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Synthesis and Reactivity of Binuclear Bis(μ-aryloxo) Complexes of Palladium and Platinum. Crystal Structure of $[NBu_4][Pt(C_6F_5)_2(OC_6H_4NO_2\text{-}p)(CO)]$

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The hydroxo complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-OH})\}_2]$ (M = Pd, Pt) react with phenols ROH (1:2 molar ratio) to give the bis(μ-aryloxo) complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-OR})\}_2]$ (M = Pd, Pt; R = C_6H_5, p-MeC_6H_4, p-$NO_2C_6H_4$, C_6F_5). The reaction of bis(μ-aryloxo) complexes with PPh_3 (1:2 molar ratio) gives the aryloxo monomer complexes $[NBu_4][M(C_6F_5)_2(OR)(PPh_3)]$ (M = Pd, Pt; R = p-$NO_2C_6H_4$, C_6F_5). The platinum monocarbonyl complexes $[NBu_4][Pt(C_6F_5)_2(OR)(CO)]$ (R = p-$NO_2C_6H_4$, C_6F_5) have also been prepared by reaction of the corresponding bis(μ-aryloxo) complexes with carbon monoxide at room temperature and normal pressure. $[NBu_4][Pd(C_6F_5)_3(CO)]$ is isolated in low yield from the reaction of $[NBu_4]_2[Pd(C_6F_5)_2(\mu\text{-}OC_6H_4NO_2\text{-}p)]$ with CO in the presence of water. The identity of the isolated complexes has been established by partial elemental analyses, conductance measurements, and spectroscopic (IR, ^1H, ^{19}F, ^{31}P) methods. A single-crystal diffraction study of $[NBu_4][Pt(C_6F_5)_2(OC_6H_4NO_2\text{-}p)(CO)]$ showed that coordination about platinum was approximately square-planar with the aryl rings tilted to avoid steric crowding.

Introduction

The chemistry of late transition metals alkoxides[1] has recently attracted growing attention partly because of their relevance to organic synthesis, where late-transition-metal alkoxides are believed to be involved,[2] and partly because of their recently discovered unique chemical reactions such as CO insertion into metal alkoxide bonds[3−6] and adduct formation with alcohols through strong hydrogen bonding.[7−11] Unfortunately, the synthesis and reactivity of palladium and platinum alkoxide and aryloxide complexes have been little explored, probably because it was thought that Pd−O and Pt−O bonds would be weak, but theoretical calculations have demonstrated that these bonds are of comparable strength to or stronger than the corresponding metal−carbon bonds.[12]

We have recently reported[13] on the synthesis of the bis(μ-methoxo) complex $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-OMe})\}_2]$, and we have now examined the reactivity of $[\{M(C_6F_5)_2(\mu\text{-OH})\}_2]^{2-}$ (M = Pd, Pt)[14,15] toward some phenols in order to form aryloxo−metal bonds. This paper deals with the synthesis of a number of bis(μ-aryloxo) complexes of palladium and platinum and their reactivity toward the neutral π-acceptor ligands triphenylphosphine and carbon monoxide, which leads to the formation of monomeric aryloxo complexes containing these ligands.

Experimental Section

Instrumental Measurements. C, H, and N analyses were performed with a Carlo Erba Model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance. Molar conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol dm^{-3}) with a Crison 525 conductimeter. The NMR spectra were recorded on a Bruker AC 200E (^1H) or Varian Unity 300 (^{19}F, ^{31}P) spectrometer, using $SiMe_4$, $CFCl_3$, and H_3PO_4 as standards, respectively. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets.

Materials. The precursors $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-OH})\}_2]$ (M = Pd, Pt) were prepared as described elsewhere.[14,15] Solvents were dried by the usual methods.

Preparation of Complexes 1−4, 7, and 8. To a solution of $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-OH})\}_2]$ (0.071 mmol) in dichloromethane

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(6 cm^3) was added the corresponding phenol, ROH (0.142 mmol), with constant stirring at room temperature for 1 h. After partial evaporation of the solvent under reduced pressure, addition of hexane caused the precipitation of white or yellowish solids which were collected by filtration and crystallized from dichloromethane−hexane. Complex **1**: yield 93%; mp 210 °C dec; Λ_M 197 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 775, 765 (Pd−C_6F_5). Anal. Calcd for $C_{68}H_{82}N_2F_{20}O_2Pd_2$: C, 52.6; H, 5.3; N, 1.8. Found: C, 52.0; H, 5.4; N, 1.8. Complex **2**: yield 90%; mp 208 °C dec; Λ_M 191 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 785, 770 (Pd−C_6F_5). Anal. Calcd for $C_{70}H_{86}N_2F_{20}O_2Pd_2$: C, 53.2; H, 5.5; N, 1.8. Found: C, 52.7; H, 5.5 N, 1.8. Complex **3**: yield 88%; mp 203 °C dec; Λ_M 199 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 795, 780 (Pd−C_6F_5). Anal. Calcd for $C_{68}H_{80}N_4F_{20}O_6Pd_2$: C, 49.7; H, 4.9; N, 3.4. Found: C, 49.1; H, 5.2; N, 3.5. Complex **4**: yield 95%; mp 230 °C dec; Λ_M 212 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 795, 780 (Pd−C_6F_5). Anal. Calcd for $C_{68}H_{72}N_2F_{30}O_2Pd_2$: C, 47.2; H, 4.2; N, 1.6. Found: C, 46.7; H, 4.5; N, 1.7. Complex **7**: yield 93%; mp 183 °C dec; Λ_M 227 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 810, 795 (Pd−C_6F_5). Anal. Calcd for $C_{68}H_{80}N_4F_{20}O_6Pt_2$: C, 44.9; H, 4.4; N, 3.1. Found: C, 44.7; H, 4.8; N, 3.1. Complex **8**: yield 90%; mp 221 °C dec; Λ_M 202 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 810, 795 (Pd−C_6F_5). Anal. Calcd for $C_{68}H_{72}N_2F_{30}O_2Pt_2$: C, 42.8; H, 3.8; N, 1.5. Found: C, 42.6; H, 4.2; N, 1.5.

Preparation of Complexes 5 and 6. To a solution of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.063 mmol) in toluene (10 cm^3) was added the corresponding phenol, ROH (0.126 mmol). The resulting solution was kept under reflux with constant stirring for 7 h. The solvent was completely evaporated under vacuum, the residue treated with 2-propanol, and then the solid collected by filtration and air-dried. Both complexes were recrystallized from dichloromethane−hexane. Complex **5**: yield 60%; mp 226 °C dec; Λ_M 198 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 805, 790 (Pt−C_6F_5). Anal. Calcd for $C_{68}H_{82}N_2F_{20}O_2Pt_2$: C, 47.2; H, 4.8; N, 1.6. Found: C, 46.8; H, 5.1; N, 1.5. Complex **6**: yield 70%; mp 215 °C dec; Λ_M 208 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 805, 790 (Pt−C_6F_5). Anal. Calcd for $C_{70}H_{86}N_2F_{20}O_2Pt_2$: C, 47.8; H, 4.9; N, 1.6. Found: C, 47.3; H, 5.1; N, 1.6.

Preparation of Complexes 9−12. To a solution of the corresponding bis(μ-aryloxo) complex **3**, **4**, **7**, or **8** (0.055 mmol) in dichloromethane (6 cm^3) was added triphenylphosphine (0.110 mmol). After being stirred for 1 h at room temperature, the solution was concentrated to dryness; the residue was treated with hexane (**9**, **11**) or ether/hexane (**10**, **12**), and the complexes were collected by filtration and air-dried. Complex **9**: yield 77%; mp 180 °C dec; Λ_M 86 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 785, 765 (Pd−C_6F_5). Anal. Calcd for $C_{52}H_{55}N_2F_{10}O_3PPd$: C, 57.7; H, 5.1; N, 2.6. Found: C, 57.7; H, 5.4; N, 2.6. Complex **10**: yield 95%; mp 198 °C dec; Λ_M 95 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 785, 765 (Pd−C_6F_5). Anal. Calcd for $C_{52}H_{51}NF_{15}OPPd$: C, 55.4; H, 4.6; N, 1.2. Found: C, 54.8; H, 4.9; N, 1.3. Complex **11**: yield 65%; mp 238 °C dec; Λ_M 96 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 880, 775 (Pt−C_6F_5). Anal. Calcd for $C_{52}H_{55}N_2F_{10}O_3PPt$: C, 53.3; H, 4.7; N, 2.4. Found: C, 52.9; H, 5.1; N, 2.3. Complex **12**: yield 65%; mp 226°C dec; Λ_M 102 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 800, 775 (Pt−C_6F_5). Anal. Calcd for $C_{52}H_{51}NF_{15}OPPt$: C, 51.3; H, 4.2; N, 1.2. Found: C, 51.8; H, 4.6; N, 1.1.

Preparation of Complexes 13 and 14. Through a dichloromethane solution (15 cm^3) of the corresponding bis(μ-aryloxo) complex **7** or **8** (0.055 mmol) at room temperature was passed CO for 20 min. The mixture was evaporated to dryness under vacuum, the residue treated with hexane, and the solid collected by filtration. Crystals were obtained by recrystallization from dichloromethane-hexane. Complex **13**: yield 95%; mp 232 °C dec; Λ_M 89 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}): 2090 (ν(CO)), 810, 795 (Pt−C_6F_5). Anal. Calcd for $C_{35}H_{40}N_2F_{10}O_4Pt$: C, 44.8; H, 4.3; N, 3.0. Found: C, 44.8; H, 4.6; N, 3.0. Complex **14**: yield 88%; mp 244 °C dec; Λ_M 93 Ω^{-1} cm^2 mol^{-1}; IR (Nujol, cm^{-1}): 2085 (ν(CO)), 810, 795 (Pt−C_6F_5). Anal. Calcd for $C_{35}H_{36}NF_{15}O_2Pt$: C, 42.8; H, 3.7; N, 1.4. Found: C, 42.5; H, 3.9; N, 1.5.

Reaction of Complex 3 with CO in the Presence of Water. CO was passed through a dichloromethane (15 cm^3) solution of complex **3** (500 mg; 0.3045 mmol) and water (10.96 μL; 0.609 mmol) at room temperature for 20 min, and the metallic palladium which formed was removed by filtration. The resulting clear solution was vacuum-concentrated to ca. one-third the original volume. On addition of hexane a yellow solid formed which was collected by filtration and was identified as the starting complex **3**. The solution was then evaporated to dryness, and the residue was extracted with 2-propanol. On addition of a small amount of hexane a white precipitate formed (60 mg). The analytical and IR data for this white product [Anal. Found: C, 47.37; H, 4.32; N, 1.61. Calcd: C, 47.85; H, 4.13; N, 1.60. IR (Nujol, cm^{-1}): 2124 ν(CO), 1504, 1058, 1044, 952 (internal vibrations of C_6F_5), 790, 770 ("X-sensitive" mode of C_6F_5), 470 ν(Pd−CO)] were in agreement with those previously reported[16] for $[NBu_4][Pd(C_6F_5)_3(CO)]$. ^{19}F NMR data ($CFCl_3$, in $(CD_3)_2CO$), δ: −114.08 (m, 4F$_o$), −114.40 (m, 2F$_o$), −163.11 (t, 2F$_p$, J_{mp} 19.75 Hz), −164.62 (t, 1F$_p$, J_{mp} 19.75 Hz), −165.16 (m, 4F$_m$), −166.55 (m, 2F$_m$). The product behaved as a 1:1 electrolyte (Λ_M 90 Ω^{-1} cm^2 mol^{-1}) in acetone solution ($c \approx 5 \times 10^{-4}$ mol dm^{-3}).

X-ray Structure Determination. A crystal suitable for a diffraction study was grown from dichloromethane−diethyl ether. Details of data collection and refinement are given in Table 1.

Results and Discussion

The ready reactivity of $[\{MR_2(\mu\text{-}OH)\}_2]^{2-}$-type complexes (M = Ni, Pd, Pt; R = pentahalophenyl) toward protic electrophiles is in agreement with the high-field proton resonance of the OH bridges,[17] and they have been used for the synthesis of complexes of the types $[\{MR_2(\mu\text{-}L\text{-}L)\}_2]^{2-}$ (L-L = exobidentate ligand),[14,15,18] $[\{MR_2(L\text{-}L)]^-$ (L-L = endobidentate ligand),[13,19] or $[\{MR_2(\mu\text{-}X)\}_2]^{2-}$ (X = monodentate ligand).[20] The hydroxo complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (M = Pd or Pt) react with 2 molar equiv of phenols to give the corresponding anionic bis(μ-aryloxo) complexes **1**−**8** shown in Scheme 1, which are isolated as the tetrabutylammonium salts. The reaction occurs smoothly at room temperature for complexes **1**−**4**, **7**, and **8**, but reflux temperature is required for the preparation of **5** and **6**.

All the isolated complexes show the characteristic infrared absorptions of the pentafluorophenyl group[21]

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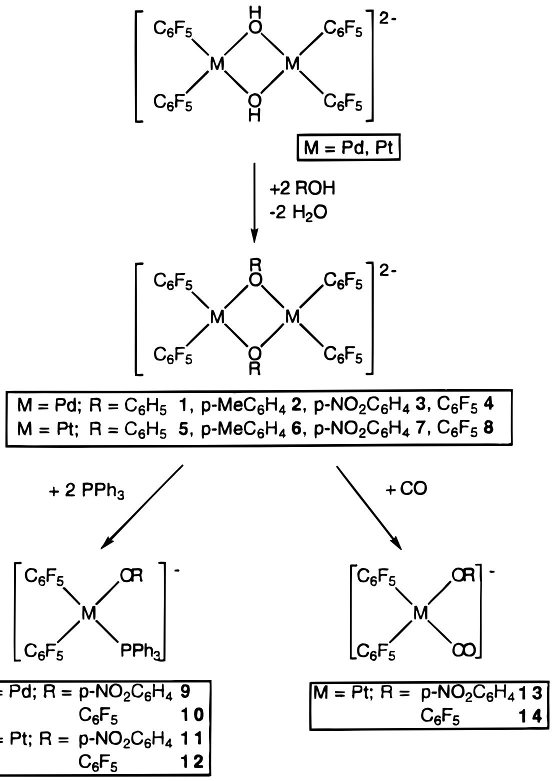
Table 1. Crystal Structure Determination Details

Crystal Data	
formula	$C_{35}H_{40}F_{10}N_2O_4Pt$
fw	937.8
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
cell dimens	
a (Å)	8.771(1)
b (Å)	21.766(3)
c (Å)	20.249(5)
α (deg)	90
β (deg)	90.97(2)
γ (deg)	90
cell vol (Å^3)	3865(1)
Z	4
D_{calc} (g cm^{-3})	1.61
F(000)	1856
monochromated Mo Kα radiation	
λ (Å)	0.710 73
μ (cm^{-1})	37.5
Data Collection	
cryst size (mm)	0.25 × 0.25 × 0.2
diffractometer	Enraf-Nonius CAD4
no. of reflns for calculating cell; θ_{min}, θ_{max} (deg)	25; 7, 10
scan mode for data collcn	$\theta - 2\theta$
data refln ranges, θ min and max (deg)	h, $0 \rightarrow 10$; k, $0 \rightarrow 25$; l, $-24 \rightarrow 24$, $2 \rightarrow 25$
tot. no. of reflns measd	7459
no. of unique reflns	6997
R_{int}	0.01
no. of significant reflns, $\lvert F^2 \rvert > 2\sigma(F^2)^a$	4673
max change in std reflns (%)	−0.9
decay corr	no
max, min abs corr	1.00, 0.86 from ψ scans
Structure Solution and Refinement	
non-H atoms located by	heavy atom methods, SHELXS-86
refinement by	full-matrix least squares, non-H atoms anisotropic, Enraf-Nonius MolEN programs
H atoms	fixed calcd posns, $U_{iso} = 1.3U_{eq}$ for parent atom
R	0.035
R'	0.036
S	1.1
no. of variables	469
no. of obsd reflcns	4673
max (Δ/σ)	0.03
max, min (Δ/ρ) (e Å^{-3})	+0.39, −0.14

[a] $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, $w = \sigma^{-2}(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized.

at ca. 1630 m, 1495 vs, 1050 s, 950 vs, and 800 cm^{-1}. The absorption at 800 cm^{-1}, which is related to the so-called "X-sensitive mode" in C_6F_5X (X = Cl, Br, I) molecules, is observed as a split band suggesting that the $M(C_6F_5)_2$ moiety has cis geometry.[22] Measurements of the molar conductivity in acetone indicate that complexes **1**−**8** behave as 2:1 electrolytes.[23] The ^1H and ^{19}F NMR spectra (Table 2) are consistent with the proposed formulae. The ^{19}F NMR spectra show the presence of four equivalent freely rotating C_6F_5 rings giving three resonances with relative intensities of 8:4:8 due to the *ortho*-, *para*-, and *meta*-F atoms, respectively. The spectra of complexes **4** and **8** show three additional signals (relative intensities of 4:4:2) from the two μ-C_6F_5O groups. As expected, the *ortho*-F signals of complexes **5**−**8** are flanked by the satellites due to coupling to ^{195}Pt.

Scheme 1



The reaction of the bis(μ-aryloxo) complexes **3**, **4**, **7**, and **8** with PPh_3 in 1:2 molar ratio leads to the formation of the monomeric aryloxo complexes $[M(C_6F_5)_2(OR)(PPh_3)]^-$ (**9**−**12**) (Scheme 1). Although the reaction of **1** with 2 molar equiv of PPh_3 was tried, the expected phenoxo−phosphine compound was not formed; instead a mixture of the previously known[24] $[Pd(C_6F_5)_2(PPh_3)_2]$ and the starting complex **1** was obtained.

Complexes **9**−**12** behave as 1:1 electrolytes[23] in acetone solution, and the *cis* arrangement of the C_6F_5 groups is supported by the split band observed in their IR spectra at ca. 800 cm^{-1}, due to the "X-sensitive" mode. The ^1H, ^{19}F, and ^{31}P NMR data for these complexes are listed in Table 3. The ^{19}F NMR spectra indicate the presence of two different pentafluorophenyl groups.

The reaction of the bis(μ-aryloxo)platinum complexes **7** and **8** with CO (1 atm) at room temperature, in dichloromethane solution, yields the monocarbonyl complexes **13** and **14** shown in Scheme 1. A wide range of platinum(II) carbonyl derivatives are known.[25] Complexes **13** and **14** are air- and moisture-stable solids which in their IR spectra show a strong absorption at ca. 2090 cm^{-1} due to ν(CO) of a terminal carbonyl ligand. The previously reported[25] *cis*-$[Pt(C_6F_5)_2X(CO)]^-$ compounds (X = Cl, Br, I) give a similar band at 2090−2080 cm^{-1}. The ^{19}F NMR spectra show two nonequivalent C_6F_5 groups corroborating the *cis* arrangement of these groups, one trans to CO and one trans to OR; this is also supported by the split band observed at ca. 800 cm^{-1}. In the ^{19}F NMR spectrum the resonance signals at lower field are assigned to the C_6F_5 group trans to CO because of the greater π-acceptor character of the

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Table 2. NMR Spectroscopic Data[a,b] (*J* in Hz) for Complexes 1−8

complex	$^1H^c$	^{19}F
1	6.48 (m, 8 H, $H_o + H_m$) 6.06 (t, 2 H, H_p, *J* 7.2)	−113.6 (d, 8 F_o, *J* 29.1) −166.6 (t, 4 F_p, *J* 19.8) −167.6 (m, 8 F_m)
2	6.42 (d, 4 H, H_o, *J* 8.3) 6.24 (d, 4 H, H_m, *J* 8.3) 1.87 (s, 6 H, CH_3)	−113.5 (d, 8 F_o, *J* 30.5) −166.8 (t, 4 F_p, *J* 21.2) −167.7 (m, 8 F_m)
3	7.54 (d, 4 H, H_o, *J* 9.0) 6.53 (d, 4 H, H_m, *J* 9.0)	−114.5 (d, 8 F_o, *J* 27.4) −164.5 (t, 4 F_p, *J* 19.8) −166.6 (m, 8 F_m)
4		−114.8 (d, 8 F_o, *J* 26.0) −156.8 (dd, 4 F_o, C_6F_5O, J_{om} 20.0, J_{op} 6.5) −164.6 (t, 4 F_p, *J* 19.8) −166.8 (m, 8 F_m) −171.8 (dd, 4 F_m, C_6F_5O, $J_{om} = J_{mp}$ 20.0) −178.6 (tt, 2 F_p, C_6F_5O, J_{mp} 20.0, J_{op} 6.5)
5	6.71 (d, 4 H, H_o, *J* 7.5) 6.54 (dd, 4 H, H_m, $J = J'$ 7.5) 6.19 (t, 2 H, H_p, *J* 7.5)	−117.8 (d, 8 F_o, *J* 26.0, J_{PtF_o} 536.0) −168.7 (t, 4 F_p, *J* 19.8) −169.2 (m, 8 F_m)
6	6.59 (d, 4 H, H_o, *J* 8.3) 6.33 (d, 4 H, H_m, *J* 8.3) 1.93 (s, 6 H, CH_3)	−117.6 (d, 8 F_o, *J* 26.0, J_{PtF_o} 531.1) −168.8 (t, 4 F_p, *J* 19.8) −169.2 (m, 8 F_m)
7	7.63 (d, 4 H, H_o, *J* 9.0) 6.78 (d, 4 H, H_m, *J* 9.0)	−118.4 (d, 8 F_o, *J* 26.0, J_{PtF_o} 527.8) −166.5 (t, 4 F_p, *J* 18.3) −168.0 (m, 8 F_m)
8		−118.9 (d, 8 F_o, *J* 24.3, J_{PtF_o} 537.3) −154.9 (d, 4 F_o, C_6F_5O, J_{om} 22.9) −166.4 (t, 4 F_p, *J* 19.8) −168.2 (m, 8 F_m) −171.0 (dd, 4 F_m, C_6F_5O, $J_{om} = J_{mp}$ 22.9) −175.4 (t, 2 F_p, C_6F_5O, J_{mp} 22.9)

[a] Chemical shifts in ppm from TMS (^1H) or from $CFCl_3$ (^{19}F). Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; tt, triplet of triplets. [b] In $(CD_3)_2CO$. [c] Additional peaks of $[NBu_4]^+$ are found at δ ca. 3.43 (t, NCH_2), 1.80 (m, NCH_2CH_2), 1.40 (m, CH_2CH_3), and 0.95 (t, CH_3), the relative intensities being 16:16:16:24, respectively.

CO ligand, and this is in agreement with the higher value of the coupling constant $J(PtF_o)$ which should correspond to the C_6F_5 group trans to the ligand with the lower trans influence.

The structure of **14** in the solid state has been determined by a single-crystal X-ray diffraction study Figure 1). The coordination about platinum is approximately square planar with small deviations which might be attributed to the low steric demand of the carbonyl ligand. There have been two previous reports of structures containing the $\{Pd(C_6F_5)_2(CO)\}$ moiety. The Pt−CO bond length is similar to those found for *cis*-$[Pt(C_6F_5)_2(CO)\{SC({=}S)P(C_6H_{11})_3\}]$ (1.910(9) Å)[26] and $[Pt(C_6F_5)_2(CO)\}\{Rh\,(CO)_2Cp\}]$ (1.860(9) Å).[27] However, the carbon−oxygen bond length is shorter (1.115(8) Å against 1.128(10) and 1.162(10) Å for the betaine and the rhodium derivatives, respectively), which is slightly surprising, since the formal negative charge might have been expected to lead to greater back-bonding. As in the rhodium complex, the Pt−C_6F_5 bond trans to the carbonyl (2.040(5) Å) is longer than than that trans to the aryloxy group (2.006(5) Å), in accord with the expected trans-influence, but both are within the normal range for (pentafluorophenyl)platinum derivatives. Mononuclear alkoxy- and (aryloxy)platinum complexes are rare, and to the best of our knowledge, this is the first to be characterized in a diffraction study.

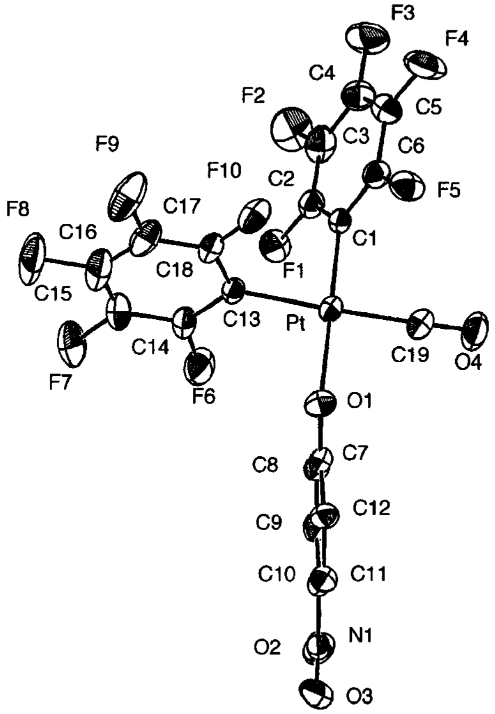

Figure 1. Molecular structure of $[Pt(C_6F_5)_2(OC_6H_4NO_2\text{-}p)(CO)]^-$. The ORTEP diagram shows the non-H atoms as 20% thermal vibration ellipsoids.

The chemical behavior of the palladium complex **3** toward CO is quite different from that above described for the platinum compounds. When CO (1 atm) was passed through a dichloromethane solution of **3**, a mixture of palladium complexes, metallic palladium, and *p*-nitrophenol was obtained. The ^1H and ^{19}F spectra gave no evidence of the formation of $C_6F_5CO_2C_6H_4NO_2$-*p*, the expected product from the insertion of carbon monoxide into the Pd−C_6F_5 or Pd−$OC_6H_4NO_2$-*p* bonds.[28] However the formation of *p*-nitrophenol requires the presence of water in the reaction mixture. Despite precautions taken to avoid water, adventitious water was always present and the experiment was therefore carried out with controlled amounts of water. In a typical experiment, CO was passed through a dichloromethane solution containing a 1:2 molar mixture of the bis(*μ*-aryloxo) complex **3** and water, respectively, until the solvent was completely evaporated. The crude material was then dissolved in $(CD_3)_2CO$ to obtain the ^1H and the ^{19}F NMR spectra which showed that 50% of complex **3** had been transformed. Figure 2 shows the

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[26] Usón, R.; Forniés, J.; Usón, M. A.; Yagüe, J. F.; Jones, P. G.; Meyer-Bäse, K. *J. Chem. Soc., Dalton Trans.* **1986**, 947.

[27] Usón, R.; Forniés, J.; Espinet, P.; Fortuño, C.; Tomás, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1988**, 3005.

[28] The reaction of CO with alkylpalladium aryloxides has previously been studied. CO inserts into the alkyl−palladium bonds to give acylmetal aryloxides which in turn undergo reductive elimination with formation of metal and the corresponding aryl ester in high yield: Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. However in the reaction of CO with the phenoxide complexes *cis*-$[PdMe(OPh)(PMe_3)_2]$ and [PdMe(OPh)(dppe)] insertion of CO into the Pd−OPh bond was suggested, and the resulting methylpalladium complex having the phenoxycarbonyl ligand reductively eliminates the ester in low yield.[9]

Table 3. NMR Spectroscopic Data[a,b] (J in Hz) for Complexes 9−14

complex	^1H[c]	^{19}F	^{31}P
9	7.60 (m, 8 H, H_o PPh_3 + H_o ArO) 7.33 (m, 9 H, H_m + H_p PPh_3) 6.49 (d, 2 H, H_m ArO, J 9.3)	−114.2 (m, 4 F_o) −164.3 (t, 1 F_p, J 19.8) −165.5 (m, 2 F_m) −165.7 (t, 1 F_p, J 19.2) −166.1 (m, 2 F_m)	20.3 (s)
10	7.81 (m, 6 H, H_o PPh_3) 7.36 (m, 9 H, H_m + H_p PPh_3)	−113.6 (d, 2 F_o, J 27.7) −114.3 (br, 2 F_o) −162.7 (m, 2 F_o, C_6F_5O) −164.7 (t, 1 F_p, J 19.8) −165.8 (m, 2 F_m) −166.3 (m, 1 F_p + 2 F_m) −172.8 (dd, 2 F_m, C_6F_5O, $J = J'$ 21.4) −186.1 (m, 1 F_p, C_6F_5O)	20.6 (s)
11	7.61 (m, 8 H, H_o PPh_3 + H_o ArO) 7.32 (m, 9 H, H_m + H_p PPh_3) 6.63 (d, 2 H, H_m ArO, J 9.3)	−117.3 (d, 2 F_o, J 25.4, J_{PtF} 497.8) −117.7 (dd, 2 F_o, J_{om}=J_{PF} 22.0, J_{PtF} 338.1) −165.0 (t, 1 F_p, J 19.8) −166.2 (m, 2 F_m) −167.7 (m, 2 F_m +1F_p)	19.1 (s, J_{PPt} 2671)
12	7.82 (m, 6 H, H_o PPh_3) 7.36 (m, 9 H, H_m + H_p PPh_3)	−116.7 (d, 2 F_o, J 26.0, J_{PtF} 500.6) −117.5 (dd, 2 F_o, J_{om} = J_{PF} 21.4, J_{PtF} 369.7) −161.5 (m, 2 F_o, C_6F_5O) −165.5 (t, 1 F_p, J 20.0) −166.7 (m, 2 F_m) −168.0 (m, 2 F_m + 1 F_p) −172.2 (dd, 2 F_m, C_6F_5O, J_{om} = J_{mp} 21.2) −183.9 (m, 1 F_p, C_6F_5O)	20.3 (s, J_{PPt} 2748)
13	7.94 (d, 2 H, H_o, J 9.3) 6.89 (d, 2 H, H_m, J 9.3)	−118.2 (d, 2 F_o, J 23.4, J_{PtF} 381.0) −119.5 (d, 2 F_o, J 24.3, J_{PtF} 338.6) −162.2 (t, 1 F_p, J 19.8) −162.9 (m, 1 F_p) −165.6 (m, 4 F_m)	
14		−117.7 (d, 2 F_o, J 24.3, J_{PtF} 431.8) −119.6 (d, 2 F_o, J 24.8, J_{PtF} 366.9) −162.5 (m, 2 F_o (C_6F_5O) + 1 F_p (C_6F_5)) −163.1 (t, 1 F_p, J 18.3) −165.8 (m, 4 F_m) −170.5 (dd, 2 F_m, C_6F_5O, J_{om} = J_{mp} 21.2) −180.8 (m, 1 F_p, C_6F_5O)	

[a] Chemical shifts from TMS (^1H), from $CFCl_3$ (^{19}F), or from H_3PO_4 (^{31}P). [b] In $(CD_3)_2CO$. [c] Additional peaks of $[NBu_4]^+$ are found at δ ca. 3.43 (t, NCH_3), 1.80 (m, NCH_2CH_2), 1.40 (m, CH_2CH_3), and 0.95 (t, CH_3), the relative intensities being 8:8:8:12, respectively.

low-field region of the ^1H NMR spectrum. It consists of four pairs of doublets at δ 8.04 and 6.85, 7.81 and 6.82, 7.78 and 6.92, and 7.56 and 6.54 with approximate relative intensities of 2:1:1:4. By comparison with genuine samples, the first and fourth pairs of doublets (a and d) could unambiguously be assigned to p-$O_2NC_6H_4OH$ and the unreacted complex **3**, respectively. The second and third pairs (b and c) could not be confidently assigned, but their spectral positions strongly suggest the presence of two additional palladium species containing Pd−$OC_6H_4NO_2$ bonds (the monomeric [*cis*-$Pt(C_6F_5)_2(OC_6H_4NO_2$-$p)(CO)]^-$ gives two doublets at δ 7.94 and 6.89). Scheme 2 shows the suggested mechanism to explain the experimental results. The cleavage of the aryloxo bridges in complex **3** by CO should produce $[Pd(C_6F_5)_2(OR)(CO)]^-$ (R = $OC_6H_4NO_2$-p) in a similar manner as that described above for platinum. Under rigourously anhydrous conditions the isolation of $[Pd(C_6F_5)_2(OR)(CO)]^-$ should be difficult because of the well-known reluctance of palladium to be involved in bonding to CO.[29] The presence of this complex is supported by two ^{19}F-NMR signals with relative intensities of 1:1 in the o-fluorine region at δ −115.4 and −116.0, respectively, and a weak CO stretching band at 2020 cm^{-1}. The pair c of ^1H-NMR signals can be assigned to this species by analogy with the corresponding platinum complex. The next step involves the nucleophilic attack of coordinated CO by an OH^- ion,[30] forming a −CO(OH) ligand, which subsequently loses CO_2. p-Nitrophenol is also formed in this step. During the decomposition of the undetected hydroxycarbonyl complex to give metallic palladium and carbon dioxide, in the presence of unreacted $[Pd(C_6F_5)_2(OR)(CO)]^-$, a C_6F_5 transfer reaction occurs to form $[Pd(C_6F_5)_3(CO)]^-$ (spectroscopic data in Experimental Section), as shown in Scheme 2. Any comment on this C_6F_5 transfer reaction would be speculative, but a palladium complex containing both terminal and bridging C_6F_5 is known.[31] Since the ^1H NMR spectrum gives no indication of the presence of free RO^-, this group should be trapped by some palladium complex present in the solution to form a new (aryloxo)palladium complex. Thus the formation of $[Pd(C_6F_5)_2(OR)_2]^{2-}$ by reaction between $[Pd(C_6F_5)_2(OR)(CO)]^-$ and RO^- is suggested, which is supported by the observation of the pair b of ^1H-NMR signals (Figure 2). Further evidence is provided by the ^{19}F NMR spectrum which shows a single resonance in the

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(29) The low stability of the palladium complexes is not due to an intrinsically thermodynamic instability but to the lability of the Pd(II)-CO bond: Dell'Amico, D. B.; Calderazzo, F.; Zandona, N. *Inorg. Chem.* **1984**, *23*, 137.

(30) This is the well-known oxidation reaction of the CO ligand in the presence of the strongly basic ligand OH^-, the net outcome being the reduction of the metal center; see, for example, Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; Oxford: Oxford, U.K., 1994; p 717.

(31) The synthesis of $[(C_6F_5)_2Pd(\mu$-$C_6F_5)_2Pd\ (C_6F_5)_2]^{2-}$ was previously reported.[16] This binuclear complex reacts with CO yielding $[Pd(C_6F_5)_3(CO)]^-$.

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2)

	x	y	z	U_{eq}
Pt	0.07648(2)	0.11529(1)	0.23180(1)	0.057(1)
F1	0.1668(5)	−0.0255(2)	0.2196(2)	0.096(3)
F2	0.2331(6)	−0.0950(2)	0.1162(3)	0.149(4)
F3	0.2277(6)	−0.0457(2)	−0.0068(2)	0.164(4)
F4	0.1498(6)	0.0733(3)	−0.0244(2)	0.144(4)
F5	0.0784(5)	0.1429(2)	0.0786(2)	0.103(3)
F6	−0.0118(5)	0.0189(2)	0.3432(2)	0.135(3)
F7	−0.2634(7)	−0.0433(2)	0.3673(3)	0.192(4)
F8	−0.5130(5)	−0.0315(3)	0.2875(3)	0.206(5)
F9	−0.4978(5)	0.0432(2)	0.1801(3)	0.174(4)
F10	−0.2445(4)	0.1048(2)	0.1547(2)	0.106(3)
O1	0.0222(4)	0.1728(2)	0.3093(2)	0.073(2)
O2	0.4046(6)	0.1414(2)	0.5687(2)	0.122(4)
O3	0.2682(6)	0.2202(3)	0.5939(2)	0.131(4)
O4	0.3663(5)	0.1825(2)	0.2023(3)	0.110(3)
N1	0.3076(6)	0.1799(3)	0.5552(2)	0.098(4)
N2	−0.1861(5)	0.3047(2)	0.1635(2)	0.061(3)
C1	0.1176(6)	0.0618(3)	0.1534(3)	0.058(3)
C2	0.1572(7)	0.0004(3)	0.1590(3)	0.075(4)
C3	0.1943(8)	−0.0354(3)	0.1073(4)	0.096(5)
C4	0.1929(9)	−0.0113(3)	0.0455(4)	0.102(5)
C5	0.1524(8)	0.0483(3)	0.0358(3)	0.093(5)
C6	0.1162(7)	0.0834(3)	0.0904(3)	0.074(4)
C7	0.0933(6)	0.1732(3)	0.3664(3)	0.065(3)
C8	0.1985(7)	0.1282(3)	0.3869(3)	0.070(4)
C9	0.2679(7)	0.1306(3)	0.4481(3)	0.077(4)
C10	0.2352(7)	0.1776(3)	0.4898(3)	0.074(4)
C11	0.1340(7)	0.2233(3)	0.4717(3)	0.080(4)
C12	0.0651(7)	0.2211(3)	0.4112(3)	0.076(4)
C13	−0.1174(6)	0.0663(3)	0.2485(3)	0.059(3)
C14	−0.1322(7)	0.0281(3)	0.3014(3)	0.087(4)
C15	−0.2602(9)	−0.0050(4)	0.3152(4)	0.114(5)
C16	−0.3829(8)	0.0002(4)	0.2755(5)	0.128(6)
C17	−0.3771(7)	0.0379(4)	0.2222(4)	0.108(5)
C18	−0.2450(6)	0.0696(3)	0.2090(3)	0.078(4)
C19	0.2580(7)	0.1583(3)	0.2140(3)	0.074(4)
C20	−0.1976(6)	0.2512(3)	0.1152(3)	0.065(3)
C21	−0.3491(7)	0.2432(3)	0.0788(3)	0.076(4)
C22	−0.3380(8)	0.1941(3)	0.0262(3)	0.094(5)
C23	−0.4899(9)	0.1769(4)	−0.0030(4)	0.118(6)
C24	−0.2153(7)	0.3655(3)	0.1288(3)	0.077(4)
C25	−0.1185(10)	0.3805(3)	0.0703(4)	0.111(6)
C26	−0.1691(14)	0.4403(5)	0.0376(5)	0.171(8)
C27	−0.2709(21)	0.4411(7)	−0.0008(7)	0.329(16)
C28	−0.3036(6)	0.2991(3)	0.2166(3)	0.072(4)
C29	−0.2953(7)	0.2420(3)	0.2577(3)	0.076(4)
C30	−0.3915(8)	0.2471(4)	0.3184(4)	0.099(5)
C31	−0.3888(10)	0.1891(4)	0.3604(4)	0.129(6)
C32	−0.0250(6)	0.3020(3)	0.1920(3)	0.066(4)
C33	0.0147(7)	0.3463(3)	0.2465(3)	0.080(4)
C34	0.1794(7)	0.3379(3)	0.2689(3)	0.092(5)
C35	0.2204(10)	0.3768(4)	0.3268(4)	0.126(6)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Intramolecular Distances (Å) and Angles (deg) for $[Pt(C_6F_5)_2(OC_6H_4NO_2\text{-}p)(CO)]^-$ with Estimated Standard Deviations in Parentheses

	Bonds		
Pt−O1	2.070(4)	Pt−C1	2.006(5)
Pt−C13	2.040(5)	Pt−C19	1.887(6)
O4−C19	1.115(8)		
	Angles		
O1−Pt−C1	176.3(2)	O1−Pt−C13	89.3(2)
O1−Pt−C19	92.9(2)	C1−Pt−C13	89.4(2)
C1−Pt−C19	88.5(2)	C13−Pt−C19	177.8(2)
Pt−C19−O4	178.0(6)		

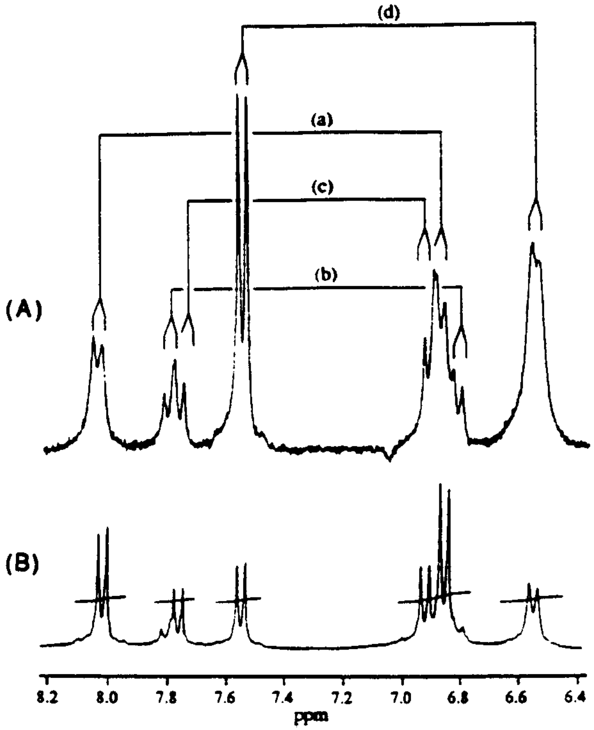
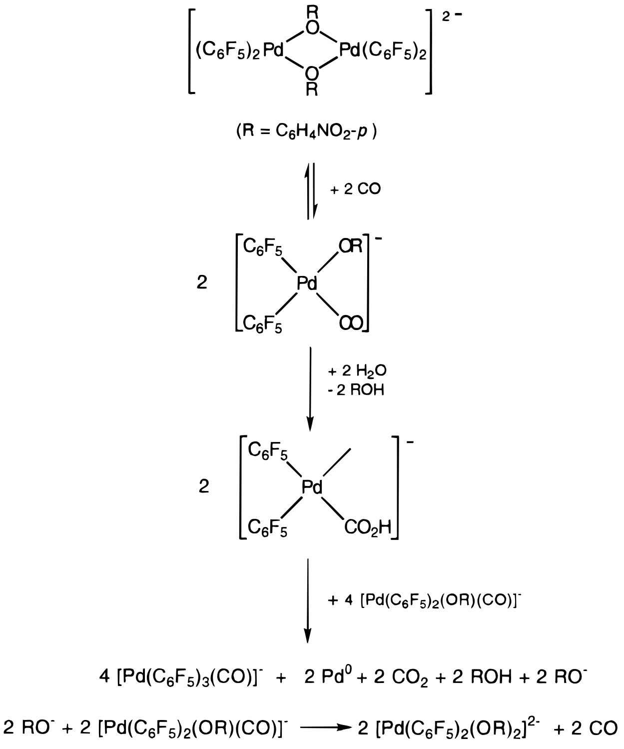


Figure 2. (A) Partial ^1H NMR spectrum of the crude material obtained from the reaction between complex **3** and CO in the presence of water (see text). (B) Partial ^1H NMR spectrum of the crude material after elimination of metallic palladium and partial precipitation with hexane. This spectrum shows that the pseudotriplet at ca. δ 7.8 and the multiplet at δ 7.0−6.8 in (A) are related to two and three different complexes, respectively.

Scheme 2



o-fluorine region at δ ca. −114.4 ppm (this signal, which is partially overlapped with the signal provided by the C_6F_5 group *trans* to CO in $[Pd(C_6F_5)_3(CO)]^-$, could be discernible in the spectrum only when it was obtained at low temperature in d_6-acetone; at room temperature the signal was completely masked by the ^{19}F peak from the C_6F_5 group *trans* to CO in $[Pd(C_6F_5)_3(CO)]^-$) and two additional peaks at δ −166.2 and −167.4 corresponding to the *p*- and *m*-fluorine atoms, respectively. The correctness of this assignment was confirmed by comparison with an authentic sample of $[NBu_4]_2[Pd(C_6F_5)_2(OR)_2]$ prepared by a different method.[32] The ^1H NMR spectrum, taken in conjunction with the ^{19}F NMR spectrum, demonstrated that the amounts of $[Pd(C_6F_5)_3(CO)]^-$, *p*-$O_2NC_6H_4OH$, and $[Pd(C_6F_5)_2(OR)_2]^{2-}$ are in the molar ratio 4:4:1, respectively, as required by the proposed reaction pathway of Scheme 2. Furthermore the experimental Pd/CO_2 molar ratio is 1:1 (carbon dioxide was controlled as $BaCO_3$ by bubbling the released gas through baryta water). It is worth noting that the C_6F_5 transfer reaction occurs with the reactants (the hydroxycarbonyl complex and $[Pd(C_6F_5)_2(OR)(CO)]^-$) in the 1:2 mol ratio which leads to the actual 4:4:1 ratio above mentioned for the reaction products. A 1:1 ratio should lead to the formation of $[Pd(C_6F_5)_3(CO)]^-$ and $[Pd(C_6F_5)_2(OR)_2]^{2-}$ in 2:1 ratio, respectively, and the concomitant liberation of 2 mol of C_6F_5H; however, only traces of C_6F_5H are observed in the ^{19}F NMR spectrum. The chemical behavior of complex **4** toward carbon monoxide was similar to that just described for complex **3**.

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Supporting Information Available: Tables of intramolecular distances and angles, hydrogen atom coordinates, anisotropic temperature factors in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$, and least squares planes for **13** (8 pages). Ordering information is given on any current masthead page.

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[32] $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ was reacted with *p*-$O_2NC_6H_4OH$ and $[NBu_4]OH$ in the molar ratio 1:4:2, respectively, in acetone; after being stirred for ca. 1 h, the solution was evaporated to dryness and the residue was treated with $MeOH-H_2O$ and filtered off to yield a yellow solid which was identified as $[NBu_4]_2[Pd(C_6F_5)_2(OC_6H_4NO_2\text{-}p)_2]$. Its ^1H and ^{19}F NMR data were coincident with those given in the text.