CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200701786

Systematic Reactions of $[Pt(PF_3)_4]$

Thomas Drews, Dieter Rusch, Stefan Seidel, Stefan Willemsen, and Konrad Seppelt*[a]

Abstract: Tetrahedral $[Pt(PF_3)_4]$ reacts with H^+ to form trigonal bipyramidal $[Pt(PF_3)_4H]^+$. This in turn looses PF_3 to form square-planar $[Pt(PF_3)_3H]^+$. The complex $[Pt(PF_3)_4]$ can be oxidized with AsF_5 to form the square-planar complex, $[Pt(PF_3)_4]^{2+}$, which can be more conveniently obtained from PtF_4 and PF_3 in HF/SbF_5 solution. $[Pt(PF_3)_4]^{2+}$ reacts with F^- in HF under cluster formation to $[Pt_4(PF_3)_8H]^+$.

Keywords: cluster compounds • ligand effects • phosphorus trifluoride complexes • platinum complexes • structure elucidation

Introduction

At times PF_3 had been considered a similar versatile ligand as CO,[1] and many metal-CO complexes have PF_3 analogues. The PF_3 liquid can be considered a weak σ donor, but a good π-acceptor ligand. Nowadays, metal phosphane complexes of organic phosphanes are numbered by the ten thousands, whereas research on metal-PF_3 complexes remains fairly dormant. There are several reasons for this: PF_3 is a very poisonous gas, is expensive or difficult to prepare and to handle, and the resulting complexes are often much less stable than their organic counterparts. Nevertheless, historically it came as a surprise that homoleptic $[Pt(PF_3)_4]$ and $[Pd(PF_3)_4]$ could be obtained,[2] whereas the corresponding carbonyl complexes are not stable.

Focusing here only on $[Pt(PF_3)_4]$, it is also evident that the chemistry of this interesting compound is largely unexplored, except that it has been tested as a precursor for platinum chemical vapor deposition (CVD) procedures many times.

Systematic chemistry is limited to ligand substitution reactions with isonitriles,[3] and recently, to the thermal decomposition into the cluster compound $[Pt_4(PF_3)_8]$.[4] At the end of this paper we will speculate on this structure of this cluster. Main topic of this work is to systematically investigate the chemistry of $[Pt(PF_3)_4]$.

Results and Discussion

$[Pt(PF_3)_4]$ is a colorless liquid, usually prepared from $PtCl_2$, PF_3, and Cu in an autoclave.[2] This procedure works well with yields around 70%, but is nevertheless tedious. It is very well characterized by physical methods, including a molecular structure determination by electron diffraction.[5] The PtP_4 framework is regular tetrahedral and the PF_3 groups are assumed to rotate freely. The Pt−P bond length is 222.9(5) pm. We have crystallized this compound from pentane, and established its structure in the solid state, in which the entire molecule obeys tetrahedral symmetry, so that the molecule is described by only one Pt, P, and F atom, all in special positions. The crystal structure determination is the most precise one we have ever encountered ($R_1 = 0.0067$), giving a Pt−P bond length of 222.4(1) pm.

Complex $[Pt(PF_3)_4H]^+$: Protonation of $[Pt(PF_3)_4]$ is possible, if the superstrong Brønsted acid HF/SbF_5 is applied. $[Pt(PF_3)_4H]^+[Sb_2F_{11}]^-$ crystallizes out of excess HF at −78 °C in colorless crystals. This compound looses PF_3 upon warming long before room temperature, especially in vacuum; so that the characterization is limited to a single crystal structure determination.

The crystal structure is shown in Figure 1, see also Table 1. The $[Pt(PF_3)_4H]^+$ unit has a trigonal bipyramidal shape with the hydrogen atom and one PF_3 group in apical positions. This fact is clearly established in spite of a twofold disorder of the cation. The equatorial PF_3 groups are bent toward the hydrogen atom with angles $P_{eq}-Pt-H = 78.9-80.5°$. In spite of the disorder the Pt−H bond distance can be established to be 160(10) pm.

Not even at −40 °C it is possible to obtain ^1H and ^{19}F NMR spectra, probably owing to rapid H^+ and F^- ex-

---

[a] T. Drews, D. Rusch, Dr. S. Seidel, Dr. S. Willemsen,
Prof. Dr. K. Seppelt
Freie Universität Berlin, Institut für Chemie und Biochemie
Fabeckstrasse 34–36, 14195 Berlin (Germany)
Fax: (+49) 30-8385-3310
E-mail: seppelt@chemie.fu-berlin.de

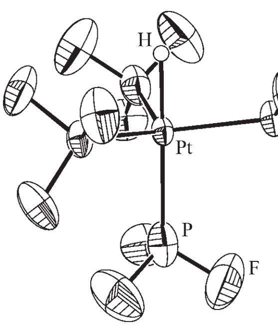

Figure 1. The cation of $[Pt(PF_3)_4H]^+[Sb_2F_{11}]^-$, ORTEP representation, 50 % probability ellipsoids.

change. The ^{31}P NMR shows nothing but a broad line and minor peaks assignable to the typical NMR spectra of the decomposition product $[Pt(PF_3)_3H]^+[Sb_2F_{11}]^-$.

The closest relative complexes to $[Pt(PF_3)_4H]^+$ are the metal hydrides $[CoH(PF_3)_4]$, $[RhH(PF_3)_4]$, and $[IrH(PF_3)_4]$, and, although they are all known,[6] in solution they are non rigid and their solid structures are unknown.[7,8]

Amongst polydentate organophosphane ligated Pt compounds $[(P)_4Pt{-}H]^+$ (P = organophosphane) there are two structures that also come out as trigonal bipyramidal with apical structured hydrogen atoms.[9,10] Here the trigonal bipyramidal structures are strongly distorted as a result of the sterical requirements of the chelating ligands.

Complex $[Pt(PF_3)_3H]^+$: The complex $[Pt(PF_3)_4H]^+[Sb_2F_{11}]^-$ easily looses PF_3 even at −78 °C if the solid material is held in vacuum. This became evident during attempts to obtain NMR spectra. The resulting complex spectra can be assigned to $[Pt(PF_3)_3H]^+$ (see below). A recrystallisation of this material in HF afforded $[Pt(PF_3)_3H]^+[Sb_2F_{11}]^-{\cdot}2HF$, which is stable at room temperature. The single crystal structure determination reveals that the cation has now the common square-planar structure of Pt^{II} complexes, see Figure 2 and Table 1. The hydrogen atom could clearly be located, and the bond length of the *trans* Pt−P bond is a little longer than the *cis* Pt−P bonds. The angle between $P_{cis}{-}Pt{-}P_{cis}$ is much smaller than 180° (157.48(5)°), owing to the small size of the hydrogen atom. Similar compounds have been isolated before with organic PR_3 ligands.

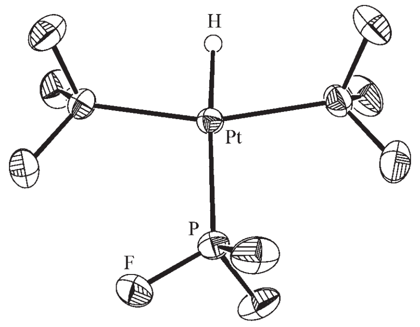

Figure 2. The cation of $[Pt(PF_3)_3H]^+[Sb_2F_{11}]^-{\cdot}2HF$, ORTEP representation, 50 % probability ellipsoids.

The atomic combination Pt/P/F/H should be ideal for NMR investigations, since all four atoms have isotopes with nuclear spin $^1/_2$. $[Pt(PF_3)_3H]^+$ shows the expected spectra, some of them are shown in Figure 3. All coupling constants of the $P_{trans}{-}Pt{-}H$ ionic fragment come out quite large, the *cis*-couplings are small and sometimes not resolvable, see the Experimental Section.

Table 1. Important bond lengths [pm] and angles [°].

	$[Pt(PF_3)_4]$		$[Pt(PF_3)_4H]^+$		$[Pt(PF_3)_3H]^+$		$[Pt(PF_3)_4]^{2+}$ [a]		$[Pt_4(PF_3)_8H]^+$ [b]
	X-ray	calcd[c]	X-ray[d]	calcd[e]	X-ray	calcd[f]	X-ray	calcd[g]	X-ray
Pt−P	222.4(1)	223.9(1)	225.7(1) 248.8(2)	228.1(3×) 232.1	221.7(1) 223.1(1) 229.0(1)	226.5(2×) 233.5	230.3(1) 230.8(1)	234.7	217.7–222.2(2)
Pt−H			161(10)	158.0	145.0(6)	157.4			187(6)
Pt−Pt									262.3–292.9(1)
P−F	154.7(2)	157.7	149.0(3)–151.8(4)	154.9–155.9	150.6–152.2(3)[h]	154.3–155.2	150.6–151.3(2)	152.9–153.3	151.3–153.7(5)
P−Pt−P	109.47	109.47	98.2(1) 100.9(1) 2 × 115.5(1) 2 × 120.1(1)[c]	97.52 118.31	100.9(1) 101.7(1) 157.4(1)	100.3(2×) 159.4	87.92(3) 92.08(3) 180	86.7 93.3 180	97.2(1) 100.2(1)
P−Pt−H			78(4) 80(2) 2 × , 2 × 177(4)		78(1) 79(1) 176(2)	79.7(2×) 179.4			103(2)(Pt−H−Pt)
F−P−F	98.2(1)	98.23	98.7(3)–101.5(2)	100.6–101.5	100.3–102.7(2)[d]	101.5–102.9	102.2–103.4(1)	104.3–104.7	97.3–100.2(1)
energy [a.u.]		−2678.6511402		−2678.9440574		−2038.9373630		−2674.7197467	

[a] $[Pt(PF_3)_4]^{2+}[(AsF_6)_2^-]{\cdot}2HF$, values in the $[Sb_2F_{11}]^-$ salt are virtually identical. [b] $[Pt_4(PF_3)_8H]^+[SbF_6]^-{\cdot}2HF$, values in the AsF_6^- salt are virtually identical. [c] Td symmetry; [d] Pt and H atoms are twofold disordered. [e] C_3 symmetry. [f] C_s symmetry. [g] The D_{2h} symmetry is taken from the crystal structure, a C_{4v} symmetric structure is calculated to be 3 kcal lower in energy. The difference corresponds to rotations of the PF_3 ligands. [h] There are two molecular units in the cell. One of them contains one twofold disordered PF_3 group. Bond length and angle data of this group are not considered in this table.

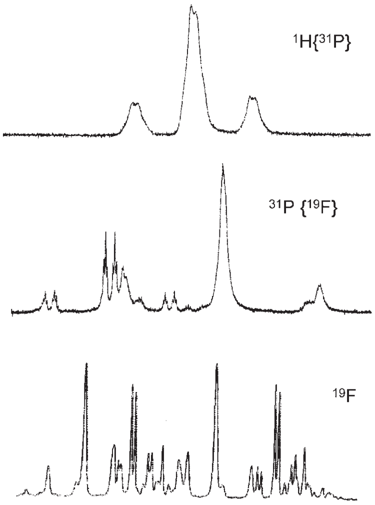

Figure 3. NMR spectra of $[Pt(PF_3)_3H]^+$.

In the Raman spectrum the Pt–H stretching vibration can easily be located at $\tilde{\nu} = 2105\ cm^{-1}$, see Figure 4.

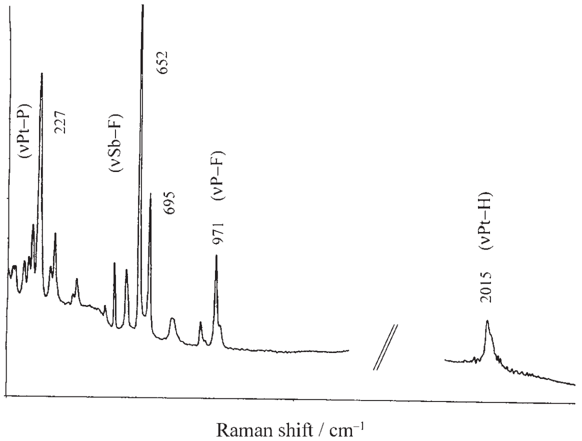

Figure 4. Raman spectrum of $[Pt(PF_3)_3H]^+[Sb_2F_{11}]^- \cdot 2\,HF$, solid, −160 °C.

Oxidation of $[Pt(PF_3)_4]$: Formally the protonation of $[Pt(PF_3)_4]$ is an oxidation, but let us turn now to the simple two electron oxidation. We keep in mind that, while $Pt(CO)_4$ is not stable under chemical conditions, $[Pt(CO)_4]^{2+}$ can be generated in super acidic media, and $[Pt(CO)_4]^{2+}[Sb_2F_{11}]_2^{2-}$ is a stable compound.[16] AsF_5 in HF is a strong enough oxidant, so that $[Pt(PF_3)_4]^{2+}[AsF_6]_2^{2-} \cdot 2\,HF$ is formed. This compound is characterized by crystal structure determination only (see Table 1). It is better to perform the oxidation by AsF_5 in presence of SbF_5, so that stable $[Pt(PF_3)_4(Sb_2F_{11})_2] \cdot 2\,HF$ is obtained.

In the course of this investigation we found a much simpler method of preparing $[Pt(PF_3)_4]^{2+}[Sb_2F_{11}]_2^{2-} \cdot 2\,HF$, namely by reacting PtF_4 with PF_3 in a HF/SbF_5 solution. So the difficult preparation of unstable $[Pt(PF_3)_4]$ can be circumvented. The square-planar $[Pt(PF_3)_4]^{2+}$ ion has, independent of the anion, the same structure, see Figure 5 and Table 1. It is important to note that the Pt–P bond length (222.4 pm) in $[Pt(PF_3)_4]$ is increased after oxidation to 230.3 pm. This effect can originate from sterical constraints, or from lesser π-bond back donation in the cation, or from both effects. It seems to be a general phenomenon that $[PtL_4]^{2+}$ ions (L = phosphane ligand) have longer Pt–L bonds of about 232–235 pm[17–19] than neutral PtL_4 compounds 222–225 pm.[20–22]

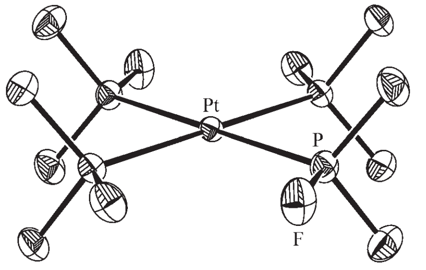

Figure 5. The cation of $[Pt(PF_3)_4]^{2+}[SbF_6]_2^{2-}$, ORTEP representation, 50 % probability ellipsoids.

We have performed calculations for the pair of complexes $[Pt(PF_3)_4]$ and $[Pt(PF_3)_4]^{2+}$ by using ab initio MP2 methods, and have qualitatively obtained a similar lengthening of the Pt–P bond upon oxidation, see Table 1.

The orientation of the PF_3 groups in the crystal obeys the D_{2h} symmetry. This is a little surprising, as a more tilted orientation, for example C_4 symmetry, should be preferred for sterical reasons; such a structure has, in our calculations, a slightly lower energy.

In general these calculations reproduce the experimental structures very well, except that all bonds to Pt atoms come out slightly longer. This is almost certainly a result of the basis set used for Pt. Owing to time limitations larger basis sets could not be used, partially because we have been limited to time expensive MP2 calculations in the electron rich species. DFT calculations, although using only 10 % of the time, do not reproduce the bond lengths well.

Complex $[Pt_4(PF_3)_8H]^+[SbF_6]^- \cdot 2\,HF$: The salts of the $[Pt(PF_3)_4]^{2+}$ cation turn orange in air. This seems to be a hydrolytic reaction followed by loss of PF_3. Adding small amounts of water to an HF solution of $[Pt(PF_3)_3]^{2+}$ salts afforded an orange solution and a small crop of crystal with the cluster cation $[Pt_4(PF_3)_8H]^+$ and varying anions, PF_6^-, AsF_6^-, SbF_6^-, and F^-. A reproducible reaction is that between $[Pt(PF_3)_4H]^+[Sb_2F_{11}]^-$ and NaF or KF in HF. At first, colorless Na/KSbF_6 crystallizes out and, after concentration, orange crystals of $[Pt_4(PF_3)_8H]^+[AsF_6]^- \cdot 2\,HF$ or $[Pt_4(PF_3)_8H]^+[SbF_6]^- \cdot 2\,HF$ are obtained. If excess of Na/KF is used, then the product is $[Pt_4(PF_3)_8H]^+[PF_6]^- \cdot 2\,HF$.

The crystal structure shows its cluster character, see Figure 6 and Table 1. Pt atoms occupy the corners of a distorted tetrahedron. We are not aware if such $[Pt_4L_8]^{2+}$ cluster have ever been observed, except, of course, the neutral $[Pt_4(PF_3)_8]$. Only $[Pt_4(PR_3)_4H_2]$ and $[Pt_4(PR_3)_4H_8]$ have been described before.[23]

The cluster is built up by four distorted square-planar $[Pt_2Pt(PF_3)_2]$ units. This can explain the differences of the

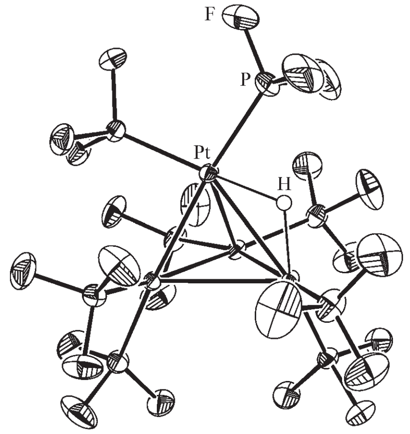

Figure 6. The cation of $[Pt_4(PF_3)_8H]^+[SbF_6]^-\cdot 2HF$, ORTEP representation, 50 % probability ellipsoids.

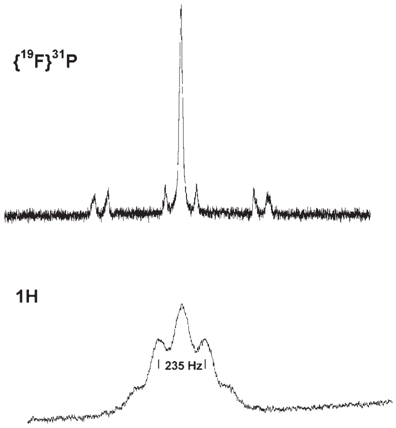

Figure 7. $\{^{19}F\}^{31}P$ NMR spectrum (above) and ^1H NMR spectrum (below) of $[Pt_4(PF_3)_8H]^+$. The calculated intensity distribution of the nine lines in the ^1H NMR spectrum is: 0.021 : 3.41 : 21.68 : 66.74 : 100 : 66.74 : 21.68 : 3.41 : 0.021.

Pt−Pt bond lengths: Within these square-planar units these bond lengths are shorter 260.7(1)–281.4(1) pm, and the remaining Pt−Pt bond is longer: 292.9(1) pm. The hydrogen atom can clearly be located. It is positioned between two Pt atoms as a symmetrical bridge. The hydrogen atom of the HF solvate molecule could not be located, however. This can be explained by two effects: Owing to the twofold disorder of the $As(Sb)F_6$ anion it is expected to be also disordered, and its positive charge makes it particularly difficult to locate by the X-ray method. In the IR spectra there are two medium to weak bands, at $\tilde{\nu} = 1620$ and $1980\,cm^{-1}$ that could be assigned to the vibrations of this hydrogen atom. A weak and broad band at $\tilde{\nu} = 3200\,cm^{-1}$ could be assigned to the HF molecule.

The compound is stable in SO_2 solution, so that NMR spectra can be recorded. Even assuming chemical equivalence of all F, P, and Pt atoms as a result of the migration of the H atom, there is a lot of magnetic inequivalence to be expected. This seems indeed to be the case. Decoupling experiments simplify the spectra enough so that a qualitative interpretation becomes possible. Of interest are the $\{^{19}F\}^{31}P$ and ^1H NMR spectra, see Figure 7 They are both composed of a single line with Pt satellite lines. In the $\{^{19}F\}^{31}P$ NMR three pairs of satellites in the ratio 1:1:1 are clearly resolved, and the fourth missing one is probably hidden in the center line as a result of its small coupling constant. The largest ^{31}P—^{195}P coupling constant could be the $^1J_{P-Pt}$, the second largest one *trans*-$^2J_{P-Pt}$, the smaller one *cis*-$^2J_{P-Pt}$. The ^1H NMR shows a multiplet a $\delta = -3.1$ ppm, which originates from the coupling with four equivalent Pt atoms. As ^{195}Pt has a natural abundance of 33 %, five isotopomers have to be considered (Pt_4H^+, $Pt_3{}^{195}PtH^+$, $Pt_2{}^{195}Pt_2H^+$, $Pt^{195}Pt_3H^+$, and $^{195}Pt_4H^+$). The calculated intensity distribution of the expected nine lines is also given in Figure 7. Evidently the hydrogen atom changes position in solution.

The ^{195}Pt NMR could not be observed. Even after ^{19}F decoupling a 16 line spectrum is expected, owing to coupling with four non equivalent phosphor atoms and the hydrogen atom.

Although chemical shifts and coupling constants of $[Pt_4(PF_3)_4H]^+$ and $[Pt_4(PF_3)_4]$ are distinctively different, there is a striking qualitative similarity of the ^{31}P NMR spectrum.[4] From this fact we conclude that the structure of the neutral cluster is similar, and is also composed of four interlinked square-planar $[Pt_2Pt(PF_3)_2]$ units. We have repeated the preparation of this material, and can confirm all results, especially that crystals by sublimation do not diffract at all. From pentane solution at −78° crystals could be obtained that are still very weakly diffracting. We could establish the unit cell ($a = 859.7(4)$, $b = 1754.8(8)$, $c = 1756.2(8)$ pm, $\alpha = 70.25(1)$, $b = 83.10(1)$, $\gamma = 83.19(1)°$, $Z = 4$) and the Pt positions, and some of the P positions. The Pt atoms form a tetrahedral cluster again. No more information should be deduced from these imperfect data, except that the Pt−Pt distance, as insecure they might be, seem on average to be shorter than in $[Pt_4(PF_3)_8H]^+$.

Conclusion

Some novel $Pt-PF_3$ compounds have been obtained. These compounds have been characterized as much as possible, and their preparation is reproducible. In the course of the search we have obtained a large number of other $Pt-PF_3$ complexes, and have resolved crystal structures for most of them. These have been little more than fortuitous findings, difficult to reproduce, and therefore incompletely characterized. Owing to ligand exchange reactions, thermal instability, high order spectra, and non-rigidity the most appealing analytical tool, namely ^{19}F, ^{31}P, ^1H, and ^{195}Pt NMR spectroscopy, is much less helpful than anticipated. Further work on these compounds is ongoing.

Experimental Section

Physical methods: NMR spectra were obtained by means of a JEOL multi nuclear 400 spectrometer. ^{1}H: 399.65 MHz (external reference TMS), ^{19}F: 376.00 MHz (external reference $CFCl_3$), ^{31}P: 161.7 MHz (external reference H_3PO_4/H_2O), ^{195}Pt: 85.36 MHz (external reference K_2PtCl_6/H_2O).

Raman spectra were recorded by using a Bruker RFS 100 FT-Raman spectrometer. IR spectra were recorded by using a 5 SXC Nicolet FT-spectrometer.

Single crystals were handled in a special device,[24] cut to an appropriate size if necessary, and mounted on a Bruker SMART CCD 1000 TU diffractometer, using $Mo_{K\alpha}$ irradiation, a graphite monochromator, a scan width of 0.3° in ω, and a measuring time of 20 s per frame. A full sphere up to $2\theta = 61°$ was usually obtained by 1800 frames. After semiempirical absorption corrections (SADABS) by equalizing symmetry equivalent reflections, the SHELX programs were used for solution and refinements.[25] Experimental details are laid down in Table 2, results in Table 1. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD: 418727 ($[Pt(PF_3)_4]$), 418724 ($[Pt(PF_3)_4H]^+[Sb_2F_{11}]^-$), 418725 ($[Pt(PF_3)_3H]^+[Sb_2F_{11}]^-\cdot 2HF$), 418727 ($[Pt(PF_3)_4(Sb_2F_{11})_2]\cdot 2HF$), 418775 ($[Pt(PF_3)_4(AsF_6)_2]\cdot 2HF$), 418728 ($[Pt_4(PF_3)_8HSbF_6]\cdot 2HF$), and 418729 ($[Pt_4(PF_3)_8\,HAsF_6]\cdot 2HF$).

Ab initio MP2 calculations were performed by using the GAUSSIAN program.[26] Basis sets for H, F, P: 6-311+G(d,p), as implemented in Ref. [26]. Pt:$s^8p^7d^6[s^6p^5d^3]$ for 18 valence electrons,[27] 60 core electrons were treated by a relativistically corrected core potential.[28]

Usually the handling of hydrolytic sensitive compounds is performed in a glove box with $p_{H_2O} < 1$ ppm.

Chemicals: AsF_5, and KHF_2, and XeF_2 are from laboratory stock. NaF and KF were heated in a vacuum to 500° to remove any water. Anhydrous HF was distilled from 98% technical HF by a stainless steel vacuum line into a stainless steel cylinder, containing $\approx$10 g BiF_5 to remove any water as $[H_3O]^+[BiF_6]^-$.

SbF_5 was distilled twice in vacuum to remove any oxyfluorides and HF. It was only used if its viscosity is high at room temperature. $PtCl_2$ was prepared according to literature.[31]

Synthesis of PF_3: PF_3 is a commercially available, but is prohibitively expensive. Here a simple procedure is given, provided that a stainless steel autoclave and a stainless steel vacuum line are at hand. A 300 mL stainless steel autoclave was filled with commercial PCl_3 (30 g, 218 mmol), and HF (13.8 g, 0.7 mol) was then condensed on it. The mixture was heated 24 hrs at 80 °C and the pressure rises to about 100 bar. After cooling to room temperature the gaseous products are blown through a water container, through a −78, and a −160 °C cold trap. With a single wash the all of the HCl and excess HF were completely absorbed by the water. The PF_3 from the −160 °C cold trap was condensed at −196 °C into a metal storage cylinder. The product was free of PCl_2F, $PFCl_2$, HCl, and HF. Yield 18.7 g (97%).

Synthesis of $[Pt(PF_3)_4]$: The literature reaction between $PtCl_2$, Cu powder, and PF_3 works well with yields up to 90%, provided the Cu powder is fine and oxide free.[2]

Synthesis of PtF_4: The most reliable synthesis so far of PtF_4 is the fluorination of Pt powder under high pressure and temperatures, and subsequently decomposing the $PtF_4/PtF_5/PtF_6$ mixture in several steps at 200° into pure PtF_4.[30] Here we present a more convenient route to PtF_4:

To Pt powder (500 mg, 2.5 mmol) in a PFA tube (poly perfluorovinylether-tetrafluoroethylene copolymer, 12 mm inner diameter), XeF_2 (3 g, 18 mmol) was added. At the metal vacuum line, HF (20 mL, anhydrous) was condensed onto the mixture, and the tube was sealed. At room temperature, gas evolution and yellow coloration was observed. The tube was shaken for 24 h at room temperature. Then a red-brown precipitate forms, and all Pt powder dissolved. The tube was then opened and the all volatile material was pumped away, and the solid residue was heated to 300 °C for 24 hrs to produce light-brown product pure PtF_4, Yield 520 mg (77%).

Synthesis of $[Pt(PF_3)_4H]^+[Sb_2F_{11}]^-$: In a PFA tube $[Pt(PF_3)_4]$ (100 mg, 0.182 mmol) was dissolved in HF (5 mL) containing SbF_5 (200 mg, 0.9 mmol). Slow cooling to −78° affords a large crop of colorless crystals of $[Pt(PF_3)_4H]^+[Sb_2F_{11}]^-$. ^{31}P NMR: $\delta = 11$ ppm (broad). Upon warming to room temperature and pumping PF_3 is liberated.

Synthesis of $[Pt(PF_3)_3H]^+[Sb_2F_{11}]^-\cdot 2HF$: The $[Pt(PF_3)_4H]^+[Sb_2F_{11}]^-$ is freed from supernatant HF by decantation and pumping at −78°, and warming slowly up to room temperature. Redisolution in HF and recrystallization affords colorless needles at −78 °C. Decantation and pumping gives pure $[Pt(PF_3)_3H]^+[Sb_2F_{11}]^-$ as colorless crystals, decomposing without melting above 60 °C. ^{1}H NMR (399.65 MHz): $\delta = -13.7$ ppm ($^{1}J_{^{1}H-^{195}Pt} = 672$ Hz, $^{3}J_{^{1}H-^{19}F} = 36$ Hz, $^{2}J_{^{1}H-^{31}P} = 314$ Hz); ^{19}F NMR (376.00 MHz, SO_2): $\delta = -24.8$ ($^{1}J_{^{19}F-^{31}P} = 1400$ Hz, $^{2}J_{^{19}F-^{195}Pt} = 329$ Hz,

Table 2. Crystallographic data from single crystal x-ray diffraction.

	$[Pt(PF_3)_4]$	$[Pt(PF_3)_4H]^+$ $[Sb_2F_{11}]^+$	$[Pt(PF_3)_3H]^+$ $[Sb_2F_{11}]\cdot 2HF$	$[Pt(PF_3)_4]^{2+}$ $[AsF_6]_2^{2-}\cdot 2HF$	$[Pt(PF_3)_4]^{2+}$ $[Sb_2F_{11}]_2^{2-}\cdot 2HF$	$[Pt_4(PF_3)_8H]^+$ $[SbF_6]^-\cdot 2HF$	$[Pt_4(PF_3)_8H]^+$ $[AsF_6]^-\cdot 2HF$
crystal system	cubic	orthorhombic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$I\bar{4}3m$	$Pmmn$	$P\bar{1}$	$Pbca$	$P2_1/n$	$C2/c$	$C2/c$
a [pm]	825.22(4)	940.8(3)	868.9(1)	926.8(2)	967.52)	1148.6(4)	1121.6(2)
b [pm]	825.22(4)	1339.8(3)	1285.9(2)	1396.4(3)	1532.5(4)	2003.4(8)	2015.6(3)
c [pm]	825.22(4)	780.6(1)	1719.8(3)	1492.9(4)	1065.9(3)	1404.8(6)	1395.2(2)
α [°]	90	90	110.48(1)	90	90	90	90
β [°]	90	90	101.09(1)	90	116.63(1)	111.73(2)	111.21(1)
γ [°]	90	90	92.19(1)	90	90	90	90
cell volume [pm^3]	591.96	983.97	1754.37	1932.3	1412.57	3002.87	2940.4
Z	2	2	4	4	2	4	4
ρ_{calcd} [g cm^{-3}]	2.232	3.377	3.455	3.317	3.508	3.846	3.867
crystal color	colorless	colorless	colorless	colorless	colorless	orange	orange
μ [mm^{-1}]	13.19	10.34	11.47	11.22	9.17	20.07	20.72
measured reflns	1574	10467	46652	24269	12906	18575	18301
independent reflns	186	1438	12622	2935	4285	4572	4493
parameters	13	104	505	156	210	222	225
goodness of fit on F^2	1.189	1.129	1.018	1.053	1.084	1.069	1.030
$R_1[F_o > 4\sigma(F_6)]$	0.007	0.024	0.030	0.019	0.017	0.023	0.031
wR_2	0.017	0.050	0.064	0.046	0.039	0.057	0.088

$^{3}J_{^{18}\mathrm{F}-^{1}\mathrm{H}} = 38$ Hz), −23.7 ($^{1}J_{^{19}\mathrm{F}-^{31}\mathrm{P}} = 1274$ Hz, $^{2}J_{^{19}\mathrm{F}-^{195}\mathrm{Pt}} = 624$ Hz), −93.9 (1F), −119.8 (8F), −142.1 ppm (2F, $Sb_2F_{14}^-$); ^{31}P{^{19}F} NMR (161.7 MHz): $\delta =$ 123.1 (^{1}P, $^{3}J_{^{31}\mathrm{P}-^{31}\mathrm{P}} = 59$ Hz, t, $^{3}J_{^{31}\mathrm{P}-^{1}\mathrm{H}} = 302$ Hz, d, $^{1}J_{^{31}\mathrm{P}-^{195}\mathrm{Pt}} = 3942$ Hz), 100.2 ppm (broad, 2P, $^{1}J_{^{31}\mathrm{P}-^{195}\mathrm{Pt}} = 6496$ Hz); Raman spectrum (solid, −160 °C): $\tilde{\nu} = 2105(10)$, 971(20), 907(5), 788(5), 695(40), 652(100), 597(15), 548(15), 508(3), 387(5), 292(15), 274(5), 227(80), 199(20), 184(5), 166(5), 129(3) cm^{-1}.

Synthesis of $[Pt(PF_3)_4]^{2+}[AsF_6]_2^{2-}\cdot 2HF$: A PFA tube was charged with $[Pt(PF_3)_4]$ (300 mg, 0.55 mmol) onto this HF (3 mL, anhydrous) and AsF_5 (200 mg, 1.2 mmol) were condensed. The mixture was then warmed to room temperature. Cooling to −78 °C affords colorless crystals. For the crystal data see Table 2. After a long period of time pumping at room temperature the elemental analysis was: calcd (%): Pt 21.10; found: 21.09. Yield approximately 250 mg (34 %), decomposing above 40 °C.

Synthesis of $[Pt(PF_3)_4]^{2+}[Sb_2F_{11}]_2^{2-}\cdot 2HF$: The above reaction carried out similarly as above, but in presence of SbF_5 (550 mg, 2.5 mmol). After crystallization at −78° colorless crystals are obtained. For further characterization see below.

Synthesis of $[Pt(PF_3)_4]^{2+}[Sb_2F_{11}]_2^{2-}\cdot 2HF$: A PFA tube was charged with PtF_4 (450 mg, 1.66 mmol) to this SbF_5 (3 g, 13.8 mmol) was added. HF (10 mL, anhydrous) was then condensed into it. Through a stainless steel valve the tube was connected to a vacuum line followed by pressurization (≈2.5 bar) with PF_3, which was slowly consumed and was refilled until a clear solution was obtained. All HF and excess SbF_5 was pumped off under vacuum and the $[Pt(PF_3)_4]^{2+}[Sb_2F_{11}]_2^{2-}$ remained a colorless powder. To free the complex from $SbF_3\cdot SbF_5$ type compounds it was recrystallised from HF at −78 °C to afford about 1 g (60 %) in the form of opaque needles. ^{19}F NMR (376.00 MHz, 25°, HF): $\delta = -29.7$ (P−F), −125 ppm (broad, Sb−F, $^{1}J_{^{19}\mathrm{F}-^{31}\mathrm{P}} = 1292$ Hz, $^{2}J_{^{19}\mathrm{F}-^{195}\mathrm{Pt}} = 524$ Hz); ^{31}P-{^{19}F} NMR (161.7 MHz): $\delta = 62.9$ ppm ($^{1}J_{^{31}\mathrm{P}-^{195}\mathrm{Pt}} = 5166$ Hz); ^{195}Pt-{^{19}F} NMR (85.36 Mhz): $\delta = -668.7$ ppm ($^{1}J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}} = 5152$ Hz); Raman spectroscopy: $\tilde{\nu} = 950$(s), 755(1090), 711(5), 567(70), 481(10), 274(40), 251(8), 201(50), 120(50) cm^{-1}; elemental analysis after pumping at room temperature to free it from HF: calcd (%): Sb 24.4, P 12.4, Pt 19.5; found: Sb 24.5, P 12.6, Pt 20.5.

Synthesis of $[Pt_4(PF_3)_8H]^{+}[SbF_6]^{-}\cdot 2HF$: A PFA tube (8 mm inner diameter) was charged with $[Pt(PF_3)_4]^{2+}[(Sb_2F_{11})]_2^{2-}$ (600 mg, 0.6 mmol). HF (10 mL, anhydrous) is then condensed into it. In a second PFA tube, KF (155 mg, 2.7 mmol; or the equivalent amounts of NaF or KHF) was dissolved in HF (5 mL). Both tubes were interconnected by a stainless steel tube, and warmed to room temperature. The two solutions were mixed and turned immediately yellow.

If NaF is used, the precipitation of $NaSbF_6$ sets in immediately. Slow cooling to −78 °C affords colorless crystals of $KSbF_6$ or further $NaSbF_6$. The remaining solution is decanted, and reduced to about one quarter. Recrystallisation from room temperature to −78° affords a mixture of large colorless cubes ($KSbF_6$, $NaSbF_6$) and orange crystals. These are sorted out under dry nitrogen. The overall yield, based on the platinum content, is small. Losses are inevitable owing to the separation procedure. The orange crystals are stable at room temperature, but react slowly under hydrolysis. The product is $[Pt_4(PF_3)_8H]^{+}[SbF_6]^{-}\cdot 2HF$. If a larger excess of KF(NaF) is used, then the SbF_6^- anion is replaced by the PF_6^-. This can be seen in the ^{19}F/^{31}P NMR spectra. ^{1}H NMR (399.65 MHz): $\delta = -3.1$ ($^{1}J_{^{1}\mathrm{H}-^{195}\mathrm{Pt}} = 253$ Hz), 10.5 ppm (HF); ^{19}F NMR (376.00 MHz, 10 °C, SO_2): $\delta = -22.9$ ($^{1}J_{^{19}\mathrm{F}-^{31}\mathrm{P}} = 1350$ Hz, $^{2}J_{^{19}\mathrm{F}-^{195}\mathrm{Pt}} = 559$ Hz), 114.6 ppm (Sb−F); ^{31}P NMR (161.7 MHz): $\delta = 138.3$ ppm, (m, $^{1}J_{^{31}\mathrm{P}-^{19}\mathrm{F}} =$ 1338.8); ^{31}P{^{19}F} NMR (85.36 Mhz): $\delta = 138.4$ ppm ($J_{^{31}\mathrm{P}-^{195}\mathrm{Pt}} = 6329$, 5313, 1135 Hz); Raman spectrum: $\tilde{\nu} = 968(10)$, 890(5), 654(100), 550(15), 274(40), 229(10), 154(50), 126(20) cm^{-1}; IR spectrum: $\tilde{\nu} = 3250$ (w), 2000 (vw), 1620 (m), 901 (s), 877 (s), 671 (vs), 532 (m), 517 cm^{-1} (m).

Acknowledgement

The authors thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for support of this work.

---

[1] T. Kruck, *Angew. Chem.* **1967**, *79*, 27–43; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 53–67.
[2] T. Kruck, H. Baur, *Angew. Chem.* **1965**, *77*, 505–506, *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 521.
[3] F. Basolo, R. B. Johnson, R. G. Pearson, *Inorg. Chem.* **1971**, *10*, 247–251.
[4] C. L. Hansmill, R. J. Clark, C. W. Ross III, A. G. Marshall, G. Schmutz, *Inorg. Chem.* **1997**, *36*, 5973–5977.
[5] C. L. Rity, L. S. Bartell, *J. Mol. Struct.* **1976**, *31*, 73–76.
[6] T. Kruck, W. Lang, N. Derner, M. Stadler, *Chem. Ber.* **1968**, *101*, 3816–3826.
[7] E. L. Muetterties, P. Meakin, J. P. Jesson, *J. Am. Chem. Soc.* **1971**, *93*, 1797–1799.
[8] P. Meakin, E. L. Muetterties, J. P. Jesson, F. N. Tebbe, *J. Am. Chem. Soc.* **1972**, *94*, 5271–5285.
[9] P. Bruegeller, *Inorg. Chem.* **1990**, *29*, 1742–1750; P. Bruegeller, *Acta Crystallogr. Sect. A* **1992**, *48*, 445–449.
[10] A. Miedaner, D. L. DuBois, C. J. Curtis, R. C. Haltiwanger, *Organometallics* **1993**, *12*, 299–303.
[11] R. E. Caputo, D. K. Mak, R. D. Willett, S. G. N. Roundhill, D. M. Roundhill, *Acta Crystallogr. Sect. A* **1977**, *33*, 215–218.
[12] H. C. Clark, M. J. Dymarski, J. B. Oliver, *J. Organomet. Chem.* **1978**, *154*, C40-C42.
[13] D. R. Russell, M. A. Mayid, P. A. Tucher, *J. Chem. Soc. Dalton Trans.* **1980**, 1737–1742.
[14] D. L. Packett, A. Syed, W. C. Trogler, *Organometallics* **1988**, *7*, 159–166.
[15] R. D. Adams, T. S. Bernard, Z. Li, L. Zhang, *Chem. Ber./Recl.* **1997**, *130*, 729–733.
[16] F. Aubke, *J. Fluorine Chem.* **1995**, *72*, 195–201.
[17] Q.-B. Bao, S. J. Geib, A. L. Rheingold, T. B. Brill, *Inorg. Chem.* **1987**, 26, 3453–3458.
[18] J. Koselka, H.-P. Luethi, E. Dubler, *Inorg. Chim. Acta* **1984**, *86*, 155–163.
[19] G. Albertin, S. Antoniutti, C. Busato, J. Castro, S. Garcia-Fontan, *Dalton Trans.* **2005**, 2641–2649.
[20] L. G. Kuy'mina, Y. T. Struchkov, L. Y. Ukhin, N. A. Dolgopolova, *Koord. Khim.* **1985**, *11*, 1694.
[21] D. J. Darensbourg, T. J. Deauir, N. W. Stafford, J. B. Robertson, J. D. Draper, J. H. Reibenspies, *Inorg. Chem.* **1997**, *36*, 4218–4226.
[22] D. J. Darensbourg, J. B. Robertson, D. L. Larkins, J. H. Reibenspus, *Inorg. Chem.* **1999**, *38*, 2473–2481.
[23] P. W. Frost, J. A. K. Howard, J. L. Spencer, D. G. Turner, D. Gregson, *J. Chem. Soc. Chem. Commun.* **1981**, 1104–1106.
[24] H. Schumann, W. Genthe, E. Hahn, M.-B. Hossein, D. van der Helm, *J. Organomet. Chem.* **1986**, *299*, 67–84.
[25] G. Sheldrick, SHELXS, Program for Crystal Structure Solution, Universität Göttingen (Germany), **1986**; G. Sheldrick, SHELXL, Program for Crystal Structure Refinement, Universität Göttingen (Germany), **1997**.
[26] Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, und J. A. Pople, Gaussian, Pittsburgh PA, **2003**.

[27] M. Kaupp, P. v. R. Schleyer, H. Stoll, H. Preuss, *J. Chem. Phys.* **1991**, *94*, 1360–1366.
[28] U. Haeussermann, M. Dolg, H. Stoll, D. Andrae, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.
[29] E. L. Muetterties, J. E. Castle, *J. Inorg. Nucl. Chem.* **1961**, *18*, 148–153.
[30] J. Slivnik, B. Zemva, *J. Fluorine Chem.* **1980**, *15*, 351–352.
[31] G. Brauer, Handbuch der präparativen Anorganischen Chemie, Band III, F. Enke Verlag Stuttgart, pp. 1710–1711, **1981**.

Received: November 13, 2007