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Volatile Methylplatinum Complexes – Formation and Reactions in Anhydrous HF

Roland Friedemann^[a] and Konrad Seppelt^{*[a]}

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 $[(CO)_2Pt(CH_3)_2]$, $[(PF_3)_2Pt(CH_3)_2]$, and $[(CF_3)_2PC_2H_4P(CH_3)_2-Pt(CH_3)_2]$ [dfmpe = $(CF_3)_2PC_2H_4P(CF_3)_2$] are obtained by ligand exchange reactions. The thermal stability of the complexes increases in the given sequence, whereas their volatility decreases. Demethylation reactions with anhydrous HF

Introduction

There is a vast number of platinum(II) compounds known that are stabilized by complex ligands. Platinum complexes are also very important in many catalytic processes. To mention just one example, (bipyrimidyl)platinum(II) in concentrated sulfuric acid catalyzes the oxidation of methane to methanol.^[1] This example shows that platinum(II) complexed by the "weak" ligand sulfuric acid is very reactive. Platinum(II) compounds with weakly basic ligands are rare. PtF₂, which should have Pt^{II} in a very ionic environment, does not even exist! Possibly the compound closest to having a naked Pt²⁺ ion is $[Pt(H_2O)_4][SbF_6]_2$, which can only be prepared in a tedious way and is barely stable at room temperature. Attempts to remove some or all of the water molecules result in complete decomposition.^[2]

One can try to obtain a partially stabilized Pt^{II} complex, for example with two ligands L_2Pt^{2+} , which may be then called "half naked" Pt^{2+} . Here, the work by Roddick et al., who used the bidentate ligand $(C_2F_5)_2P-C_2H_4-P(C_2F_5)_2$ for this purpose, should be mentioned.^[3]

In the present work, we used CO, PF_3 , $F_2P(CH_2)_{1,2}PF_2$ and $(CF_3)_2PC_2H_4P(CF_3)_2$ (dfmpe) as protecting ligands. The other ligands are two methyl groups, which should be eliminated in HF solution as methane in the hope of generating L_2Pt^{2+} complexes with very weakly coordinated anions.

Results and Discussion

[(CO)₂Pt(CH₃)₂] and Its Reactions

 $[(CO)_2Pt(CH_3)_2]$ has previously been identified in solution by NMR and IR spectroscopy but has not been iso-

cleave one methyl group. The addition of AsF_5 and SbF_5 often cleaves both methyl groups. The resulting L_2Pt^{2+} compounds are obtained in crystalline form with the corresponding $[AsF_6]^-$, $[SbF_6]^-$, $[Sb_2F_{11}]^-$, and $[B_{12}F_{12}]^{2-}$ anions. Bridged dimeric or trimeric platinum complexes are also formed.

lated.^[4] We achieved its isolation by modification of a wellknown procedure, namely the reaction of a diene complex with gaseous CO:

 $[(\text{diene})\text{Pt}(\text{CH}_3)_2] + 2 \text{ CO} \rightarrow [(\text{CO})_2\text{Pt}(\text{CH}_3)_2].$

The resulting $[(CO)_2Pt(CH_3)_2]$ is very volatile, which hampered its isolation. In particular, the separation from the commonly used dienes such as norbornadiene (nbd) or cyclooctadiene (cod) proved to be impossible. Therefore, we used 7-phenylnorbornadiene as the diene as it has a very low vapor pressure.^[5] For details of the starting compound $[C_6H_5-C_7H_7Pt(CH_3)_2]$ see the Experimental Section.

Pure $[(CO)_2Pt(CH_3)_2]$ thus obtained is a yellow crystalline solid with a m.p. of 5 °C that slowly decomposes above 0 °C. Its crystal structure is shown in Figure 1.



Figure 1. Crystal structure of $[(CO)_2Pt(CH_3)_2]_2$. ORTEP representation, 50% probability ellipsoids. The molecules pack in an almost linear columnar structure with Pt–Pt distances of 338.0 pm.

 $[(CO)_2Pt(CH_3)_2]$ reacts in anhydrous HF to result in the cleavage of one Pt–CH₃ bond:

$$[(CO)_2Pt(CH_3)_2] \rightarrow [(CO)_2Pt(CH_3)]^+ + CH_4$$

HF



 [[]a] Freie Universität Berlin, Institut für Chemie und Biochemie, Fabeckstraße 34-36, 14195 Berlin, Germany Fax: +49-30-838-54289
 E-mail: seppelt@chemie.fu-berlin.de





Figure 2. Crystal structure of $[(PF_{3})_2Pt(CH_{3})_2]$. ORTEP representation, 50% probability ellipsoids. The three crystallographically independent but otherwise identical molecules are shown. The columnar arrangement has Pt–Pt distances between 393.2 and 409.9 pm. $r_{av}(Pt-C) = 210(1) \text{ pm}, r_{av}(Pt-P) = 220.1(5) \text{ pm}, \text{ average } C-Pt-C 84.0(5)^{\circ}, \text{ average } P-Pt-P 99.9(1)^{\circ}.$

The cation could only be identified by NMR spectroscopy in solution. It decomposes upon warming and also after the addition of SbF_5 , which ought to give $[SbF_6]^-$ or $[Sb_2F_{11}]^-$ -containing compounds.

Decomposition always produces finely divided Pt powder. According to an X-ray powder analysis the average crystal size is 50 nm.

[(PF₃)₂Pt(CH₃)₂] and Its Reactions

The preparation of $[(PF_3)_2Pt(CH_3)_2]$ is completely analogous to that of the carbonyl complex, except that PF₃ is used instead of CO. Again, it was necessary to start with $[(7\text{-phenylnorbornadiene})Pt(CH_3)_2]$ to obtain a pure product. $[(PF_3)_2Pt(CH_3)_2]$ is a little less volatile but thermally and chemically more stable. Its crystal structure is shown in Figure 2. The spectroscopic data, especially the various NMR spectroscopic data (see Figure 3 and the Experimental Section), are in accordance with the crystal structure.



Figure 3. ¹⁹⁵Pt NMR spectrum of $[(PF_3)_2Pt(CH_3)_2]$; first-order spectrum of a binominal triplet of septets of septets. Chemical shift values are in ppm relative to K_2PtCl_6/H_2O .



Figure 4. Crystal structures of $[(PF_3)PtCH_3][BF_4]$ (top) and $[(PF_3)_2-PtCH_3][SbF_6]$ (bottom). ORTEP representations, 50% probability ellipsoids.



The reaction of $[(PF_3)_2Pt(CH_3)_2]$ with anhydrous HF can be interpreted by NMR spectroscopy, but no crystalline products can be isolated. There are two new products formed in an intensity ratio of 2.9:1. The NMR spectra (³¹P, ¹⁹F, ¹H) of the minor compound is very similar to that of the cation in $[(PF_3)_2Pt(CH_3)][BF_4]$ or $[(PF_3)_2Pt(CH_3)][SbF_6]$ (see below). Here, the two PF₃ groups are chemically and magnetically no longer equivalent. The major compound has similar spectra, except that all lines are broadened. We assume this is due to a dimeric cation such as $[(PF_3)_2(CH_3)-Pt-F-Pt(CH_3)(PF_3)_2]^+$. It was not possible to crystallize any of these compounds, and the platinum compounds decompose above -78 °C.

Upon addition of BF_3 or SbF_5 , however, thermally unstable crystalline complexes of $[(PF_3)_2Pt(CH_3)][BF_4]$ and



Figure 5. Crystal structures of $[(PF_3)_2Pt][SbF_6]_2$ (top) and of the cation in $[(PF_3)_2PtF]_3[SbF_6]_3$ ·HF (bottom). ORTEP representation, 50% probability ellipsoids.

 $[(PF_3)_2Pt(CH_3)][SbF_6]$ are isolated below -35 °C. HF solutions of these complexes show spectra similar to that of the minor compound observed for $[(PF_3)_2Pt(CH_3)_2]$ in HF.

The crystal structures of the two salts are shown in Figure 4. It is obvious that ionic formulations do not fully describe the structures; in fact, the compounds appear as ion pairs with a close contact between the platinum atom and one fluorine atom of the anions. The Pt–F distance is 208(2) pm in the [BF₄]⁻ compound and 215.6(8) pm in the [SbF₆⁻] compound. This shows clearly the more ionic character of [(PF₃)₂Pt(CH₃)][SbF₆] owing to the higher fluoride ion affinity (Lewis acidity) of SbF₅ than BF₃.

After warming the $[(PF_3)_2Pt(CH_3)][SbF_6]$ sample in HF and $[SbF_5]$, two new compounds were found that are stable at room temperature. The main product is $[(PF_3)_2Pt]$ - $[SbF_6]_2$ (see Figure 5). This compound is again best described as an ion pair. Here the Pt–F distances come down to 206.0(5) and 208.9(4) pm, which shows that the "half naked" $[(PF_3)_2Pt]^{2+}$ cation competes well in terms of fluoride ion affinity with SbF₅.

The high fluoride ion affinity of the $[(PF_3)_2Pt]^{2+}$ ion also explains the formation of a minor side product, which has only been characterized by a single-crystal structure determination, namely the trimeric $[(PF_3)_2PtF]_3[SbF_6]_3$ ·HF (see Figure 5). The cation has Pt–F bond lengths (203–208 pm) similar (or even shorter) than those of $[(PF_3)_2Pt][SbF_6]_2$.

$[(F_2PCH_2)_2Pt(CH_3)_2]$ and $[(F_2P)_2CH_2Pt(CH_3)_2]_2$

To arrive at more stable (fluorophosphane)dimethylplatinum complexes, we checked the ligands $F_2PC_2H_4PF_2$ and $F_2PCH_2PF_2$. Both were prepared according to a literature procedure from the corresponding chlorides.^[6] The platinum precursor for the ligand exchange reaction is [codPt(CH₃)₂].

 $[(F_2PCH_2)_2Pt(CH_3)_2]$ is formed in solution and can be identified by ¹H, ¹³C, ¹⁹F, ³¹P, and ¹⁹⁵Pt NMR spectroscopy. Concentration of such solution results in an insoluble material that is probably polymeric.



Figure 6. Crystal structure of dinuclear $[(PF_2)_2CH_2Pt(CH_3)_2]_2$. ORTEP representation, 50% probability ellipsoids. The intra- and intermolecular Pt–Pt distances are 351.8 and 381.0 pm.



The reaction of $F_2PCH_2PF_2$ and $[codPt(CH_3)_2]$ results in a dinuclear complex (see Figure 6). This compound slowly dissolves in HF at -50 °C with the evolution of gas. The NMR spectra indicate the loss of one methyl group per platinum atom and the nonequivalency of the two phosphorus atoms at each platinum center. Attempts to obtain crystalline materials failed. The addition of BF₃ or AsF₅ provides colorless precipitates that are unstable above -50 °C.

[(dfmpe)Pt(CH₃)₂] and Its Reactions

The ligand $(CF_3)_2PC_2H_4P(CF_3)_2$ (dfmpe) has been prepared by a modification of a known procedure (Scheme 1).^[7]

 $Cl_{2}P-C_{2}H_{4}-PCl_{2} \xrightarrow{C_{g}H_{g}OH, El_{2}N} (C_{6}H_{5}O)_{2}P-C_{2}H_{4}-P(OC_{6}H_{5})_{2} \xrightarrow{CF_{3}-Si(CH_{3}J_{3}CSF)} (CF_{3})_{2}P-C_{2}H_{4}-P(CF_{3})_{2} ("dfmpe")$

Scheme 1.

This is then treated with $[codPt(CH_3)_2]$ to form the title compound. The ligand $(CF_3)_2PC_2H_4P(CF_3)_2$ is very similar to $(C_2F_5)_2PC_2H_4P(C_2F_5)_2$, which has been used by Roddick et al.^[3] The advantage of complexes that contain CF_3 groups is that they form crystals of better quality as they have a lower tendency for disorder. In the following, we will abbreviate $(CF_3)_2PCH_2CH_2P(CF_3)_2$ as dfmpe, in analogy to $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, which has been abbreviated as dfepe by Roddick.^[3] [(dfmpe)Pt(CH_3)_2] is thermally much more stable than [(CO)_2Pt(CH_3)_2] and [(PF_3)_2Pt(CH_3)_2]. It can be sublimed at 80–90 °C/14 mbar.

This compound dissolves in anhydrous HF with the formation of one new compound, which decomposes upon warming to room temperature. In the ³¹P NMR spectrum, the two phosphorus atoms are nonequivalent. It is, therefore, safe to assume that only one methyl group has been cleaved.

Upon addition of AsF_5 to such a solution, the second methyl group is also cleaved, and the compound [(dfmpe)-Pt](AsF₆)₂·HF is formed (see Figure 7).

If the excess AsF_5 is removed before the crystallization, a dinuclear complex, [(dfmpe)PtF₂Pt(dfmpe)][AsF₆]₂, is formed (see Figure 8).

 SbF_5 acts similarly to AsF_5 ; the first product [(dfmpe)-Pt][SbF₆]₂·2HF differs only from the AsF_6 compound in the HF content (Figure 7). A larger excess of SbF_5 , to reach the less basic Sb_2F_{11} ion, results in the formation of [(dfmpe)-Pt][SbF₆]·[Sb₂F₁₁]·3HF, in which the coordination sphere around Pt is now completed by [SbF₆] and HF, and the [Sb₂F₁₁] anion is separate from the cation. Coordination of the [Sb₂F₁₁] anion to the platinum atom is only achieved if the crystallization is done in the absence of HF (see Figure 9).

This complex is possibly the one with the least basic ligand so far, namely $[Sb_2F_{11}]$, which is considered even less basic than SbF_6 and HF.

The product distribution varies depending on the reaction conditions, especially when SbF_5 is used as the fluoride



Figure 7. Crystal structure of [(dfmpe)Pt][AsF₆]₂·HF. One AsF₆⁻ anion is a complex ligand and the other is a discrete anion. ORTEP representation, 50% probability plot. [(dfmpe)Pt][SbF₆]₂(HF)₂ and [(dfmpe)Pt][SbF₆][Sb₂F₁₁](HF)₃ have similar structures, except that in the former there is one additional HF in the lattice, and in the latter an exchange of the external [SbF₆]⁻ anion by the [Sb₂F₁₁]⁻ anion.



Figure 8. Structure of the $[(dfmpe)PtF]_2^{2+}$ ion. ORTEP representation, 50% probability plot. Counterions are $([AsF_6]^-)_2$ or $[B_{12}F_{12}]^{2-}$ HF (see below).



Figure 9. $[(dfmpe)Pt][Sb_2F_{11}]^+$ complex. ORTEP representation, 50% probability plot. There are two independent molecules in the unit cell, which are essentially identical. Counterions are $[Sb_2F_{11}]^-$.

ion acceptor. For example, after long reaction times between $[(dfmpe)Pt(CH_3)_2]$ and SbF₅, small amounts of the dihydridodiplatinum complex $[(dfmpe)PtH_2Pt(dfmpe)]$ - $[Sb_2F_{11}]_2$ are formed. Similar complexes have been described before, both as dicationic complexes such as here^[8] and as neutral complexes.^[9] In this dinuclear compound, the separation between the platinum atoms is now 260 pm, in contrast to the distances in the fluorine-bridged dinuclear and trinuclear complexes, so that a Pt–Pt interaction can be discussed (see Figure 10).



Figure 10. Structure of the $[(dfmpe)PtH]_2^{2+}$ ion; the counterion $[Sb_2F_{11}]^-$ is not shown. ORTEP representation, 50% probability plot.

One attempt has been made to arrive at cationic complexes with a completely different weakly coordinating anion, namely $[B_{12}F_{12}]^{2-}$, by salt metathesis (see Figure 8).

Under these conditions, a dimeric platinum complex with two fluorine bridges is formed and is similar to one of the products in the $[AsF_6]^-$ series.

Conclusions

The molecules [(CO)₂Pt(CH₃)₂] and [(PF₃)₂Pt(CH₃)₂] present highly volatile small platinum complexes. Owing to their instability, their use in further synthetic chemistry is rather limited. Reactions with the cyclic compound [(dfmpe)Pt(CH₃)₂] are more successful. In no case has it been possible to arrive at a platinum centre that is so weakly coordinated that it would react with elemental xenon, as has been shown with Au^I, Au^{II}, Au^{III}, and Hg^{II} centers.^[10] This would demand different anions and should not be tried in the presence of anhydrous HF. Reactions in the presence of HF and xenon always lead to HF bound to Pt.

Experimental Section

General: The handling of hydrolytically sensitive compounds was performed in a glove box with $p_{H2O} < 1$ ppm and $p_{O2} = 1$ ppm. Reactions with anhydrous HF were performed by its distillation into PFA tubes (PFA = perfluorovinylether tetrafluoroethylene copolymer) by using a stainless steel vacuum line.

Physical Methods: NMR spectra were obtained with a JEOL multinuclear 400 spectrometer; ¹H: 399.656 MHz (external reference TMS), ¹⁹F: 376.00 MHz (external reference CFCl₃), ³¹P: 161.7 MHz (external reference H₃PO₄/H₂O), ¹⁹⁵Pt: 85.36 MHz (external reference K₂PtCl₆/H₂O). Raman spectra were recorded with a Bruker RFS 100 FT Raman spectrometer. IR spectra were recorded with a 5 SXC Nicolet FT spectrometer. Single crystals were handled with the exclusion of moisture and at low temperatures in a special device^[11] and cut to an appropriate size if necessary, and data were measured with a Bruker SMART CCD 1000 TU diffractometer by using $Mo-K_{\alpha}$ irradiation, a graphite monochromator, a scan width of $\omega = 0.3^{\circ}$, and a measuring time of 20 s per frame. A full sphere mostly up to $2\theta = 61^{\circ}$ was usually obtained by 2400 frames. After semiempirical absorption corrections (SADABS) by equalizing symmetry-equivalent reflections, the SHELX programs were used for solution and refinements.^[12] Experimental details are summarized in Tables 1, 2, 3, and 4. CCDC-895923 {for $[(CO)_2Pt(CH_3)_2]$ }, -895924 {for $[(PF_3)_2Pt(CH_3)_2]$ }, -895929 {for [(PF₃)₂PtCH₃][BF₄]}, -895925 {for [(PF₃)₂Pt-CH₃][SbF₆]}, -895930 {for [(PF₃)₂Pt][SbF₆]₂}, -895928 {for [(PF₃)₆- $Pt_3F_3[SbF_6]_3$ ·HF}, -895916 {for $[CH_2(PF_2)_2Pt(CH_3)_2]$ }, -895921 {for $[C_6H_5C_7H_7Pt(CH_3)_2]$ }, -895918 {for $[(dfmpe)Pt(CH_3)_2]$ }, -895926 {for [(dfmpe)PtHF][AsF₆]₂}, -895917 {for [(dfmpe)PtF]₂- $[(AsF_6)]_2(HF)_2$, -895920 {for $[(dfmpe)PtHF][SbF_6] \cdot 2HF$ }, -895919 {for [(dfmpe)PtHF][SbF₆]·[Sb₂F₁₁]·HF}, -895927 {for [(dfmpe)Pt]- $[Sb_2F_{11}]_2$, -895922 {for $[(dfmpe)Pt]_2[Sb_2F_{11}]_2$ }, and -895915 {for $[(dfmpe)PtF]_{2}[B_{12}F_{12}](HF)_{2}\}$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.

Chemicals: AsF₅, CsF, and CO were from laboratory stock. Anhydrous HF was distilled from 98% technical HF, by using a stainless steel vacuum line, into a stainless steel cylinder containing BiF5 (ca. 10 g) to remove any water as $[H_3O]^+[BiF_6]^-$. $Cl_2PCH_2PCl_2$ was purchased from Acros Chemicals, and Cl2PCH2CH2PCl2 was purchased from aber Co, Germany. SbF5 was distilled twice in vacuo to remove any oxyfluorides and HF. It was only used if its viscosity was high at room temperature. PF₃ is commercially available but is prohibitively expensive. We prepared it by a simple procedure published recently.^[13] A 300 mL stainless steel autoclave was filled with commercial PCl₃ (30 g, 218 mmol), and HF (13.8 g, 0.7 mol) was then condensed into it. The mixture was heated at 80 °C for 24 h, during which time the pressure increased to about 100 bar. After cooling to room temperature, the gaseous products were blown through a water container and -78 and -160 °C cold traps. With a single wash, all of the HCl and excess HF were completely absorbed by the water. The PF3 from the -160 °C cold trap was condensed at -196 °C into a metal storage cylinder. The product was free of PCl₂F, PFCl₂, HCl, and HF. Yield 18.7 g (97%). [codPt(CH₃)₂],^[14] 7-phenylnorbornadiene,^[5] 1,2-bis(difluorophosphanyl)ethane,^[6] 1,2-bis(difluorophosphanyl)methane,^[6] 1,2-bis(diphenoxyphosphanyl)ethane,^[15] and Cs₂-closo-B₁₂F₁₂^[16] were prepared according to literature procedures.

Dichlorido(7-phenylnorbornadiene)platinum(II): Potassium tetrachloroplatinate(II) (3.76 g, 9.06 mmol) was dissolved in a warm solution of water, acetic acid, and hydrochloric acid, and 7-phenylnorbornadiene (3.05 g, 18.1 mmol) was added. The red mixture was heated under reflux for 30 min. The solution became colorless, and a yellow solid precipitated. The solid was removed by filtration at room temperature, washed with water and ethanol, and dried in high vacuum. Yield 3.65 g (89%). ¹H NMR ([D₈]THF): δ = 3.53 (s, 1 H), 4.77 (m, 2 H), 5.25 (m, ²J_{H,Pt} = 69 Hz, 2 H), 5.47 (m, ²J_{H,Pt} = 69 Hz, 2 H), 7.20–7.42 (m, 5 H) ppm. IR: \tilde{v} = 3067 (w),



Table 1. Crystal parameters, data collection, and refinement details for the single-crystal X-ray determinations of [(CO) ₂ Pt(CH ₃) ₂], [(PF	$(r_3)_2$ -
$Pt(CH_3)_2], [(PF_3)_2Pt(CH_3)][BF_4], and [(PF_3)_2Pt(CH_3)][SbF_6].$	

	[(CO) ₂ Pt(CH ₃) ₂]	[(PF ₃) ₂ Pt(CH ₃) ₂]	[(PF ₃) ₂ Pt(CH ₃)][BF ₄]	[(PF ₃) ₂ Pt(CH ₃)][SbF ₆]
Empirical formula	C ₄ H ₆ O ₂ Pt	$C_2H_6F_6P_2Pt$	CH ₃ BF ₁₀ P ₂ Pt	CH ₃ F ₁₂ P ₂ PtSb
M	281.2	401.1	472.9	621.8
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	Pbca	$P2_1/c$	$P2_1/m$	$P2_{1}2_{1}2_{1}$
a [pm]	1302.8(7)	1379.2(5)	736.1(2)	892.7(1)
<i>b</i> [pm]	675.5(4)	826.3(3)	792.3(2)	893.3(1)
<i>c</i> [pm]	1446.5(9)	2371.8(10)	834.1(2)	1514.0(2)
a [°]	90	90	90	90
β [°]	90	106.67(1)	104.97(2)	90
γ [°]	90	90	90	90
$V \times 10^{6} [pm^{3}]$	1273.0	2589.5	487.2	1207.4
Z	8	12	2	4
$D_{\text{calcd.}}$ [Mgm ³]	2.934	3.087	3.223	3.421
$\mu \text{ [mm^{-1}]}$	21.94	16.66	14.84	14.20
Crystal size [mm]	$0.4 \times 0.05 \times 0.01$	$0.3 \times 0.2 \times 0.05$	$0.05 \times 0.05 \times 0.01$	$0.05 \times 0.04 \times 0.04$
Color	yellow	colorless	colorless	colorless
Independent data	1946	7869	1752	3259
R _{int}	0.0857	0.0310	0.1134	_
Parameters	66	307	89	157
R_1, wR_2	0.0450, 0.1266	0.0405, 0.1067	0.0727, 0.1909	0.0556, 0.1435
Flack parameter	-	_	_	0.466

Table 2. Crystal parameters, data collection, and refinement details for the single-crystal X-ray determinations of $[(PF_3)_2Pt][SbF_6]_2$, $[(PF_3)_6-Pt_3F_3][SbF_6]_3$, HF, $[CH_2(PF_2)_2Pt[CH_3]_2]_2$, and $[(dfmpe)Pt[CH_3]_2]$.

	$[(PF_3)_2Pt][SbF_6]_2$	$[(PF_3)_6Pt_3F_3][SbF_6]_3 \cdot HF$	$[CH_2(PF_2)_2Pt[CH_3]_2]_2$	[(dfmpe)Pt[CH ₃] ₂]
Empirical formula	F ₁₈ P ₂ PtSb	F ₄₀ P ₆ Pt ₃ Sb	$C_6H_{16}F_8P_4Pt_2$	$C_4H_{10}F_{12}P_2Pt$
M	842.5	1896.34	754.25	591.2
Crystal system	monoclinic	monoclinic	triclinic	Tetragonal
Space group	$P2_1/n$	$P2_1/n$	$P\overline{1}$	P42
a [pm]	832.3(1)	1148.5(1)	773.4(2)	979.7(1)
b [pm]	1251.6(1)	1393.9(1)	883.9(2)	979.7(1)
c [pm]	1427.3(2)	2037.0(2)	1329.7(3)	849.7(2)
	90	90	77.68(1)	90
β [°]	94.91(1)	90.5(1)	83.54(1)	90
γ [°]	90	90	65.20(1)	90
$V \times 10^{6} [\text{pm}^{3}]$	1481.4	3260.8	805.8	850
Z	4	4	2	2
$D_{\rm calcd.}$ [Mg m ³]	3.778	3.863	3.109	2.407
$\mu \text{ [mm^{-1}]}$	13.44	15.80	17.80	8.91
Crystal size [mm]	$0.4 \times 0.4 \times 0.2$	$0.3 \times 0.05 \times 0.05$	$0.15 \times 0.15 \times 0.06$	$0.3 \times 0.2 \times 0.1$
Color	colorless	colorless	colorless	Colorless
Independent data	5321	7289	4776	2493
R _{int}	_	0.0620	0.0265	0.0284
Parameters	209	470	186	107
R_1, wR_2	0.0498, 0.1329	0.0734, 0.1916	0.0219, 0.0531	0.0239, 0.0657
Flack parameter	-	_	_	0.243

3050 (w), 2894 (vw), 1730 (w), 1596 (w), 1496 (w), 1448 (w), 1394 (w), 1340 (w), 1293 (m), 1228 (w), 1198 (w), 1163 (w), 1141 (w), 1078 (w), 1032 (w), 975 (m), 932 (w), 908 (w), 883 (w), 861 (w), 844 (w), 831 (w), 817 (w), 789 (w), 741 (s), 698 (s), 647 (w), 622 (w), 608 (w) cm⁻¹. Raman: $\tilde{v} = 83$ (s), 211 (w), 151 (m), 211 (w), 244 (w), 266 (w), 322 (w), 334 (w), 572 (w), 883 (w), 941 (w), 1004 (w), 1029 (w), 1078 (w), 1140 (w), 1157 (w), 1191 (w), 1228 (w), 1418 (w), 1582 (w), 1602 (w), 3034 (w), 3050 (w), 3059 (w), 3066 (w), 3076 (w) cm⁻¹. MS (EI, 190 °C): m/z = 434 [M]⁺⁻, 398 [M – HCl]⁺⁻, 168 [Ph-nbd]⁺⁻, 167 [Ph₂CH]⁺⁻, 165 [C₁₃H₉]⁺⁻.

Dimethyl(7-phenylnorbornadiene)platinum(II): Dichlorido(7-phenylnorbornadiene)platinum(II) (1.5 g, 3.45 mmol) was dissolved in diethyl ether (25 mL) at 0 °C, and methyllithium (5.4 mL, 1.6 M) was slowly added to the mixture. A cold saturated ammonium chloride solution (5 mL) was added within 2 h. After warming the mixture to room temperature, the phases were separated. The aqueous phase was washed three times with diethyl ether. The combined organic phases were dried with sodium sulfate, which was removed by filtration, and the solvent was removed. The resulting brown residue was dissolved in pentane, and – after cooling the solution to -80 °C – a yellow solid was obtained. Single crystals were obtained by slow evaporation of the pentane at room temperature. Yield 1.1 g (81%). ¹H NMR (CDCl₃): $\delta = 0.77$ (s, ²J_{H,Pt} = 90 Hz, 3 H), 0.81 (s, ²J_{H,Pt} = 90 Hz, 3 H), 3.39 (s, 1 H), 4.28 (m, 2 H), 4.84 (m, ²J_{H,Pt} = 38 Hz, 2 H), 5.15 (m, ²J_{H,Pt} = 40 Hz, 2 H), 7.04 (m, 2 H), 7.17–7.30 (m, 3 H) ppm. ¹³C{¹H} NMR: $\delta = 6.5$ (s, ¹J_{Pt,C} = 809 Hz), 6.7 (s, ¹J_{Pt,C} = 812 Hz), 53.3 (s, ²J_{Pt,C} = 39 Hz), 86.0 (s,

Table 3. C	Crystal parameters,	data collection,	and refinement	details for the	single-crystal 2	X-ray determinations	of [(dfmpe)PtHF][A	$sF_6]_2$
[(dfmpe)F	PtHF][SbF ₆] ₂ HF, [(dfmpe)PtHF][Sb	F ₆]·[Sb ₂ F ₁₁](HF)2, and [(dfmp	$e)PtF]_2[AsF_6]_2($	$(HF)_2$.		

	[(dfmpe)PtHF][AsF ₆] ₂	[(dfmpe)PtHF][SbF ₆] ₂ HF	$[(dfmpe)PtHF][SbF_6] \cdot [Sb_2F_{11}](HF)_2$	[(dfmpe)PtF] ₂ [AsF ₆] ₂ (HF) ₂
Empirical formula	$C_6H_5As_2F_{25}P_2Pt$	C ₆ H ₄ F ₂₆ P ₂ PtSb ₂	$C_6H_7F_{32}P_2PtSb_3$	$C_{12}H_{10}AsF_{40}P_4Pt_2$
M	954.0	1070.6	1306.4	1576.1
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	C_c	C_c	$P2_1/n$	PĪ
a [pm]	1008.4(2)	1611.5(2)	1189.6(3)	969.8(3)
b [pm]	1520.6(3)	1302.9(2)	1711.2(4)	987.7(3)
<i>c</i> [pm]	1494.6(3)	1100.0(2)	1372.8(3)	1072.4(3)
a [°]	90	90	90	83.64(1)
β[°]	106.76(1)	90.142	101.801(4)	84.79(1)
γ [°]	90	90	90	65.33(1)
$V \times 10^{6} [\text{pm}^{3}]$	2194.5	2309.6	2730.2	926.6
Z	4	4	4	1
$D_{\text{calcd.}}$ [Mg m ³]	2.903	3.079	3.174	2.824
$\mu [{\rm mm}^{-1}]$	9.74	8.71	8.37	9.70
Crystal size [mm]	$0.4 \times 0.05 \times 0.05$	$0.3 \times 0.3 \times 0.2$	$0.3 \times 0.2 \times 0.03$	$0.1 \times 0.1 \times 0.1$
Color	yellow	yellow	light yellow	yellow
Independent data	5791	5328	7271	5503
R _{int}	0.0249	0.0330	0.0481	0.0341
Parameters	337	334	398	272
R_1, wR_2	0.202, 0.0435	0.0228, 0.0507	0.0442, 0.1202	0.0356, 0.0871
Flack parameter	0.169	0.0	_	-

Table 4. Crystal parameters, data collection, and refinement details for the single-crystal X-ray determinations of $[(dfmpe)Pt][Sb_2F_{11}]_2$, $[(dfmpe)PtH]_2[Sb_2F_{11}]_2$, $(dfmpe)[PtF]_2[B_{12}F_{12}](HF)_2$, and $[C_6H_5C_7H_7Pt(CH_3)_2]$.

	$[(dfmpe)Pt][Sb_2F_{11}]_2$	$[(dfmpe)PtH]_2[Sb_2F_{11}]_2$	$(dfmpe)[PtF]_2[B_{12}F_{12}](HF)_2$	$[C_6H_5C_7H_7Pt(CH_3)_2]$
Empirical formula	C ₆ H ₄ F ₃₄ P ₂ PtSb ₄	C ₁₂ H ₁₀ F ₄₆ P ₄ Pt ₂ Sb ₄	$C_{12}H_{10}B_{12}F_{40}P_4Pt_2$	C ₁₅ H ₁₈ Pt
M	1466.1	2029.3	1557.9	393.48
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_{1}/c$
<i>a</i> [pm]	1274.3(7)	1008.4(3)	1106.6(2)	1104.9(4)
<i>b</i> [pm]	1469.1(8)	2094.2(5)	1369.3(3)	653.6(2)
<i>c</i> [pm]	1711.2(7)	1048.1(2)	1382.9(3)	1747.7(6)
a [°]	77.08(5)	90	90	90
β [°]	69.94(5)	98.93(1)	91.75(1)	103.12(1)
γ [°]	89.94(4)	90	90	90
$V \times 10^{6} [\text{pm}^{3}]$	2922.9	2186.52	2094.3	1229.3
Ζ	4	2	2	4
$D_{\text{calcd.}} [\text{Mg}\text{m}^3]$	3.332	3.082	2.470	2.126
$\mu \text{ [mm^{-1}]}$	8.75	9.17	7.01	11.38
Crystal size [mm ⁻¹]	$0.2 \times 0.1 \times 0.05$	$0.1 \times 0.03 \times 0.03$	$0.3 \times 0.2 \times 0.1$	$0.3 \times 0.05 \times 0.01$
Color	light yellow	orange	colorless	light yellow
Independent data	14023	6215	6384	3424
$R_{ m int}$	0.0533	_	0.0240	0.0442
Parameters	850	313	330	147
$\frac{R_1, wR_2}{}$	0.0719, 0.2053	0.0558, 0.1661	0.0198, 0.0483	0.0264, 0.0915

 $^{1}J_{\rm Pt,C}=48$ Hz), 87.3 (s, $^{3}J_{\rm Pt,C}=44$ Hz), 88.3 (s, $^{1}J_{\rm Pt,C}=48$ Hz), 126.8 (s), 128.0 (s), 128.4 (s) ppm. $^{195}{\rm Pt}\{^{1}{\rm H}\}$ NMR: $\delta=-3551$ (s, $^{1}J_{\rm Pt,C}=812$ Hz) ppm. IR: $\tilde{\nu}=3080$ (vw), 3056 (w), 3018 (w), 2919 (w), 2863 (w), 2781 (w), 1596 (w), 1575 (w), 1495 (w), 1441 (w), 1300 (w), 1260 (w), 1170 (w), 1089 (m), 1073 (m), 1030 (w), 937 (w), 812 (w), 757 (w), 726 (s), 694 (s), 645 (m), 572 (m) cm^{-1}. Raman: $\tilde{\nu}=83$ (s), 143 (m), 163 (m), 184 (m), 236 (m), 256 (w), 531 (w), 554 (w), 574 (m), 619 (w), 647 (w), 859 (w), 899 (w), 920 (w), 937 (w), 991 (w), 1003 (m), 1031 (w), 1041 (w), 1089 (w), 1135 (w), 1155 (w), 1170 (w), 1197 (w), 1209 (w), 1228 (w), 1289 (w), 1305 (w), 1340 (w), 1436 (w), 1457 (w), 1580 (w), 1602 (w), 2868 (w), 2905 (w), 3001 (w), 3010 (w), 3038 (w), 3061 (w), 3078 (w) cm^{-1}. MS (EI, 50 °C): m/z = 393.3 [M]+, 168 [Ph-nbd]+, 167 [Ph₂CH]+, 165 [C₁₃H₉]+.

cis-Dicarbonyldimethylplatinum(II): [PtMe₂(Ph-nbd)] (490 mg, 1.25 mmol) and dimethyl ether (5 mL) were added into a glass vessel equipped with a Teflon valve, and carbon monoxide (3.1 mmol) was condensed at -196 °C into the mixture. The contents were warmed to room temperature, and a clear solution formed. A trapto-trap condensation in vacuo (-15, -78, and -196 °C) gave the title compound in high purity in the -78 °C trap. Yield 250 mg (71%). Single crystals were obtained by slow cooling of a dichloromethane solution to -80 °C. M.p. 5 °C. ¹H NMR (CD₂Cl₂): δ = 0.88 (s, ²J_{H,Pt} = 78 Hz) ppm. ¹³C{¹H} NMR: δ = -2.1 (¹J_{C,Pt} = 592 Hz),178.2 (¹J_{C,Pt} = 908 Hz) ppm. ¹⁹⁵Pt NMR: δ = -4255 (sept, ²J_{Pt,H} = 77 Hz) ppm. I^R (gas): \tilde{v} = 462 (m), 2044 (w), 2079 (vs), 2121 (vs), 2128 (vs), 2830 (w), 2907 (m), 2968 (m) cm⁻¹. Raman: \tilde{v}



= 83 (s), 117 (m), 287 (w), 411 (m), 460 (w), 544 (m), 561 (m), 1232 (w), 1418 (w), 2063 (w), 2118 (w), 2821 (w), 2896 (w), 2960 (w) cm⁻¹. MS (EI, 30 °C): $m/z = 281 [M]^{+}$, 266 [M – CH₃]⁺, 251 [M – 2 CH₃]⁺, 238 [M – CH₃ – CO]⁺, 209 [PtCH₂]⁺.

cis-Dicarbonyldimethylplatinum(II) in Anhydrous HF (aHF): [PtMe₂(CO)₂] (80 mg, 0.28 mmol) and aHF (0.5 mL) were condensed into a 4 mm PFA tube at -196 °C. At -80 °C, the complex dissolved with the evolution of gas, and a yellow solution formed. The gas was removed under vacuum, and the tube was sealed. ¹H NMR (aHF, -80 °C): $\delta = 0.83$ (br. s, ²J_{H,Pt} = 60 Hz) ppm. ¹³C{¹H} NMR: $\delta = -17.6$ (s, ¹J_{C,Pt} = 319 Hz), 161.9 (s, ¹J_{C,Pt} = 1780 Hz), 172.1 (s, ¹J_{C,Pt} = 866 Hz) ppm. ¹⁹⁵Pt{¹H} NMR: $\delta = -4273$ (s) ppm. At room temperature, the solution turns brown within 10 min. Warming the solution to 50 °C for 5 h quantitatively produces nanocrystalline platinum.

cis-Dimethylbis(trifluorophosphane)platinum(II): [PtMe₂(Ph-nbd)] (827 mg, 2.10 mmol) was added into a glass vessel equipped with a Teflon valve. Dimethyl ether (ca. 5 mL) and phosphorus trifluoride (500 mg, 5.7 mmol) were condensed into the vessel at -196 °C. The mixture was warmed to room temperature, and a clear yellow solution formed. After 1 h, fractional condensation through -10, -78, and -196 °C cold traps afforded the pure title compound in the -78 °C trap. Yield 750 mg (89%). M.p. -54 °C. ¹H NMR (CD₂Cl₂): $\delta = 0.99$ (t, ${}^{3}J_{H,P} = 22$, ${}^{2}J_{H,Pt} = 74$ Hz) ppm. ${}^{31}P$ NMR: $\delta = 125.3$ (q, ${}^{1}J_{P,F}$ = 1380, ${}^{1}J_{P,Pt}$ = 3300 Hz) ppm. ${}^{19}F$ NMR: δ = -34.6 (m) ppm. ¹³C{¹H} NMR: δ = 1.2 (d m, ² $J_{C,P}$ = 151, ¹ $J_{C,Pt}$ = 564 Hz) ppm. ¹⁹⁵Pt NMR: δ = 4704 (tseptsept, ¹ $J_{Pt,P}$ = 3270, ² $J_{Pt,F}$ = 292, ${}^{2}J_{\text{Pt,H}}$ = 77 Hz) ppm. IR (gas): \tilde{v} = 515 (s), 528 (m), 547 (w), 877 (vs), 907 (vs), 919 (vs), 926 (vs), 1217 (w), 2827 (w), 2910 (w), 2971 (w) cm⁻¹. Raman: $\tilde{v} = 83$ (s), 96 (s), 225 (m), 236 (m), 297 (w), 389 (w), 527 (m), 550 (s), 626 (w), 741(w), 864 (w), 922 (w), 1211 (w), 1234 (w), 1428 (w), 2820 (w), 2902 (w), 2958 (w) cm⁻¹. MS (EI, 30 °C): $m/z = 401 \, [M]^{+}$, 386 $[M - CH_3]^+$, 371 $[M - 2 \, CH_3]^+$, 298 $[M - CH_3 - PF_3]^+$, 283 $[M - 2 CH_3 - PF_3]^+$, 209 $[PtCH_2]^+$, 88 [PF₃]^{+.} HRMS: calcd. for [M]^{+.} 399.9476; found 399.9487.

cis-Dimethylbis(trifluorophosphane)platinum(II) in aHF: A 4 mm PFA tube was filled with [PtMe₂(PF₃)₂] (100 mg, 0.25 mmol), and aHF (0.5 mL) was condensed into it. At -78 °C, the platinum complex reacted within 1 h to result in a colorless solution and the evolution of gas. The gas was removed under vacuum, and the tube was sealed. ¹H NMR (aHF, -80 °C): $\delta = 0.8$ (br. m) ppm. ³¹P NMR (aHF, -80 °C): major product: $\delta = 59.9$ (br. q, $^{1}J_{\rm P,Pt} = 9970$, $^{1}J_{\rm P,F} = 1290$ Hz), 145.5 (br. q, $^{1}J_{\rm P,Pt} = 3350$, $^{1}J_{\rm P,F} = 1260$, $^{2}J_{\rm P,P} = 55$ Hz), 137.8 (qd, $^{1}J_{\rm P,Pt} = 3370$, $^{1}J_{\rm P,F} = 1430$, $^{2}J_{\rm P,P} = 55$ Hz) ppm. ¹⁹F NMR (aHF, -80 °C): major product: $\delta = -42.3$ (br. d, $^{1}J_{\rm F,P} = 1440$, $^{2}J_{\rm F,Pt} = 271$ Hz), -33.8 (br. d, $^{1}J_{\rm F,P} = 1250$, $^{2}J_{\rm F,Pt} = 1240$ Hz); minor product: $\delta = -40.7$ (d, $^{1}J_{\rm F,P} = 1430$, $^{2}J_{\rm F,Pt} = 269$ Hz), -34.7 (d, $^{1}J_{\rm F,P} = 1260$, $^{2}J_{\rm F,Pt} = 1160$ Hz) ppm.

Methylbis(trifluorophosphane)platinum(II) Tetrafluoridoborate: Into the colorless solution described above, boron trifluoride (0.3 mmol) was condensed at -78 °C. A colorless precipitate formed immediately. The excess BF₃ was removed under vacuum, and the tube was sealed. At -60 °C, the solid dissolved, and a yellow solution formed that slowly turned brown. Slow cooling of the solution to -80 °C afforded crystals. NMR (aHF, -60 °C): ¹H NMR: $\delta = 0.9$ (br. m) ppm. ³¹P NMR: $\delta = 49.5$ (qd, ¹ $J_{P,Pt} = 12140$, ¹ $J_{P,P} = 1250$, ² $J_{P,P} = 56$ Hz), 154.1 (qd, ¹ $J_{P,P} = 1440$, ¹ $J_{P,Pt} = 3680$, ² $J_{P,P} = 56$ Hz) ppm. ¹⁹F NMR: $\delta = -41.3$ (d, ¹ $J_{P,P} = 1440$, ² $J_{P,Pt} = 306$ Hz), -32.5 (d, ¹ $J_{P,P} = 1260$, ² $J_{P,Pt} = 1400$ Hz) ppm.

two-chamber 4 mm PFA tube, and antimony pentafluoride (250 mg, 1.2 mmol) was added to the other part. aHF (0.5 mL) was condensed into the part of the tube containing the platinum complex. At -78 °C, a colorless solution formed within 1 h with the evolution of gas. The gas was removed under vacuum, and the contents of the two parts of the tube were combined. A colorless precipitate immediately formed and dissolved completely at -35 °C. The tube was sealed, and slow cooling of the solution to -80 °C afforded crystals. ¹H NMR (aHF, -35 °C): $\delta = 0.8$ (br. m) ppm. ¹⁹F NMR (aHF, -35 °C): $\delta = -40.8$ (d, ¹ $J_{\rm FP} = 1440$, ² $J_{\rm F,Pt} = 312$ Hz), -31.8 (d, ¹ $J_{\rm F,P} = 1260$, ² $J_{\rm F,Pt} = 1430$ Hz), -94.4 (br.), -120.7 (br.), -143.4 (br.) ppm. ³¹P NMR (aHF, -35 °C): $\delta = 47.9$ (qd, ¹ $J_{\rm F,Pt} = 3740$, ² $J_{\rm F,P} = 55$ Hz) ppm.

Bis(trifluorophosphane)platinum(II) Bis(hexafluoridoantimonate): A reaction mixture as described above was warmed to room temperature, and a second gas evolution occurred. The compounds [Pt(PF₃)₂][SbF₆]₂ and (possibly) [PtMe(PF₃)₃]⁺ formed in a ratio of 3:2. [Pt(PF₃)₂][SbF₆]₂ crystallized after slow cooling of the solution to -30 °C. Recrystallization of [Pt(PF₃)₂][SbF₆]₂ in aHF produced some [Pt(PF₃)₂F]₃[SbF₆]₃·HF. Yield of [Pt(PF₃)₂][SbF₆]₂: 20 mg (20%). [Pt(PF₃)₂][SbF₆]₂: ¹⁹F NMR (aHF): δ = -33.5 (d, ¹J_{F,P} = 1300, ${}^{2}J_{\text{E,Pt}}$ = 827 Hz) ppm. ³¹P NMR (aHF): δ = 8.5 (q, br, ${}^{1}J_{\text{P,Pt}}$ = 8640, ${}^{1}J_{\rm PF}$ = 1310 Hz) ppm. Raman: \tilde{v} = 83 (s), 119 (w), 218 (w), 232 (m), 281 (m), 300 (w), 390 (w), 411 (w), 560 (w), 587 (w), 649 (s), 985 (m), 1047 (w) cm⁻¹. [PtMe(PF₃)₃]⁺: ¹H NMR (aHF): $\delta = 1.06$ (q, ${}^{3}J_{\text{H,P}} = 8$, ${}^{2}J_{\text{H,Pt}} = 53$ Hz) ppm. ${}^{19}\text{F}$ NMR (aHF): $\delta =$ -33.1 (d, ${}^{1}J_{F,P} = 1400$, ${}^{2}J_{F,Pt} = 285$ Hz, 3 F), -41.1 (m, 6 F) ppm. ³¹P NMR (aHF): δ = 122.4 (qt, ¹J_{P,F} = 1400, ²J_{P,P} = 78, ¹J_{P,Pt} = 3640 Hz, 1 P), 96.5 (m, 2 P) ppm.

[1,2-Bis(difluorophosphanyl)ethane]dimethylplatinum(II): 1,2-Bis(difluorphosphanyl)ethane (150 mg, 0.9 mmol) and (cyclooctadiene)dimethylplatinum(II) (300 mg, 0.9 mmol) were separately dissolved in diethyl ether (5 mL). The phosphane solution was added slowly under vigorous stirring to the other solution, and a colorless solid formed. Contact with air, too high concentration or cooling resulted in the formation of an insoluble yellow solid. The reaction can also be performed in dichloromethane or tetrahydrofuran. ¹H NMR (CD₂Cl₂): $\delta = 0.73$ (t, ${}^{3}J_{H,P} = 9$, ${}^{2}J_{H,Pt} = 68$ Hz), 2.28 (m) ppm. ³¹P NMR (CD₂Cl₂): $\delta = 206.4$ (t, ${}^{1}J_{P,F} = 1160$, ${}^{1}J_{P,Pt} =$ 2640 Hz) ppm. ¹⁹F NMR (CD₂Cl₂): $\delta = -74.8$ (d, ${}^{1}J_{F,P} = 1160$, ${}^{2}J_{F,Pt} = 193$ Hz) ppm. ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 0.1$ (d, ${}^{2}J_{C,P} =$ 127, ${}^{1}J_{C,Pt} = 540$ Hz), 26.7 (m) ppm. ¹⁹⁵Pt{¹⁹F} NMR (CD₂Cl₂): $\delta = 4528$ (t, ${}^{1}J_{Pt,P} = 2650$, ${}^{2}J_{Pt,H} = 66$ Hz) ppm.

Bis{bis(difluorophosphanyl)methaneldimethylplatinum(II)}: (Cyclooctadiene)dimethylplatinum(II) (510 mg, 1.5 mmol) was added to an ampoule with a valve. At -196 °C, dichloromethane (ca. 10 mL) and bis(difluorophosphanyl)methane (240 mg, 1.6 mmol) were condensed into the ampoule. The valve was closed, and the ampoule was warmed to room temperature. A milky suspension formed. A clear solution was obtained by carefully warming of the suspension to 50 °C. Upon cooling of the solution to 5 °C, yellow crystals formed. The crystals were dried in high vacuum. Yield 400 mg (70%). ¹H NMR (CDCl₃): $\delta = 0.80$ (t, ³ $J_{H,P} = 10$, ² $J_{H,Pt} =$ 69 Hz), 3.11 (br. s) ppm. ³¹P NMR (CDCl₃): δ = 192.6 (m) ppm. ¹⁹F NMR (CDCl₃): δ = -60.6 (m), -74.7 (m) ppm. ¹³C{¹H} NMR $(CD_2Cl_2, 50 \text{ °C}): \delta = 0.1 \text{ (d, } {}^2J_{C,P} = 130, {}^1J_{C,Pt} = 560 \text{ Hz}), 45.3 \text{ (m)}$ ppm. ¹⁹⁵Pt{¹H} NMR (CD₂Cl₂, 50 °C): δ = 4427 (tquint, ¹J_{Pt,P} = 2770, ${}^{2}J_{\text{Pt,F}}$ = 183 Hz) ppm. IR: \tilde{v} = 708 (s), 774 (s), 841 (s), 893 (m), 1065 (w), 1139 (m), 1216 (w), 1347 (m), 1424 (w), 2814 (w), 2899 (m), 2957 (w) cm⁻¹. Raman: $\tilde{v} = 83$ (s), 99 (w), 119 (vw), 158 (w), 223 (w), 243 (m), 272 (m), 417 (vw), 433 (w), 518 (m), 532 (s),



708 (vw), 720 (vw), 770 (vw), 796 (vw), 807 (vw), 841 (vw), 882 (vw), 895 (vw), 1066 (vw), 1147 (vw), 1204 (vw), 1228 (vw), 1346 (vw), 2812 (vw), 2899 (w), 2956 (vw) cm⁻¹. MS (EI, 30 °C): m/z = 739 [M - CH₃]⁺, 709 [M - CH₃ - HF]⁺. HRMS: calcd. for [M - CH₃]⁺ 738.9125; found 738.9102.

Bis{[bis(difluorophosphanyl])methane]dimethylplatinum(II)} in aHF: Bis{[bis(difluorophosphanyl])methane]dimethylplatinum(II)} (120 mg, 0.16 mmol) and aHF (0.5 mL) were combined in a 4 mm PFA tube. The platinum complex dissolved at -50 °C within 1 h to form a yellow solution. The evolved gas was removed under vacuum, and the tube was sealed. ¹H NMR (aHF, -60 °C): $\delta = 1.87$ (br. m, 3 H), 4.04–4.44 (m, 2 H) ppm. ³¹P NMR (aHF, -60 °C): $\delta = 126.2$ (m, ¹*J*_{P,Pt} = 7.6 kHz), 211.7 (m) ppm. ¹⁹F NMR (aHF, -60 °C): $\delta = -81.5$ (m), -72.2 (m), -61.7 (m), -50.1 (m) ppm. ¹³C{¹H} NMR (aHF, -60 °C): $\delta = 9$ (br. m), 45 (br. m) ppm. ¹⁹FPt{¹H, ¹⁹F} NMR (aHF, -60 °C): $\delta = -4120$ (m, br) ppm.

1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane (dfmpe): Cesium fluoride (0.50 g, 3.3 mmol) and 1,2-bis(diphenoxyphosphanyl)ethane (5.00 g, 10.8 mmol) were added to a 100 mL glass vessel equipped with a Teflon valve, and diethyl ether (10 mL) was added. CF₃Si(CH₃)₃ (10.0 mL, 67.5 mmol) was then carefully added. The vessel was closed, and the contents were stirred slowly for 24 h. The surface of the CsF quickly turned brown, and finally the whole suspension became brown. All volatiles including the product were distilled in vacuo. Yield 1.67 g (42%) in 12.8 g of solution according to the ¹H and ¹⁹F NMR spectra. ¹H NMR: δ = 2.29–2.31 (m) ppm. ³¹P NMR: $\delta = -1.5$ to -4.5 (m) ppm. ³¹P{¹⁹F} NMR: $\delta =$ -2.9 (s) ppm. ¹³C{¹H, ¹⁹F} NMR: δ = 14.4, 128.2 (dd, ¹J_{CP} = 9, ${}^{2}J_{\text{C},\text{P}}$ = 10 Hz) ppm. ${}^{19}\text{F}\{{}^{31}\text{P}\}$ NMR: δ = -55.2 (s) ppm. ${}^{19}\text{F}$ NMR: $\delta = -56.3$ (m) ppm.

{1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}dimethylplatinum(II) {[(dfmpe)Pt(CH₃)₂]}: (Cyclooctadiene)dimethylplatinum(II) (1.53 g, 4.60 mmol) was added to a solution of 1,2-bis[bis(trifluoromethyl)phosphanyl]ethane (1.67 g, 4.58 mmol) in diethyl ether (12.8 g, see above). After 20 h, the solvent was removed under vacuum. The remaining brown oil was dissolved in perfluorohexane at 50 °C. Only a little of the brown oil remained undissolved. A large part of the perfluorohexane was removed under vacuum, and a colorless solid precipitated. This was sublimed at 80-90 °C/14 mbar. Yield 1.08 g (40%). M.p. 65–67 °C. ¹H NMR ([D₆]acetone): $\delta = 1.15$ (t, ${}^{3}J_{\rm H,P} = 8$, ${}^{2}J_{\rm H,Pt} = 80$ Hz), 2.87 (d, ${}^{2}J_{\rm H,P} = 13$, ${}^{3}J_{\rm H,Pt} = 13$ Hz) ppm. 19 F NMR ([D₆]acetone): $\delta = -59.1$ (d, ${}^{2}J_{\rm F,P} = 75$, ${}^{3}J_{\rm F,Pt} = 20$ Hz) ppm. ³¹P{¹⁹F} NMR ([D₆]acetone): δ = 68.0 (t, ²J_{P,H} = 13, ¹J_{P,Pt} = 1430 Hz) ppm. ³¹P NMR ([D₆]acetone): δ = 64.9 (sept, ²J_{P,F} = 75, ${}^{1}J_{P,Pt}$ = 1430 Hz) ppm. ${}^{13}C{}^{1}H$ NMR ([D₆]acetone): δ = 1.9 (m, ${}^{1}J_{C,Pt}$ = 314 Hz), 20.8 (dd, ${}^{1}J_{C,P}$ = 20, ${}^{2}J_{C,P}$ = 19 Hz), 122.2 (dq and fine structure, ${}^{1}J_{C,P} = 55$, ${}^{1}J_{C,F} = 320 \text{ Hz}$) ppm. ${}^{195}\text{Pt}\{{}^{19}\text{F}\}$ NMR ([D₆]acetone): $\delta = -4514$ (tsept, ${}^{1}J_{Pt,P} = 1470$, ${}^{2}J_{Pt,H} = 78$ Hz) ppm. IR: $\tilde{v} = 529$ (m), 561 (st), 631 (w), 663 (m), 703 (m), 751 (w), 814 (m), 880 (w), 904 (w), 972 (w), 1027 (w), 1086 (st), 1119 (st), 1141 (st), 1184 (st), 1262 (w), 1287 (w), 1318 (w), 1413 (w), 2814 (w), 2901 (w), 2976 (w) cm⁻¹. Raman: $\tilde{v} = 176$ (55), 195 (15), 218 (70), 250 (5), 272 (15), 285 (30), 351 (5), 371 (20), 409 (2), 464 (10), 507 (10), 540 (100), 704 (10), 749 (30), 982 (2), 1145 (5), 1194 (15), 1220 (5), 1413 (5), 2811 (2), 2902 (5), 2924 (5), 2974 (10) cm⁻¹. MS (EI, 40 °C): $m/z = 575.9 [M - Me]^+$, 560.8 $[M - 2 Me]^+$, 491.8 $[M - 2 Me]^+$ 2 Me – CF_3]⁺⁻, 441.7 [M – 2 Me – C_2F_5]⁺⁻. HRMS: calcd. for [M – Me]⁺ 575.94794; found 575.94812.

Reaction of {1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}dimethylplatinum(II) {[(dfmpe)Pt(CH₃)₂]} with aHF: {1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}dimethylplatinum(II) (0.1 g, 0.2 mmol) was treated with aHF (0.15 mL) in a 4 mm o.d. PFA tube at -196 °C. At -78 °C, the colorless compound dissolved, gas evolved, and a yellow solution formed. The gas was removed under vacuum, and the PFA tube was sealed. ¹H NMR (-70 °C): δ = 2.11 (br. m), 3.36 (br. m), 3.64 (br. m) ppm. ¹⁹F NMR (-70 °C): major product: $\delta = -57.5$ (d, ${}^{2}J_{\rm F,P} = 88$, ${}^{3}J_{\rm F,Pt} = 70$ Hz), -59.7 (d, ${}^{2}J_{\rm F,P} = 97$, ${}^{3}J_{\rm F,Pt} = 93$ Hz); minor product: -57.5 (d, ${}^{2}J_{\rm F,P} = 88$, ${}^{3}J_{\rm F,Pt} = 70$ Hz) ppm. ³¹P{¹⁹F} NMR (-70 °C): major product $\delta = 78.0$ (s, ${}^{1}J_{\rm P,Pt} = 1580$ Hz), 53.0 (s, ${}^{1}J_{\rm P,Pt} = 5600$ Hz); minor product: 74.3 (s, ${}^{1}J_{\rm P,Pt} = 1580$ Hz), 56.2 (s, ${}^{1}J_{\rm P,Pt} = 5300$ Hz) ppm. ¹³C{¹H, ¹⁹F} NMR (-70 °C): major product: $\delta = -4373$ (dd, ${}^{1}J_{\rm Pt,P} = 1580$, ${}^{1}J_{\rm Pt,P} = 5500$ Hz); minor product: -4400 (dd, ${}^{1}J_{\rm Pt,P} = 1560$, ${}^{1}J_{\rm Pt,P} = 5600$ Hz), -4536 (dd, ${}^{1}J_{\rm Pt,P} = 1570$, ${}^{1}J_{\rm Pt,P} = 5300$ Hz) ppm.

{1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}(hydrogen fluoride)platinum(II) Bis(hexafluoridoarsenate) {[(dfmpe)PtHF][AsF₆]₂}: Into the solution described above that had been kept at -78 °C, arsenic pentafluoride (ca. 0.5 mmol) was condensed at -196 °C. The tube was sealed and warmed to -78 °C. A yellow precipitate formed that dissolved at -20 °C. Slow cooling of the solution to -80 °C afforded yellow crystals.

Bis{1,2-bis[bis(trifluoromethyl)phosphanyl]ethane}di- μ -fluoridodiplatinum(II) Bis(hexafluoridoarsenate) {[(dfmpe)PtF₂Pt(dfmpe)]-[AsF₆]₂: 1,2-{Bis[bis(trifluoromethyl)phosphanyl]ethane}dimethylplatinum(II) (49 mg, 0.083 mmol) was treated with aHF (0.2 mL) at -78 °C in a PFA tube. The gas that formed was removed under vacuum, and arsenic pentafluoride (50 mL, 600 mbar, 20 °C) was condensed into the mixture. After warming the mixture to -20 °C, the excess AsF₅ was pumped off, and the tube was sealed. Storage of the mixture at -30 °C overnight produced a yellow solid that dissolved only at 40 °C. Slow cooling of the solution to room temperature afforded yellow crystals.

{1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}platinum(II) Bis-(hexafluoridoantimonate) {[(dfmpe)Pt][SbF₆]₂}: {1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}dimethylplatinum(II) (330 mg, 0.56 mmol) and antimony pentafluoride (300 mg,1.4 mmol) were added to a 4 mm o.d. PFA tube. aHF (ca. 0.4 mL) was condensed into the mixture at -196 °C. At -78 °C, vigorous gas evolution occurred, and a yellow solid precipitated from the yellow solution. The solid dissolved at -20 °C, at which point NMR spectra were measured (see below). Slow cooling of the solution to -100 °C resulted in the formation of yellow crystals of $[(dfmpe)Pt]^{2+}(SbF_6)$ $_{2}$ ·2HF. ¹H NMR (-20 °C): δ = 3.40 (m) ppm. ¹⁹F NMR (-20 °C): $\delta = -55.7$ (d, ${}^{2}J_{\rm EP} = 114$, ${}^{3}J_{\rm EPt} = 45$ Hz), -128.6 (br. s) ppm. ³¹P{¹⁹F} NMR (-20 °C): δ = 59.7 (s, ¹J_{P,Pt} = 4700 Hz) ppm. ³¹P NMR (-20 °C): δ = 59.6 (septsept, ${}^{2}J_{P,F}$ = 115, ${}^{5}J_{P,F}$ = 14, ${}^{1}J_{P,Pt}$ = 4700 Hz) ppm. ¹³C{¹H, ¹⁹F} NMR (-20 °C): δ = 19.5 (m), 117.0 (m) ppm. ¹⁹⁵Pt{¹⁹F} NMR (-20 °C): δ = -4360 (t, ¹*J*_{Pt,P} = 4700 Hz) ppm. The following three compounds were obtained in low yields and are considered to have formed from accidental crystallizations.

{1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}platinum(II) Bis(undecafluoridodiantimonate) {[(dfmpe)Pt][Sb₂F₁₁]₂}: At -196 °C, a thick-walled glass ampoule of 2 mm inner diameter was filled with {1,2-bis[bis(trifluoromethyl)phosphanyl]ethane} platinum(II) bis(hexafluoridoantimonate) (23 mg, 0.022 mmol) and antimony pentafluoride (700 mg, 3.2 mmol). Xenon (6 mmol) was condensed into the mixture at -196 °C and the ampoule was sealed. Antimony pentafluoride and xenon mixed at 0 °C as a colorless solution, but





the platinum complex remained undissolved. The ampoule was kept in an ultrasound bath at 0 °C for 20 min. At 40 °C, a homogeneous yellow solution formed. The mixture was stored at 5 °C for 1 month, and colorless single crystals formed.

Bis{1,2-bis[bis(trifluoromethyl)phosphanyl]ethane}di-µ-hydridodiplatinum(II) Bis(undecafluoridodiantimonate) {[(dfmpe)PtH₂Pt-(dfmpe)][Sb₂F₁₁]₂}: The same reaction as described above but performed in a PFA tube in the presence of HF (600 mg, 30 mmol) and kept solely at -30 °C produced the title compound as orange crystals.

Bis{1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}di-µ-fluoridodi-Dodecafluoridododecaboranate platinum(II) {[(dfmpe)PtF₂Pt- $(dfmpe)|[B_{12}H_{12}]\cdot HF\}:$ {1,2-Bis[bis(trifluoromethyl)phosphanyl]ethane}platinum(II) bis(hexafluoridoantimonate) (40 mg, 40 nmol) and cesium dodecafluoridododecaboranate (50 mg, 80 mmol) were added to a 4 mm o.d. PFA tube, aHF (1.5 mL) was condensed in, and the tube was sealed. After the solution was warmed to room temp., the supernatant colorless liquid was separated from the insoluble remainder and cooled slowly to -80 °C. Two types of colorless crystals formed: cubic-shaped CsSbF₆ and needle-shaped platinum dodecafluoridododecaboranate. ¹⁹F NMR (aHF): $\delta = -54.5$ (br. m, 24 F), -267 (br. m, 12 F) ppm. Crystal structure details are summarized in Tables 1, 2, 3 and 4.

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