The equivalence of the hydrogen nuclei for the NH$_2$ fragment indicates that a mirror plane is present in the molecule on the NMR time scale. This mirror plane can also be inferred from the ^{19}F NMR spectra in which the two pentafluorophenyl groups are inequivalent, displaying an AA′MM′X spin system.

Crystal Structure of the Complex *cis*-[Pt(C$_6$F$_5$)$_2$(R−I)]·$^1/_4$CHCl$_3$ (2·1/4CHCl$_3$). There are two molecules of **2** in the crystallographic asymmetric unit. A drawing of these two molecules (**2a** and **2b**) showing the atom labeling scheme used is depicted in Figure 1 (top and bottom, respectively). Selected bond distances and angles for **2a** and **2b** are given in Table 2. Fractional atomic coordinates and their estimated standard deviation are listed in Table 3. The structural features of **2a**

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(7) Crystallytics Company, P.O. Box 82286, Lincoln, NE.

(8) Sheldrick, G. M. SHELXTL 93. *J. Appl. Crystallogr.*, in press.

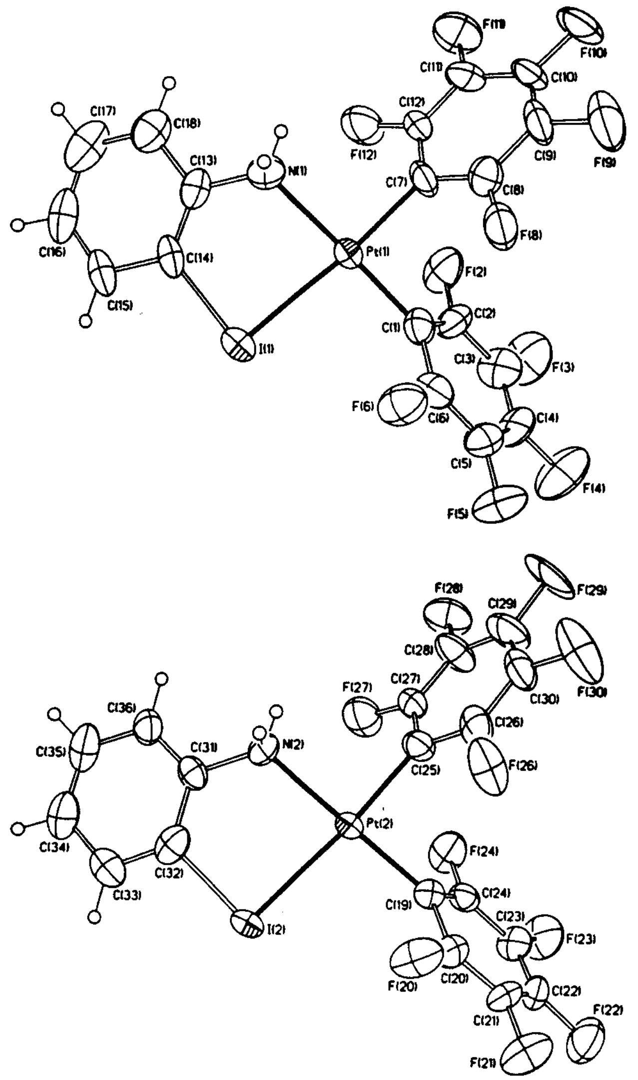

Figure 1. Drawing of the two molecules of complex **2** showing the atom-labeling scheme.

Table 2. Selected Bond Distances and Angles for Complex **2**

molecule 1		molecule 2	
	Distances (Å)		
Pt(1)−I(1)	2.620(1)	Pt(2)−I(2)	2.610(1)
Pt(1)−C(1)	1.990(13)	Pt(2)−C(19)	2.013(13)
Pt(1)−C(7)	1.990(13)	Pt(2)−C(25)	1.981(13)
Pt(1)−N(1)	2.132(12)	Pt(2)−N(2)	2.128(11)
I(1)−C(14)	2.101(15)	I(2)−C(32)	2.092(14)
Pt(1)⋯H(2b)	2.77(1)	Pt(2)⋯H(1b)	2.79(1)
	Angles (deg)		
C(1)−Pt(1)−C(7)	88.4(6)	C(19)−Pt(2)−C(25)	89.0(6)
C(1)−Pt(1)−N(1)	177.2(5)	C(19)−Pt(2)−N(2)	177.9(5)
C(7)−Pt(1)−N(1)	91.8(5)	C(25)−Pt(2)−N(2)	90.2(5)
I(1)−Pt(1)−C(1)	96.9(4)	I(2)−Pt(2)−C(19)	96.7(4)
I(1)−Pt(1)−C(7)	174.7(4)	I(2)−Pt(2)−C(25)	174.3(4)
I(1)−Pt(1)−N(1)	83.0(3)	I(2)−Pt(2)−N(2)	84.1(3)
Pt(1)−I(1)−C(14)	88.1(3)	Pt(2)−I(2)−C(32)	89.0(4)

and **2b** are very similar. In both cases, the platinum atom has a slightly distorted square-planar environment formed by the two *cis* pentafluorophenyl groups and the iodoaniline which is acting as a chelating didentate ligand. The Pt−C_{ipso} distances are in the range found in other pentafluorophenyl platinum complexes.[9] The Pt−N distances are also similar to those shown in previously reported complexes.[2i,10]

The Pt−I distances are 2.620(1) Å for **2a** and 2.610(1) Å for **2b**. As far as we know, no structure containing a bond between Pt and the iodine of an iodocarbon has previously been reported. In addition, very few structures of iodocarbon complexes of any transition metal can be found in the literature,[11] and the Pt−I distances found in **2a** and **2b** are shorter than any other M−I−(C). In fact, these distances are similar or even shorter than Pt−I distances found in complexes in which the iodine ligand is acting in either a bridging or a terminal fashion.[12] The I−C distance and Pt−I−C angles in **2** are similar to those found in other transition metal-iodocarbon ligand complexes.

Molecules **2a** and **2b** lie in parallel planes [the dihedral angle between the two square-planar environments is 0.6(3)°]. The amminic hydrogen atoms have been placed geometrically, assuming an sp^3 hybridization for the nitrogen and a N−H distance of 0.90 Å. The distances between the platinum atom of one molecule and one of the amminic hydrogen atoms of the other are Pt(1)−H(2b) 2.79 Å and Pt(2)−H(1b) 2.79 Å, and the angles Pt(1)−H(2b)−N(2) 161° and Pt(2)−H(1b)−N(1) 160° (see Figure 2). These short distances suggest that an intermolecular Pt⋯H interaction is present. The origin of such interaction is due to the basic character of the metal center (which is able to donate electron density from its $5d_z{}^2$ orbital) and the slightly weak acid characteristics of the amminic hydrogen. There are few examples of this kind of interaction $M \rightarrow H$,[13] which formally would possess a hydrogen-bonding type of three center−four electron electronic configuration.

The existence of the Pt⋯H interaction and concomitant proximity of the two molecules require that the dihedral angles between the best planes of the square-planar environment of the platinum and the corresponding C_6F_5 groups take a value lower (around 60°) than that usually found in other pentafluorophenyl platinum(II) complexes (70−80°).[9]

There is no evidence of the presence of the Pt⋯H interaction in solution since, as previously mentioned, the ^1H NMR spectrum of **2** shows only one signal for both amminic hydrogen atoms with ^{195}Pt satellites due to the Pt−N bond. In any event, the presence of the Pt⋯H interaction in solution seems very unlikely.

Reaction of *cis*-$[M(C_6X_5)_2(THF)_2]$ (M = Pd, Pt; X = F, Cl) with 2-Benzoylpyridine ($C_{12}H_9NO$, R−C(O)Ph). Reactions identical to those described for the preparation of complexes **1** and **2**, but using the ligand 2-benzoylpyridine ($C_{12}H_9NO$, R−C(O)Ph−see Chart 1b), lead to the preparation

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) for **2**$\cdot{}^1/_4CHCl_3$^{a}

	x	y	z	U_{eq}
Pt(1)	1881(1)	1215(1)	2417(1)	35(1)
Pt(2)	1888(1)	4401(1)	2709(1)	33(1)
I(1)	−371(1)	908(1)	2302(1)	49(1)
I(2)	−353(1)	4016(1)	2717(1)	44(1)
C(1)	2043(12)	415(10)	3498(10)	43(3)
C(2)	2646(14)	−314(12)	3475(11)	56(4)
C(3)	2774(15)	−853(12)	4237(13)	65(5)
C(4)	2245(16)	−621(14)	5072(12)	70(5)
C(5)	1625(14)	125(13)	5135(11)	60(4)
C(6)	1510(12)	630(12)	4378(11)	52(4)
F(2)	3177(8)	−603(8)	2677(6)	73(3)
F(3)	3395(11)	−1581(9)	4145(9)	105(4)
F(4)	2358(12)	−1130(9)	5815(8)	104(4)
F(5)	1097(9)	375(8)	5963(6)	84(3)
F(6)	894(8)	1361(7)	4496(6)	67(3)
C(7)	3588(11)	1543(11)	2421(11)	46(4)
C(8)	4242(12)	2051(11)	3199(11)	49(4)
C(9)	5433(12)	2271(12)	3182(12)	57(4)
C(10)	6002(12)	1937(14)	2433(14)	64(5)
C(11)	5362(13)	1421(14)	1609(12)	62(5)
C(12)	4195(12)	1246(13)	1637(10)	53(4)
F(8)	3755(7)	2412(7)	3987(6)	64(3)
F(9)	6037(8)	2784(8)	3967(8)	86(3)
F(10)	7158(7)	2145(9)	2426(8)	89(4)
F(11)	5930(9)	1106(10)	837(8)	103(4)
F(12)	3636(8)	731(9)	836(6)	79(3)
N(1)	1706(10)	1996(9)	1224(9)	56(3)
C(13)	729(11)	1660(10)	571(9)	40(3)
C(14)	−264(11)	1184(10)	872(10)	44(4)
C(15)	−1281(12)	887(12)	282(11)	55(4)
C(16)	−1176(15)	1068(13)	−658(12)	64(5)
C(17)	−160(18)	1515(12)	−990(11)	70(5)
C(18)	776(14)	1798(12)	−388(11)	57(4)
C(19)	1992(11)	5220(10)	1616(9)	37(3)
C(20)	1480(12)	4827(11)	694(10)	45(3)
C(21)	1562(12)	5358(12)	−42(9)	47(4)
C(22)	2077(12)	6324(12)	63(10)	47(4)
C(23)	2540(13)	6759(11)	938(11)	51(4)
C(24)	2478(11)	6183(11)	1679(9)	42(3)
F(20)	946(8)	3876(6)	545(6)	62(2)
F(21)	1070(9)	4938(7)	−905(6)	73(3)
F(22)	2103(9)	6880(8)	−658(6)	74(3)
F(23)	3085(9)	7707(7)	1076(7)	77(3)
F(24)	2983(8)	6651(7)	2535(6)	65(3)
C(25)	3589(11)	4609(11)	2804(11)	46(4)
C(26)	4268(12)	4247(11)	2094(11)	49(4)
C(27)	4222(11)	5177(12)	3595(10)	45(4)
C(28)	5383(12)	5336(13)	3692(12)	60(5)
C(29)	6012(13)	4950(15)	2980(14)	73(5)
C(30)	5450(12)	4391(12)	2177(13)	57(4)
F(26)	3757(7)	3699(7)	1308(7)	71(3)
F(27)	3644(7)	5583(8)	4316(6)	69(3)
F(28)	5950(8)	5901(9)	4466(7)	93(4)
F(29)	7164(7)	5067(9)	3084(9)	102(4)
F(30)	6051(8)	4004(9)	1469(9)	104(4)
N(2)	1803(10)	3584(9)	3898(8)	46(3)
C(31)	819(10)	3572(9)	4494(9)	34(3)
C(32)	−227(12)	3710(10)	4127(9)	43(3)
C(33)	−1204(12)	3645(12)	4677(11)	53(4)
C(34)	−1101(15)	3464(13)	5630(11)	64(5)
C(35)	−59(14)	3347(12)	5994(11)	62(5)
C(36)	889(12)	3419(10)	5423(9)	45(3)
C(40)	5973(26)	7913(16)	2054(15)	127(18)
Cl(1)	6037(27)	6891(15)	1317(17)	135(6)
Cl(2)	6080(28)	8945(16)	1540(20)	135(6)
Cl(3)	6187(26)	7964(18)	3201(14)	135(6)
Cl(4)	7122(22)	7451(23)	2465(24)	199(11)
Cl(5)	6284(26)	9164(16)	2241(27)	199(11)
Cl(6)	5732(24)	7436(27)	897(18)	199(11)

^{a} U(eq) is defined as one-third the trace of the orthogonalized U_{ij} tensor.

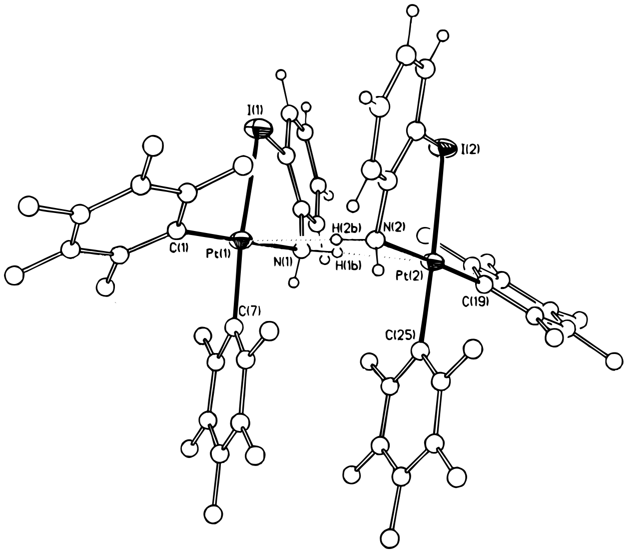

Figure 2. Perspective of the two molecules of complex **2** showing the Pt−H interactions.

of the complexes *cis*-[M(C_6F_5)$_2${R−C(O)Ph}] [M = Pd, X = F (**3**); M = Pt, X = F (**4**), Cl (**5**)]. Compounds **3**−**5** are obtained as strongly colored solids, yellow for the palladium and red for the platinum complexes.

In a previous work we reported the preparation and structural characterization of *cis*-[Pt(C_6F_5)$_2$(R-CH_2Ph)] (R-CH_2Ph = 2-benzylpyridine; see Chart 1c) in which the four coordination of the platinum center is achieved through an η^2-phenyl−Pt interaction.[2i] The ligand 2-benzoylpyridine is structurally similar to bzpy. Nevertheless, for R−C(O)Ph, besides the phenyl group there is also an oxygen atom that is able to donate electron density in the same way as the iodine atom in R−I. Due to the higher basicity of the O atom with respect to the phenyl group and the higher rigidity of the py−CO−Ph skeleton in R−C(O)Ph than that of py-CH_2-Ph, it is more likely that in complexes **3**−**5** a bond Pt−O=C is present. Infrared spectra of **3**−**5** confirm the existence of this bond since there is a decrease in ν(CO) from 1671 cm^{-1} in the free ligand to about 1550 cm^{-1} in the complexes since the coordination of the oxygen atom to the metal center causes the CO bond to weaken.[14]

The most important feature in the ^{1}H NMR spectra of **3**−**5** is the absence of signals for THF, which has been completely displaced by the ligand R−C(O)Ph. ^{19}F NMR spectra of **3** and **4** show the inequivalence of the two C_6F_5 groups, which appear as AA′MM′X spin systems. Again, these spectra suggest the existence of a symmetry plane on the NMR time scale that would contain the square-planar environment of the metal atom.

Crystal Structure of Complex *cis*-[Pd(C_6F_5)$_2${R−C(O)Ph}] (3). In this case, as for compound **2**, there are two almost identical molecules in the crystallographic asymmetric unit. Figure 3 shows a drawing of both molecules (**3a** (left) and **3b** (right)) with the atom-labeling scheme. Tables 4 and 5 list

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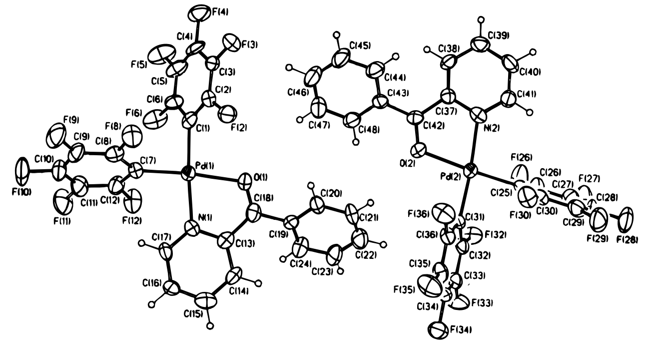

Figure 3. Drawing of the two molecules of complex **3** as they appear in the crystal structure showing the atom-labeling scheme.

Table 4. Selected Bond Distances and Angles for **3**

molecule 1		molecule 2	
	Distances (Å)		
Pd(1)−O(1)	2.156(6)	Pd(2)−O(2)	2.117(6)
Pd(1)−C(1)	2.012(9)	Pd(2)−C(25)	1.988(8)
Pd(1)−C(7)	1.984(9)	Pd(2)−C(31)	1.990(8)
Pd(1)−N(1)	2.099(7)	Pd(2)−N(2)	2.103(7)
C(18)−O(1)	1.224(10)	C(42)−O(2)	1.228(9)
	Angles (deg)		
C(1)−Pd(1)−C(7)	88.3(4)	C(25)−Pd(2)−C(31)	85.3(3)
C(1)−Pd(1)−N(1)	174.5(3)	C(31)−Pd(2)−N(2)	174.7(3)
C(7)−Pd(1)−N(1)	97.1(3)	C(25)−Pd(2)−N(2)	99.2(3)
O(1)−Pd(1)−C(1)	97.1(3)	O(2)−Pd(2)−C(31)	98.4(3)
O(1)−Pd(1)−C(7)	174.1(3)	O(2)−Pd(2)−C(25)	176.1(3)
O(1)−Pd(1)−N(1)	77.5(3)	O(2)−Pd(2)−N(2)	77.0(3)
Pd(1)−O(1)−C(18)	113.3(6)	Pd(2)−O(2)−C(42)	117.6(6)
Pd(1)−N(1)−C(13)	114.3(6)	Pd(2)−N(2)−C(37)	113.5(6)
Pd(1)−N(1)−C(17)	127.6(6)	Pd(2)−N(2)−C(41)	126.2(7)
N(1)−C(13)−C(18)	113.9(8)	N(2)−C(37)−C(42)	114.9(8)
O(1)−C(18)−C(13)	120.6(8)	O(2)−C(42)−C(37)	116.4(8)
O(1)−C(18)−C(19)	119.8(9)	O(2)−C(42)−C(43)	120.3(8)
C(13)−C(18)−C(19)	119.6(9)	C(37)−C(42)−C(43)	123.3(8)

selected bond distances and angles and fractional atomic coordinates with their estimated standard deviations.

In both molecules the palladium atom has a slightly distorted square-planar environment formed by the two *cis* C_6F_5 groups and the 2-benzoylpyridine ligand acting as a chelating didentate ligand. The Pd−C[9] and Pd−N[2i,10] distances are in the range found in similar compounds. The Pd(1)−O(1) and Pd(2)−O(2) distances are 2.156(6) and 2.117(6) Å, respectively. These values are similar or slightly higher than others found in Pd complexes containing chelate ligands of the type Pd−C∼C=O or Pd−N∼C=O.[15] The C(18)−O(1) and C(42)−O(2) distances are 1.224(10) and 1.228(9) Å, slightly shorter than those reported in related complexes.[15] The mean value given in the literature for a C=O bond in C_{ar}−CO−C_{ar} surroundings in pure organic compounds is 1.230 Å.[16] From these values it is possible to deduce that the coordination of the oxygen atom to the metal center does not affect perceptibly the length of the C−O bond.

The five-membered rings formed by the Pd, O, and N atoms and the two C atoms bonded to the latter [C(13) and C(18) for **3a** and C(37) and C(42) for **3b**] are almost perfectly planar and are coplanar with the square-planar environment of the metal (dihedral angles are 0.4(2)° for **3a** and 1.0(2)° for **3b**). This structural feature, due to the characteristics of the R−C(O)Ph ligand and its coordination in a chelate fashion, requires that some angles around the atoms involved in the five-membered ring be slightly distorted with respect to the ideal geometry (O(1)−Pd(1)−N(1), 77.5(3)°; O(2)−Pd(2)−N(2), 77.0(3)°; Pd(1)−N(1)−C(13), 114.3(6)°; Pd(2)−N(2)−C(37), 113.7(6)°).

Finally, **3a** and **3b** are almost coplanar (dihedral angle 6.3(2)°), but in this case no intermolecular interaction is observed.

Reactivity of Complexes 1−5 toward Neutral and Anionic Ligands. A proof of the weakness of the N$\frown$X→M bond is obtained when neutral or anionic ligands are added to solutions of complexes **1**−**5**. In most of the cases, the new ligand L added is able to displace the iodine or oxygen interaction forming a new M−L bond. Thus, when CO is bubbled through a solution of the iodocarbon complex **2** in CH_2Cl_2 for 5 min, the removal of the solvent yields a solid that is identified as *cis*-[Pt(C_6F_5)$_2$(R−I)(CO)] (**6**). The presence of the ligand CO coordinated to the platinum center is confirmed by the infrared spectrum that shows a sharp absorption at 2123 cm^{-1} corresponding to ν(CO). Under the same conditions it is not possible to prepare the analogous *cis*-[Pd(C_6F_5)$_2$(R−I)(CO)]. Nevertheless, this behavior is more likely due to the lack of stability of the Pd−CO bond rather than to the strength of the N$\frown$X→Pd one.[2b] The ^{1}H NMR spectrum of **6** shows that the ligand R−I is still bonded to the metal atom because of the presence of ^{195}Pt−^{1}H coupling in the amminic proton signal ($^2J_{Pt-H}$ = 35 Hz). The ^{19}F NMR spectrum indicates the presence of a molecular mirror plane on the NMR time scale, even at −70 °C, since two AA′MM′X spin systems are observed, one for each pentafluorophenyl group.

If the bubbling of CO through solutions of **2** is maintained over longer periods, the carbon monoxide is even able to displace completely the ligand R−I, resulting in the formation of *cis*-[Pt(C_6F_5)$_2$(CO)$_2$].[2b] Even in short duration reactions, complex **6** is always impurified with small amounts of the bis(carbonyl) complex, the signals of which can be identified and discarded in the NMR and infrared spectra.

The lability not only of the M−I bond but also of the M−N bond in **1** and **2** becomes apparent once more in their reactions with CH_3CN and Br$^-$. The addition of an excess of CH_3CN to solutions of **1** and **2** produces the complete displacement of the iodoaniline ligand and the formation of the corresponding complexes *cis*-[M(C_6F_5)$_2$(CH_3CN)$_2$].[17] If CH_3CN is added in a 1:1 molar ratio, a mixture of *cis*-[M(C_6F_5)$_2$(CH_3CN)$_2$], *cis*-[M(C_6F_5)$_2$(R−I)(CH_3CN)], and starting material is obtained. Reaction of **2** with NBu_4Br in a 1:1 molar ratio results in the formation of [NBu_4]$_2$[Pt_2(μ-Br)$_2$(C_6F_5)$_4$],[18] also with elimination of R−I due to the ability of the Br$^-$ to act as a bridging ligand.

The cleavage of the Pt−O bond in **4** is also easily induced by CO and PPh_3 ligands. When CO is bubbled or PPh_3 is added in a 1:1 molar ratio to solutions of **4** in CH_2Cl_2, the strong red color fades almost instantaneously. The removal of the solvent yields solids identified as *cis*-[Pt(C_6F_5)$_2${R−C(O)Ph}L] [L = CO (**7**) or PPh_3 (**8**)]. The presence of the new ligands in complexes **7** and **8** is confirmed by their infrared spectra, especially for the carbonyl complex for which a sharp ν(CO) absorption is observed at 2128 cm^{-1}. Moreover, for both complexes the signal due to the ketonic group of the R−C(O)Ph ligand shows a displacement to higher frequencies (1681 cm^{-1}) with respect to the starting complex **4** (1558 cm^{-1}) indicating that the C=O→Pt bond is no longer present. Again, the preparation of the complex analogous to **7**, *cis*-[Pd(C_6F_5)$_2${R−C(O)Ph}(CO)], is not possible under the same conditions for the reasons mentioned above. It is also noteworthy that the Pt−N(pyridine) bond is more robust than the Pt−N(aniline)

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Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **3**[a]

	x	y	z	U_{eq}		x	y	z	U_{eq}
Pd(1)	857(1)	10532(1)	199(1)	35(1)	C(36)	1682(3)	4634(9)	2655(3)	38(2)
Pd(2)	1628(1)	2365(1)	2125(1)	35(1)	C(37)	1917(3)	1716(9)	1264(3)	36(2)
C(1)	1084(3)	9559(9)	−306(3)	36(2)	C(38)	2044(3)	1005(9)	920(3)	42(3)
C(2)	1525(4)	8867(9)	−278(3)	42(3)	C(39)	2203(4)	−225(10)	974(3)	50(3)
C(3)	1694(4)	8148(9)	−607(3)	44(3)	C(40)	2230(4)	−694(10)	1379(3)	51(3)
C(4)	1413(5)	8089(10)	−982(3)	51(3)	C(41)	2064(4)	17(10)	1714(3)	45(3)
C(5)	959(4)	8751(11)	−1027(3)	53(3)	C(42)	1754(3)	3067(9)	1245(3)	35(2)
C(6)	814(3)	9479(10)	−696(3)	44(3)	C(43)	1790(3)	3852(8)	867(3)	35(2)
C(7)	829(3)	12062(8)	−164(3)	38(2)	C(44)	2203(4)	3754(10)	602(3)	50(3)
C(8)	1248(3)	12610(9)	−329(3)	41(2)	C(45)	2219(5)	4576(11)	270(3)	64(3)
C(9)	1237(4)	13701(10)	−568(3)	47(3)	C(46)	1861(5)	5489(12)	194(3)	72(4)
C(10)	784(5)	14316(10)	−628(3)	58(3)	C(47)	1451(4)	5597(10)	457(3)	64(3)
C(11)	343(4)	13809(11)	−478(3)	57(3)	C(48)	1429(4)	4789(9)	795(3)	45(3)
C(12)	375(4)	12682(10)	−256(3)	47(3)	F(2)	1821(2)	8876(5)	91(2)	52(2)
C(13)	627(3)	10611(9)	1099(3)	36(2)	F(3)	2148(2)	7527(5)	−563(2)	67(2)
C(14)	544(3)	11031(9)	1501(3)	39(2)	F(4)	1560(3)	7353(6)	−1305(2)	76(2)
C(15)	412(3)	12302(10)	1559(3)	47(3)	F(5)	680(2)	8707(7)	−1397(2)	83(2)
C(16)	381(3)	13067(9)	1207(3)	41(2)	F(6)	374(2)	10123(6)	−763(2)	65(2)
C(17)	492(3)	12591(9)	813(3)	41(2)	F(8)	1713(2)	12048(5)	−262(2)	59(2)
C(18)	753(3)	9287(9)	1000(3)	42(2)	F(9)	1660(2)	14185(6)	−715(2)	73(2)
C(19)	707(3)	8300(9)	1332(3)	38(2)	F(10)	752(3)	15412(6)	−845(2)	84(2)
C(20)	1103(4)	7433(9)	1395(3)	49(3)	F(11)	−103(2)	14415(6)	−546(2)	85(2)
C(21)	1078(4)	6530(10)	1708(3)	61(3)	F(12)	−67(2)	12250(5)	−109(2)	62(2)
C(22)	660(5)	6448(10)	1947(4)	65(3)	F(26)	954(2)	87(6)	2413(2)	73(2)
C(23)	250(5)	7262(11)	1872(3)	67(3)	F(27)	1046(3)	−1404(7)	3091(2)	92(2)
C(24)	275(4)	8201(11)	1569(3)	57(3)	F(28)	1848(3)	−1162(6)	3670(2)	88(2)
C(25)	1697(3)	1214(8)	2623(3)	33(2)	F(29)	2544(2)	692(6)	3564(2)	74(2)
C(26)	1355(4)	263(9)	2692(3)	46(3)	F(30)	2454(2)	2228(5)	2889(2)	57(2)
C(27)	1403(4)	−514(10)	3042(3)	54(3)	F(32)	586(2)	2635(5)	2643(2)	54(2)
C(28)	1814(5)	−376(11)	3327(3)	56(3)	F(33)	328(2)	4378(5)	3205(2)	65(2)
C(29)	2150(4)	547(11)	3268(3)	52(3)	F(34)	975(2)	6276(5)	3435(2)	64(2)
C(30)	2097(4)	1334(9)	2923(3)	41(2)	F(35)	1883(2)	6462(5)	3059(2)	70(2)
C(31)	1382(3)	3620(8)	2536(3)	30(2)	F(36)	2140(2)	4768(5)	2479(2)	59(2)
C(32)	920(3)	3582(9)	2737(3)	37(2)	O(1)	898(2)	9000(6)	649(2)	43(2)
C(33)	782(4)	4458(9)	3027(3)	47(3)	O(2)	1588(2)	3506(6)	1572(2)	42(2)
C(34)	1109(4)	5432(9)	3142(3)	43(2)	N(1)	625(3)	11386(7)	758(2)	34(2)
C(35)	1562(3)	5524(9)	2952(3)	41(2)	N(2)	1916(3)	1180(7)	1658(2)	34(2)

[a] *U*(eq) is defined as one-third the trace of the orthogonalized U_{ij} tensor.

since the ligand R−C(O)Ph is not completely displaced from complex **4** when CO is bubbled through its solutions for longer periods.

The NMR spectra of **7** show a dynamic behavior for this complex in solution. In the ^{1}H NMR spectrum at room temperature all the hydrogen nuclei of the R−C(O)Ph phenyl group in homologous positions are equivalent probably because it rotates about the C(O)−C_{ipso} bond. This rotation is not stopped even at −90 °C. The ^{19}F NMR spectrum at room temperature shows one AA′MM′X spin system for each pentafluorophenyl group. However, at −90 °C the spectrum shows two AFMRX spin systems since all the fluorine nuclei are inequivalent. These spectra suggest that the C_6F_5 groups rotate at room temperature and that at −90 °C this rotation is stopped or slow enough for the NMR technique to distinguish all the different fluorine nuclei. The ^{19}F NMR spectrum of **8** at room temperature shows the signals for two AFMRX spin systems, indicating that in this complex the C_6F_5 groups do not rotate probably because the triphenylphospine ligand is bulkier than carbon monoxide.

Conclusions

The behavior of the "*cis*-$M(C_6X_5)_2$" fragment as a moderate Lewis acid makes possible the use of the substrates *cis*-$[M(C_6X_5)_2(THF)_2]$ in the preparation of complexes containing unusual $N\frown X \rightarrow M$ bonds. The family of 2-haloanilines has been used for this purpose as nucleophiles. The number of known complexes containing halocarbon ligands is small mainly because of the limited basic character of the halogen atoms. This characteristic has been confirmed in this work since only for a haloaniline containing iodine is it possible to prepare and isolate the corresponding complex *cis*-$[M(C_6F_5)_2(R{-}I)]$ [M = Pd (**1**) or Pt (**2**)] because of the more basic nature of the iodine atom with respect to the other halogens. Complexes **1** and **2** are among the very few known halocarbon complexes of Pd and Pt. In any case, the M−I bonds in **1** and **2** are weak and easily broken by the addition of ligands such as CO, CH_3CN, or Br^-. The ketonic oxygen atom of the ligand 2-benzoylpyridine acts in a similar way as the iodine atom in R−I, which allows the synthesis of the complexes *cis*-$[M(C_6F_5)_2\{R{-}C(O)Ph\}]$ [M = Pd, X = F (**3**); M = Pt, X = F (**4**), Cl (**5**)]. Also, the M−O bond is easily displaced by the addition of ligands such as CO or PPh_3.

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Supporting Information Available: For the crystal structures of **2** and **3**, tables of crystal data and structure refinement, anisotropic displacement parameters, full tables of bond distances and angles, and tables of coordinates and isotropic thermal parameters for the hydrogen atoms (15 pages). Ordering information is available on any current masthead page.

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