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Electron transfer reactions involving *trans*-[$PtH_2(PCy_3)_2$] and fluorinated benzonitriles

Samuel Hintermann, Paul S. Pregosin, Heinz Rüegger
Laboratorium für Anorganische Chemie, Eidgenössische Technische Hochschule,
CH-8092 Zürich (Switzerland)

and Howard C. Clark
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3 (Canada)

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Abstract

The complex *trans*-[$PtH_2(PCy_3)_2$] reacts with activated benzonitriles such as 4-R-C_6F_4CN (R = F, H, CN, OCH_3) bearing electron-withdrawing substituents to give the new platinum(II) aryl complexes *trans*-[$PtH(RC_6F_3CN)(PCy_3)_2$], which have been isolated and fully characterized, and a hydridofluoride *trans*-[PtH("F")($PCy_3)_2$], where "F" is either F or HF_2, which has been detected in solution. These complexes and related by-products from the reaction have been characterized by one- and two-dimensional multinuclear NMR spectroscopy. A reaction mechanism involving rate-determining electron transfer from the dihydride complex to the organic substrate is postulated on the basis of (i) the relative reaction rates for the nitriles (p-$C_6F_4(CN)_2 > C_6F_5CN >$ p-$C_6HF_4CN >$ p-$C_6F_4(OCH_3)CN >$ o,o-$C_6H_3F_2CN$), which parallel their electron affinities, and (ii) the observation of a radical by ESR spectroscopy after "spin-trapping" with PBN.

Introduction

During the investigation [1] of the mechanism of the insertion of acetylenes into the platinum–hydride bond it was recognized that *trans*-[$PtH_2(PCy_3)_2$] initially reacts with acetylene bearing electron-withdrawing groups, such as dimethylacetylene dicarboxylate (DMA) and hexafluorobutyne, to form a charge transfer complex which then undergoes electron transfer from the metal to the alkyne. The mechanism of this reaction was deduced [1] from:

(a) the occurrence of exclusive *trans*-addition of the platinum and the hydride to the triple bond;

Correspondence to: Dr. H. Rüegger, Laboratorium für Anorganische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

(b) the observation of regioselectivity in the case of unsymmetrical acetylenes such as PhC≡CR and HC≡CR (R = CN, $COOCH_3$ and CF_3), with which the R group always ends up in the geminal position with respect to the platinum; and

(c) the observation of a transient charge transfer band in the initial stages of the reaction and of a strongly colored stable platina-cyclopropene radical as a side product.

The occurrence of an electron transfer reaction as opposed to other well-known processes, such as those involving a four-center transition state [2] or free radicals [3], depends on the donor properties [4] of the platinum hydride (*trans*-$[PtH_2(PCy_3)_2]$ > *trans*-$[PtH(Me)(PCy_3)_2]$ > *trans*-$[PtHCl(PCy_3)_2]$) and the acceptor properties [1] of the acetylene (*e.g.* $CH_3OOCC{\equiv}CCOOCH_3$ > $PhC{\equiv}CCOOCH_3$ > $HC{\equiv}CCOOCH_3$ > $CH_3C{\equiv}CCOOCH_3$). From reduction potentials [5,6] it was concluded that benzonitriles bearing electronegative substituents should have similar acceptor properties to those of acetylenes, and we report here on the reaction of *trans*-$[PtH_2(PCy_3)_2]$ with *para*-XC_6F_4CN (X = H, F, CN and OCH_3).

Experimental

Materials

Pentafluorobenzonitrile, tetrafluoroterephthalonitrile and pentafluoronitrobenzene were obtained from Aldrich Chemical Co. and used without further purification, but 2,3,5,6-tetrafluorobenzonitrile was prepared via 4-hydrazinotetrafluorobenzonitrile from pentafluorobenzonitrile [7] and 4-methoxytetrafluorobenzonitrile was obtained from pentafluorobenzonitrile and sodium methoxide [8].

All reactions were carried out under an inert atmosphere.

trans-$[PtH_2(PCy_3)_2]$

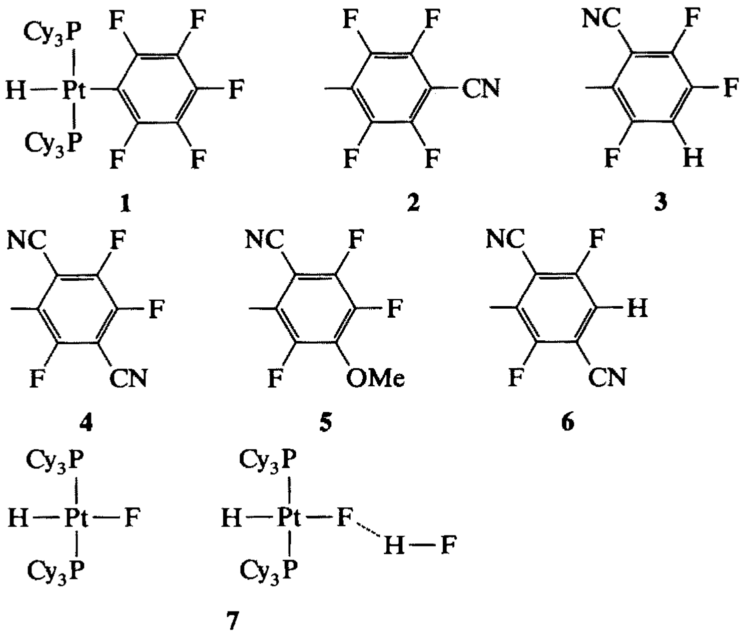
The *trans*-$[PtH_2(PCy_3)_2]$ was prepared from *trans*-$[PtCl_2(PCy_3)_2]$ by published methods [9–11], and most succesfully in the following way:

To a suspension of *trans*-$[PtCl_2(PCy_3)_2]$ (1.00 g, 1.20 mmol) and PCy_3 (0.13 g, 0.36 mmol) in 2 ml of tetrahydrofuran (THF) was added dropwise a solution of sodium-naphthalenide prepared from 0.50 g of sodium and 2.20 g of naphthalene in 50 ml of THF. The addition was halted at the point at which the dark green color of the naphthalenide persisted. After 2 h stirring the solvent was evaporated *in vacuo* and the naphthalene partially removed by sublimation. The residue was extracted with hexane, and after filtration the extract containing $[Pt(PCy_3)_2]$ was transferred to an autoclave, which was then charged with 180 atm of hydrogen. After 3 d storage the product *trans*-$[PtH_2(PCy_3)_2]$ was filtered off and recrystallized from toluene/methanol. Yield: 0.56 g, 62%.

Scheme 1 shows the various substitution patterns for the products *trans*-$[PtH(fluoroaryl)(PCy_3)_2]$.

trans-$[PtH(C_6F_5)(PCy_3)_2]$ *(1)*. The complex *trans*-$[PtH(C_6F_5)(PCy_3)_2]$ was synthesized from $[Pt(PCy_3)_2]$ (prepared as above), and pentafluorobenzene by oxidative addition as previously described [11]. IR (Nujol, cm^{-1}): ν(Pt–H) = 2050m, 2032m.

trans-$[PtH(C_6F_4CN)(PCy_3)_2]$ *(2)*. Pentafluorobenzonitrile (40 mg, 0.20 mmol) was added to a solution of *trans*-$[PtH_2(PCy_3)_2]$ (76 mg, 0.10 mmol) in 1 ml of benzene. Crystals of *trans*-$[PtH(C_6F_4CN)(PCy_3)_2]$ separated when the mixture was



Scheme 1.

set aside, and after 5 h methanol (5 ml) was slowly added to complete the crystallization. The product was separated from the mother liquor by decantation, washed with 2 × 0.5 ml portions of cold methanol, and dried *in vacuo*. Yield: 32 mg (34%). Analytical data (%) (calculated for $C_{43}H_{67}F_4NP_2Pt$): C, 55.78 (55.47); H, 7.54 (7.25); F, 8.41 (8.16). IR (Nujol, cm^{-1}): $\nu(C\equiv N) = 2244w, 2225m$; $\nu(Pt\text{-}H) = 2085w, 2066m, 2054m, 2037m$.

The compound was also synthesized by oxidative addition of *p*-H-C_6F_4CN to $[Pt(PCy_3)_2]$.

The following complexes were prepared analogously from the dihydride and the relevant substituted-benzonitrile:

trans-$[PtH(C_6HF_3CN)(PCy_3)_2]$ *(3).* From *trans*-$[PtH_2(PCy_3)_2]$ and 2,3,5,6-tetrafluorobenzonitrile. Analytical data (%) (calculated for $C_{43}H_{68}F_3NP_2Pt$): C, 55.77 (56.57); H, 7.50 (7.51); F, 6.03 (6.24).

trans-$[PtH(C_6F_3(CN)_2)(PCy_3)_2]$ *(4).* From *trans*-$[PtH_2(PCy_3)_2]$ and tetrafluoroterephthalonitrile. Analytical data (%) (calculated for $C_{44}H_{67}F_3N_2P_2Pt$): C, 55.54 (56.34); H, 7.20 (7.20).

trans-$[PtH(C_6F_3(CN)(OCH_3))(PCy_3)_2]$ *(5).* From *trans*-$[PtH_2(PCy_3)_2]$ and 4-methoxy-2,3,5,6-tetrafluorobenzonitrile.

Halogen metathesis

trans-$[PtH_2(PCy_3)_2]$ and C_6F_5CN were allowed to react in toluene-d_8 as described above for *trans*-$[PtH(C_6F_4CN)(PCy_3)_2]$ (2) and the product was filtered off. The filtrate containing *trans*-[PtH("F")$(PCy_3)_2$] (7) was shaken with aqueous solutions of KCl, KBr, KCN, and $NaNO_2$, respectively, to give *trans*-$[PtHX(PCy_3)_2]$

(X = Cl, Br, CN and NO_2). These complexes were not isolated; instead the toluene solution was separated, dried over $MgSO_4$, and used directly for the NMR studies.

Microanalysis

Analytical data were obtained from Guelph Chemical Laboratories Ltd, Guelph, Ontario, Canada and Organisch Chemisches Institut, ETH-Z, Zürich.

Physical measurements

^1H, ^{19}F and ^{31}P NMR spectra were recorded on Bruker AC-200, CXP-200, AC-250, AM-250, WH-400, AMX-400 and AMX-500 instruments in the Fourier transform mode. One-dimensional spectra were processed by resolution enhancement techniques for ^1H and ^{19}F and exponential weighting for ^{31}P data. Heteronuclear shift correlation NMR data ($^{195}Pt-^1H$) were acquired using standard techniques for inverse correlation [12,13] on the AC-250 and the AMX-400 instruments.

Results and discussion

Reactions of trans-[PtH$_2$(PCy$_3$)$_2$] with fluorobenzonitriles

Addition of an activated fluorinated-benzonitrile to a colorless benzene or toluene solution of the platinum dihydride complex produces an immediate yellowish color. The course of the reaction is easily monitored by interleaved * ^{31}P, ^{19}F and ^1H NMR spectroscopy. In the early stages two new phosphorus-containing species develop. One of these is associated with a ^1H hydride signal at $\delta \approx -8$ ppm, and proved to be stable for weeks in solution. This complex type was isolated in moderate yields, and fully characterized as *trans*-[PtH(fluoro-cyano-aryl)(PCy$_3$)$_2$] (*vide infra*). Relevant NMR parameters are summarized in Table 1 for ^1H and Table 2 for other nuclei.

The second component, which shows broad ^{31}P resonances at room temperature and is associated with hydride resonances at $\delta \approx -27$ ppm, is formulated as

Table 1

^1H NMR data for platinum aryl complexes [a]

Complex	Aryl	$\delta(^1H)$	$^1J(Pt, H)$	$^2J(P, H)$	$^4J(F, H)$	$^5J(F, H)$
1	Pentafluorophenyl	−8.83	733	15.2	14.9	6.1
2	4-Cyano-2,3,5,6-tetrafluorophenyl	−8.56	719	14.2	14.1	6.1
3	2-Cyano-3,4,5-trifluorophenyl [b]	−8.44	656	15.6	9.8	2.0
4	2,5-Dicyano-3,4,6-trifluorophenyl	−8.70	676	15.7	9.9	3.0
5	2-Cyano-5-methoxy-3,4,6-trifluorophenyl [c]	−8.51	666	16.7	11.8	4.0
6	2,5-Dicyano-3,6-difluorophenyl [d]	−8.53	662	15.6	10.0	2.7

[a] Data were measured at room temperature in C_6D_6, chemical shifts are in ppm relative to TMS and coupling constants are in Hz. [b] $\delta(H_{aryl}) = 6.12(t)$. [c] $\delta(H_{methoxy}) = 3.44(t)$. [d] $\delta(H_{aryl}) = 5.85(d \times d)$.

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* Interleaved measurements for fast reactions can be performed by using the relaxation delay of one measurement (*e.g.* ^{31}P) to record the spectrum of a second nucleus. In the present case blocks of 64 scans were acquired for ^{31}P, ^{19}F and ^1H, and stored before repetition of the sequence.

Table 2

^{31}P and ^{19}F NMR data for platinum aryl complexes [a]

Complex	$\delta(^{31}P)$	$^{1}J(Pt, P)$	$\delta(^{19}F_{ortho})$	$\delta(^{19}F_{meta})$	$\delta(^{19}F_{para})$	$^{3}J(Pt, F_{ortho})$	$^{4}J(Pt, F_{meta})$
1	38.1	2752	−119.6	−172.8	−173.0	302	
2 [b]	38.8	2735	−117.7	−146.3		296	
3	37.2	2753	−93.0	−151.4	−148.2	266	30
4	37.5	2715	−85.9	−147.0	−145.8	277	
5	37.1	2755	−110.1	−167.4	−144.7	302	38
6	37.5	2722					

[a] Chemical shifts are in ppm relative to 85% H_3PO_4 (^{31}P) and $CFCl_3$ (^{19}F), respectively. Coupling constants are in Hz. [b] $\delta(^{195}Pt) = -4970$ ppm (relative to Na_2PtCl_6).

trans-[PtH("F")(PCy$_3$)$_2$] on the basis of findings outlined below. The "F" notation means that the ligand is mostly fluoridic in nature but probably interacts dynamically with dissolved hydrofluoric acid to form coordinated $F(HF)^-$. Attempts to isolate the complex were unsuccessful. However, addition of other halides, *e.g.* Cl^-, Br^-, NO_2^- and CN^-, converts the intermediates to stable complexes which were characterized by NMR spectroscopy (Table 3). The broad ^{31}P resonance observed at room temperature splits into two lines at 203 K with relative intensities of approximately 4 to 1. At the same time there are corresponding changes in the ^{1}H and ^{19}F spectra. Surprisingly, the changes in the ^{1}H spectrum are not restricted to the hydride region alone, but also involve a low field resonance ($\delta = 12.8$ ppm, $^{1}J(F, H) = 392$ Hz) which we assign to "HF". This resonance, presumably from solvated HF, shows no platinum coupling, but disappears upon addition of D_2O.

In addition to the two organometallic complexes described, there is concurrent formation of new benzonitriles, *e.g.* 2,3,5,6-tetrafluorobenzonitrile and 2,3,5-trifluoro-terephthalonitrile in the reactions with pentafluorobenzonitrile and tetrafluoroterephthalonitrile, respectively. There are, however, no indications [14–16] of nitrile reduction, and so the reactions can be summarized as in the eqns. 1 and 2:

$$\textit{trans}\text{-}[PtH_2(PCy_3)_2] + C_6F_4R(CN) \longrightarrow \textit{trans}\text{-}[PtH\{C_6F_3R(CN)\}(PCy_3)_2] + HF \qquad (1)$$

$$\textit{trans}\text{-}[PtH_2(PCy_3)_2] + C_6F_4R(CN) \longrightarrow \textit{trans}\text{-}[PtHF(PCy_3)_2] + C_6HF_3R(CN) \qquad (2)$$

(R = F (**2**), H (**3**), CN (**4**) and OCH_3 (**5**))

Table 3

NMR data for complexes *trans*-[PtHX(PCy$_3$)$_2$] [a]

X	$\delta(^{195}Pt)$	$\delta(^{31}P)$	$\delta(^{19}F)$	$\delta(^{1}H)$	$^{1}J(Pt, P)$	$^{1}J(Pt, F)$	$^{1}J(Pt, H)$	$^{2}J(P, F)$	$^{2}J(P, H)$	$^{2}J(F, H)$
F	−4538	43.2	−383	−26.4	2881	560	1330	n.r. [b]	15	113
Cl		39.3		−17.8	2813		1247		12.7	
Br		38.6		−16.61	2786		1303		11.8	
CN		39.8		−8.34	2654		770		13.9	
NO_2		38.6		−20.22	2856		971		14.1	

[a] Measured at room temperature in toluene-d_8. Chemical shifts are in ppm relative to Na_2PtCl_6(^{195}Pt), H_3PO_4(^{31}P), $CFCl_3$(^{19}F) and TMS(^{1}H), respectively. Coupling constants are in Hz. [b] n.r. = not resolved.

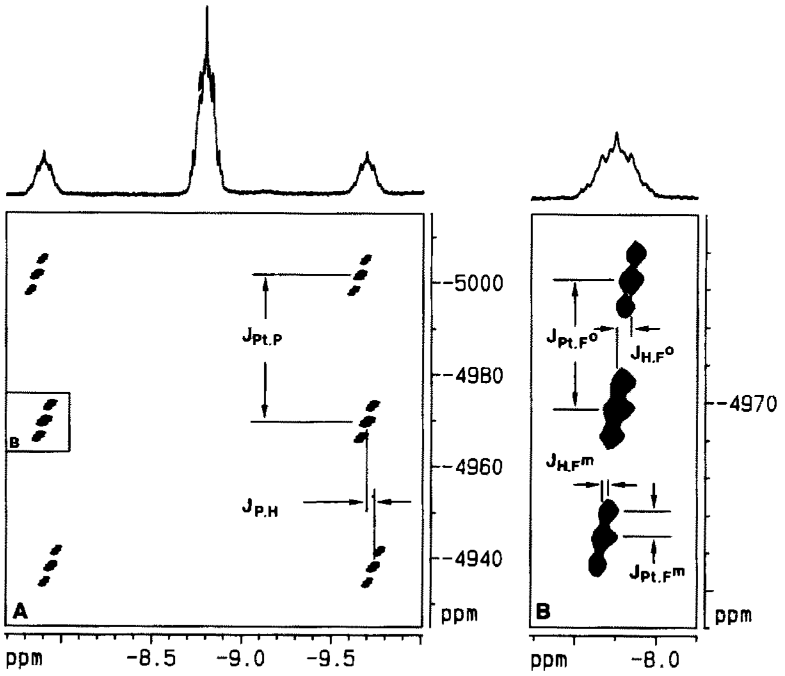


Fig. 1. ^{195}Pt–^{1}H heteronuclear correlation (9.4 Tesla) for *trans*-[PtH(C_6F_4CN)(PCy_3)$_2$] recorded in $CDCl_3$ showing in ω_1 the t×t×t multiplicity due to two ^{31}P spins (A) and F_{ortho} and F_{meta} (B). The hydride region of a conventional ^{1}H spectrum is shown above the contour maps.

The relative reaction rates depend strongly on the nature of the aromatic reactant, being fastest with the most strongly electron accepting substituents. The following qualitative reactivity sequence is observed: tetrafluoroterephthalonitrile > pentafluorobenzonitrile > 2,3,5,6-tetrafluorobenzonitrile ≫ 4-methoxy-2,3,5,6-tetrafluorobenzonitrile ⋙ 2,6-difluorobenzonitrile. The dihydride reacts smoothly during a period of minutes to hours with 4-RC_6F_4CN (R = F, H, CN, OCH_3), whereas the complexes *trans*-[PtHCl(PCy_3)$_2$], *trans*-[PtH("F")(PCy_3)$_2$] (*in situ*) and *trans*-[PtH{C_6F_3R(CN)}(PCy_3)$_2$] do not react even with a large excess of nitrile.

Spectroscopic identification of reaction products

Platinum fluoroaryls. The characterization of this type of complex is best illustrated by taking *trans*-[PtH(C_6F_4CN)(PCy_3)$_2$] (2) as a typical example. The hydride region of the ^{1}H NMR spectrum (see top trace in Fig. 1A) shows a complicated multiplet at $\delta = -8.56$ with associated platinum satellites, $^{1}J(^{195}$Pt, ^{1}H) = 719 Hz. This coupling constant indicates a ligand in *trans* position with a considerable *trans* influence [17,18], whereas the complexity suggests the presence of additional NMR active nuclei apart from ^{31}P. The metal part of the (^{1}H observed) ^{195}Pt–^{1}H correlation reveals spin–spin interaction to two ^{31}P spins (Fig. 1A) as well as splitting by two *ortho* and two *meta* ^{19}F spins (see expansion, Fig. 1B). The presence of the η^1-C_6F_4 CN ligand is further confirmed by the ^{19}F spectrum, and the appearence of nitrile stretching vibrations in the IR spectrum (ν(C≡N) = 2249–2225 cm^{-1}).

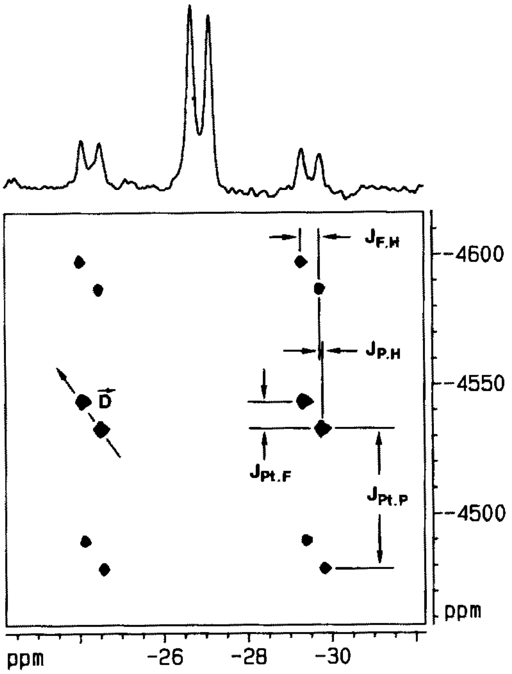


Fig. 2. Part of the conventional ^1H spectrum and the contour plot of the $^{195}Pt-^1H$ heteronuclear correlation (5.9 Tesla) for *trans*-[PtH("F")PCy$_3$)$_2$] recorded in toluene-d_8. The orientation of the displacement vector D results from unlike signs of $^1J(^{195}Pt, ^{19}F)$ and $^2J^{19}F, ^1H)$.

The structures of the analogous complexes **1** and **3–6** were derived by analysis of the ^{31}P and hydride ^1H NMR data, with the aromatic substitution pattern (see Scheme 1) derived from the ^{19}F spectra. Typical aromatic ^1H resonances were observed for complexes **3** and **6**. The relevant shift and coupling data are listed in Tables 1 and 2.

Platinum hydrofluoride. The identification of the second transition metal compound is somewhat hampered by the broadness of the resonances due to exchange processes. Nevertheless, the main features of the molecule can be discussed in terms of Fig. 2 which shows the platinum–hydrogen correlation and the conventional ^1H spectrum. The hydride resonance at room temperature consists of a doublet with a separation $^2J(F, H) = 113$ Hz accompanied by the expected platinum satellites $^1J(Pt, H) = 1330$ Hz. The multiplicity in the metal dimension of the correlation spectrum is determined by the presence of two equivalent phosphines and one fluorine spin, with scalar coupling constants $^1J(Pt, P)$ of 2881 and $^1J(Pt, F)$ of 560 Hz, respectively. The former coupling constant is normal for two phosphorus spins in a *trans* arrangement [19], but there is a dearth of reference data for platinum(II) fluorides. However, data for $^1J(Pt, F)$ in Pt^{IV} compounds are somewhat more common; this coupling is, *e.g.*, 2003 in PtF_6^{2-} and 1077 Hz in $PtCl_3F_3^{2-}$ [20]. In the light of the expected [17] increase in this parameter upon going from Pt^{IV} to Pt^{II}, the observed value of 560 Hz seems to be surprisingly small for a one-bond interaction between platinum(II) and fluorine. However, Dixon and co-workers [21] found $^1J(Pt, F)$ to be 66 Hz in the complex $[PtF(PPh_3)_3]^+$

and 250 Hz in $[PtF(PEt_3)_3]^+$. An interesting observation concerns the relative signs of the coupling constants $^{1}J(Pt, F)$ (assumed to be positive) and $^{2}J(F, H)$ obtainable from the $^{195}Pt-^{1}H$ correlation. The orientation of the displacement vector D relative to the ω_1 axis in Fig. 2 reveals unlike signs for $^{1}J(Pt, F)$ and $^{2}J(F, ^{1}H_{Hydride})$. In general, two-bond coupling constants involving spins which are in a mutual *cis* arrangement on platinum have a negative sign, whereas those from *trans*-ordered spins are positive, *i.e.* we would expect $^{2}J(F, H)$ to be positive. Since we have only one complex we refrain from attributing much significance to these observations, and note that many other one-bond couplings involving fluorine are reported to have a negative sign [22].

Organic reaction products. The organic reaction products can be readily detected and characterized by ^{19}F and ^{1}H NMR spectroscopic methods. The main organic by-product in all the reactions studied is a new benzonitrile having one of the fluorines replaced by a hydrogen atom. The fluorine substitution pattern on the aromatic nucleus follows exactly that observed for the platina-aryls **2**–**5**; *e.g.* 2,3,5,6-tetrafluorobenzonitrile is formed from pentafluoronitrile and 2,3,5-trifluoroterephthalonitrile from tetrafluoroterephthalonitrile.

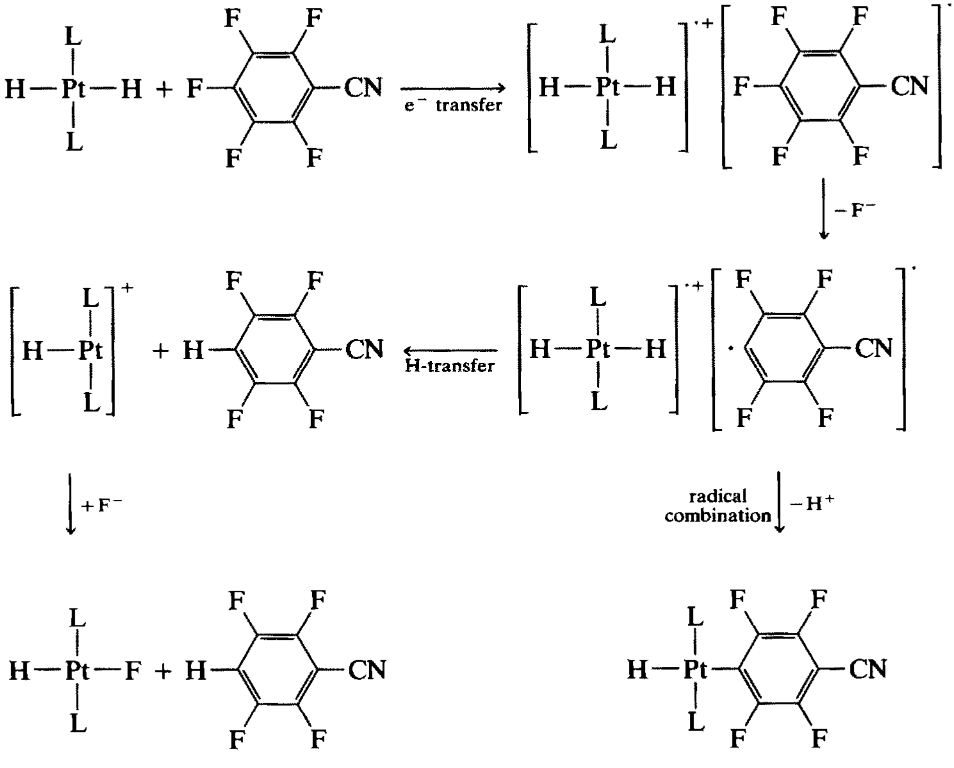
Inorganic reaction products. The ^{1}H NMR spectrum shows a broad doublet resonance at low field ($\delta = 12.8$ ppm, $J(F, H) = 392$ Hz) which is associated with a doublet in the ^{19}F spectrum ($\delta = -182.0$ ppm). The latter collapses into a singlet upon selective irradiation at the center of the proton low field signals. In view of the large magnitude of $J(F, H)$ we assign these resonances to hydrogen fluoride, which might take part in exchange either with water contained in toluene-d_8 or with the complex *trans*-[PtH("F")(PCy$_3$)$_2$] (see above). The literature gives values for $^{1}J(F, H)$ in HF ranging from 120 Hz [23] in 70% HF in pyridine to 521 Hz [24] in a mixture of HF and BF_3 in acetone.

Comments on the reaction mechanism

Nitriles [14] and isonitriles [15,16] can react with metal hydrides to form MN=CHR and MC(R)=NH complexes, respectively. Compounds of these types are easily recognized in the ^{1}H NMR spectra by the low field resonance for the imidoyl or imine proton. The absence of such lines in the proton NMR spectra and the presence of cyano bands in the infrared spectra ($\nu(C\equiv N) = 2249$–$2225\ cm^{-1}$) show these that substituents remain intact during the reaction. Instead, the complex *trans*-[PtH$_2$(PCy$_3$)$_2$] reacts with fluorinated benzonitriles to give platinum hydridofluoroaryl and platinum hydridofluoride complexes, according to eqns. 1 and 2.

The observed products can be accounted for in terms of two alternative reaction mechanisms, one involving an electron transfer process as depicted in Scheme 2, and the other oxidative addition of the fluorobenzonitrile and subsequent reductive elimination of either the fluoroaryl or HF. The latter pathway, involving the oxidative addition of a C–F bond to platinum, does not seem likely since oxidative addition of a C–H bond is normally favored over that of a C–F bond. In support of this we note that pentafluorobenzene adds smoothly to the Pt^0 compound $[Pt(PCy_3)_2]$ to give exclusively *trans*-[PtH(C$_6$F$_5$)(PCy$_3$)$_2$] [11] and no *trans*-[PtF(C$_6$HF$_4$)(PCy$_3$)$_2$] (hexafluorobenzene does not react under similar conditions).

It is noteworthy that *trans*-[PtH$_2$(PCy$_3$)$_2$] preferably adds the pentafluorobenzonitrile and not the tetrafluorobenzonitrile which is formed as a by-product in the



Scheme 2.

reaction. Only where substoichiometric amounts of the nitrile are used, *e.g.* as with tetrafluoroterephthalonitrile, is *trans*-[PtH{$C_6HF_2(CN)_2$}$(PCy_3)_2$] (6) observed in addition to *trans*-[PtH{$C_6F_3(CN)_2$}$(PCy_3)_2$] (4). This suggests a dependance of the relative reaction rates upon the electron affinities of the nitrile substrates, and the following qualitative sequence of decreasing reactivity is found: p-$C_6F_4(CN)_2$ > C_6F_5CN > p-C_6HF_4CN > p-$C_6F_4(OCH_3)CN$ ≫ o,o-$C_6H_3F_2CN$. Further support for an electron transfer mechanism arises from the fact that the substitution pattern for the resulting nitriles is consistent with the known electrochemistry of such species; *e.g.* reduction of C_6F_5CN with sodium produces the anionic π-radical $C_6F_5CN^{\cdot -}$, which by expulsion of a fluoride is converted into the σ-radical $C_6F_4CN^{\cdot}$, whose structure is known [25] to have the unpaired electron *para* to the nitrile. This radical can combine with the platinum species to form the aryl complexes or capture a hydrogen atom to form the secondary benzonitriles. When the reaction of *trans*-[$PtH_2(PCy_3)_2$] with C_6F_5CN is carried out in the presence of phenyl-t-butyl-nitrone (PBN), a known [26] spin trapping agent for radicals, an ESR spectrum is observed that contains a somewhat broadened doublet of a triplet attributable to a nitroxide radical of the form PhCHR(^{t}Bu)NO$^{\cdot}$. Comparison of the hyperfine splittings $a_N = 13.5$ and $a_H = 2.75$ G with values in the literature [27,28] suggests that the trapped species is a carbon-centered radical. The broadness of the resonance lines may be due to unresolved fluorine hyperfine splittings in the spin adduct PhCH{p-C_6F_4CN}(^{t}Bu)NO$^{\cdot}$. However, the addition of the PBN spin trap does not alter either the course or the rate of the reaction. Consequently a radical chain mechanism, such as is observed [3] in the reaction of *trans*-[PtHCl(PEt$_3$)$_2$] with acetylenes in non-coordinating solvents, can be excluded. We believe that formation of a tight radical ion pair within a solvent cage as an intermediate is most likely in our reaction. The presence of oxygen does not influence the main features of the reaction, but leads to some additional hydridic by-products.

In conclusion, we think that the course of the reaction between *trans*-[PtH$_2$(PCy$_3$)$_2$] and activated benzonitriles is most easily rationalized by assuming an electron transfer process as the rate-determining step, involving a tight radical ion and radical pairs, as depicted in Scheme 2. A similar reaction path was postulated recently [29] for the activation of the C–F bond in the addition of hexafluorobenzene-to [Ir(CH$_3$)(PEt$_3$)$_3$].

Acknowledgments

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