Behavior of Neutral Phosphido Derivatives of Platinum and Palladium toward Silver Centers

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Ⓢ *Supporting Information*

ABSTRACT: The reaction of the neutral binuclear complexes $[(R_F)_2Pt(\mu\text{-}PPh_2)_2M(phen)]$ (phen = 1,10-phenanthroline, $R_F = C_6F_5$; M = Pt, **1**; M = Pd, **2**) with $AgClO_4$ or $[Ag(OClO_3)(PPh_3)]$ affords the trinuclear complexes $[AgPt_2(\mu\text{-}PPh_2)_2(R_F)_2(phen)(OClO_3)]$ (**7a**) or $[AgPtM(\mu\text{-}PPh_2)_2(R_F)_2(phen)(PPh_3)][ClO_4]$ (M = Pt, **8**; M = Pd, **9**), which display an "open-book" type structure and two (**7a**) or one (**8**, **9**) Pt—Ag bonds. The neutral diphosphine complexes $[(R_F)_2Pt(\mu\text{-}PPh_2)_2M(P-P)]$ (P—P = 1,2-bis(diphenylphosphino)methane, dppm, M = Pt, **3**; M = Pd, **4**; P—P = 1,2-bis(diphenylphosphino)ethane, dppe, M = Pt, **5**; M = Pd, **6**) react with $AgClO_4$ or $[Ag(OClO_3)(PPh_3)]$, and the nature of the resulting complexes is dependent on both M and the diphosphine. The dppm Pt—Pt complex **3** reacts with $[Ag(OClO_3)(PPh_3)]$, affording a silver adduct **10** in which the Ag atom interacts with the Pt atoms, while the dppm Pt—Pd complex **4** reacts with $[Ag(OClO_3)(PPh_3)]$, forming a 1:1 mixture of $[AgPdPt(\mu\text{-}PPh_2)_2(R_F)_2(OClO_3)(dppm)]$ (**11**), in which the silver atom is connected to the Pt—Pd moiety through Pd—$(\mu\text{-}PPh_2)$—Ag and Ag—P(k^1-dppm) interactions, and $[AgPdPt(\mu\text{-}PPh_2)_2(R_F)_2(OClO_3)(PPh_3)_2][ClO_4]$ (**12**). The reaction of complex **4** with $AgClO_4$ gives the trinuclear derivative **11** as the only product. Complex **11** shows a dynamic process in solution in which the silver atom interacts alternatively with both Pd—μPPh_2 bonds. When P—P is dppe, both complexes **5** and **6** react with $AgClO_4$ or $[Ag(OClO_3)(PPh_3)]$, forming the saturated complexes $[(PPh_2C_6F_5)(R_F)Pt(\mu\text{-}PPh_2)(\mu\text{-}OH)M(dppe)][ClO_4]$ (M = Pt, **13**; Pd, **14**), which are the result of an oxidation followed by a PPh_2/C_6F_5 reductive coupling. Finally, the oxidation of trinuclear derivatives $[(R_F)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}L_2]$ (L_2 = phen, **15**; L = PPh_3, **16**) by $AgClO_4$ results in the formation of the unsaturated 46 VEC complexes $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{III}(\mu\text{-}PPh_2)_2Pt^{II}L_2][ClO_4]_2$ (**17** and **18**, respectively) which display Pt(III)—Pt(III) bonds.
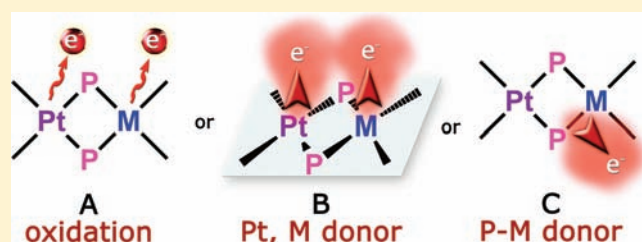
INTRODUCTION

Heteropolynuclear complexes of palladium and platinum containing Ag(I) centers are well-known today.[1–10] In some cases, the d^8-d^{10} derivatives show M—Ag (M = Pt or Pd throughout the paper) donor—acceptor bonds.[11–25] These types of complexes have been also proposed as unstable intermediates both in halide abstraction processes, with elimination of AgX, and in oxidation processes, with the formation of Ag^0.[26–33] In the course of our current research on phosphido derivatives, we have studied the behavior of the dinuclear complexes of platinum and palladium(II) of the general formula $[(R_F)_2Pt(\mu\text{-}PPh_2)_2ML_2]^{n-}$ ($R_F = C_6F_5$) toward silver derivatives obtaining either complexes with M(II)—Ag(I) bond or M(III)—M(III) binuclear complexes. For n = 2, M = Pt, and L = R_F, the electron transfer process affords a Pt(III)—Pt(III) complex of the type **A** (Scheme 1).[34] Surprisingly, this type of complex displays the Pt(III) centers in square planar environments with Pt—Pt and Pt—ligand bonds lying in the same plane. When

n = 1 and 2 L = acetylacetonate, acac, the formation of "open book" type **B** complexes, with one or two M—Ag bonds (Scheme 1),[17] was observed. Finally, when n = 0, M = Pt, and L = PPh_3, the silver ion inserts into the M—PPh_3 bond of the neutral starting material, giving rise to a type **C** cluster (Scheme 1) with a planar core in which a M—$(\mu\text{-}P)$ bond of a bridging phosphido group acts as a donor to the silver center in a 3c—2e bond.[35] In Table 1 are reported the known examples of types **A**—**C** complexes.

In this paper, we describe the reactions of other platinum or palladium phosphido complexes toward silver derivatives in an attempt to gain insights into the factors which address the reactions toward the formation of **A**, **B**, or **C** type complexes.
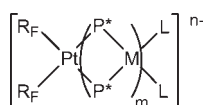
Scheme 1

R_F = C_6F_5
P* = PPh_2
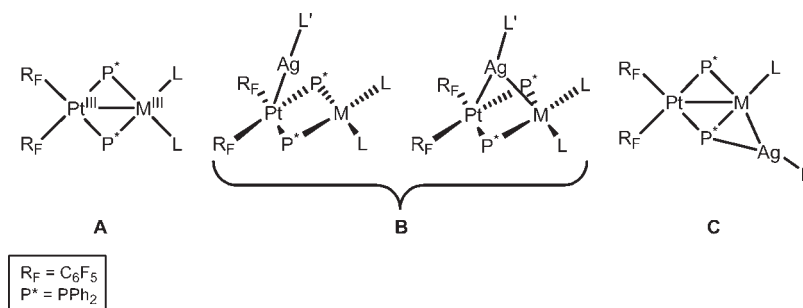
Table 1. Reaction of Platinum or Palladium Phosphido Derivatives Towards Silver Salts

$$\left[\begin{array}{c} R_F \\ Pt \\ R_F \end{array}\!\!\!\!\begin{array}{c} P^* \\ \\ P^* \end{array}\!\!\!\!\begin{array}{c} L \\ M \\ L \end{array}_m\right]^{n-}$$

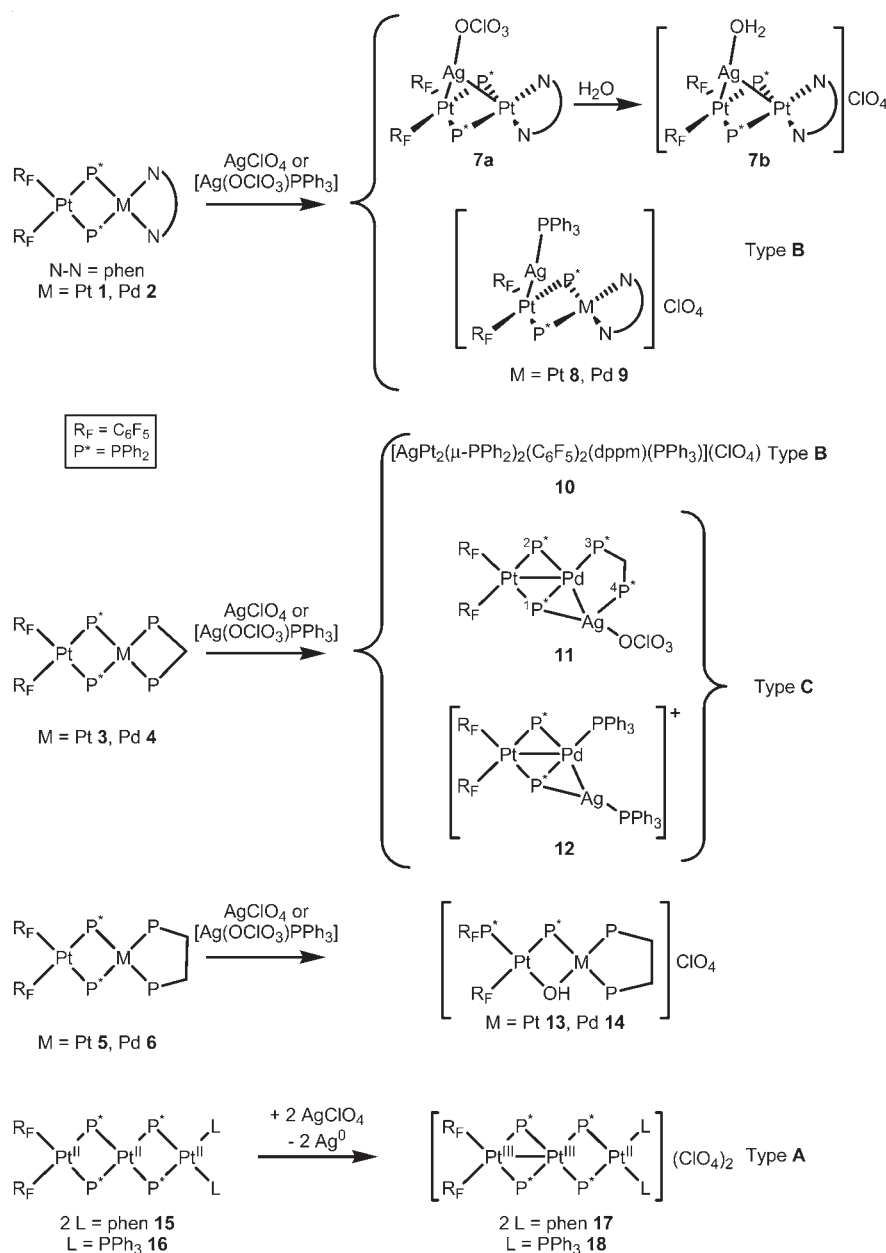| entry	m	2 L	M	n	type	ref
1	1	$2R_F$	Pt	2	A	34
2	1	acac	Pt	1	B	17
3	1	acac	Pd	1	B	17
4	1	$2PPh_3$	Pt	0	C	35
5	1	$2PPh_3$	Pd	0	C	35
6	1	phen	Pt	0	B	this work
7	1	phen	Pd	0	B	this work
8	1	dppm	Pt	0	B	this work
9	1	dppm	Pd	0	C	this work
10	2	$2R_F$	Pt	2	A	39
11	2	acac	Pt	1	A	28
12	2	phen	Pt	0	A	this work
13	2	$2PPh_3$	Pt	0	A	this work

■ RESULTS AND DISCUSSION

Behavior of Dinuclear Derivatives toward Ag(I). The results of the study on dinuclear phosphido bridged derivatives toward silver salts carried out so far (Table 1, entries 1−5) point out that the platinum center of a monoanionic derivative is basic enough to form stable donor−acceptor platinum−silver bonds in the complexes of type **B** (Table 1, entries 2 and 3).[17] Nevertheless, for a complex carrying two negative charges (Table 1, entry 1), the putative Pt−Ag bond is a result of electron transfer from the platinum center to the silver one, affording a Pt(III)−Pt(III) complex of type **A**.[34] Interestingly, for neutral phosphido bridged Pt−M derivatives (Table 1, entries 4 and 5), the $(\mu$-P)−M bond competes with the metal centers as a basic site, and an unusual 3c−2e bond between the $(\mu$-P)−M bond and the silver cation is formed.[35] In order to establish whether the neutral nature of the starting material reduces the basic nature of the platinum or palladium centers and warrants the formation of the aforementioned 3c−2e bond, we have explored the reactivity of the neutral complexes $[(R_F)_2Pt(\mu\text{-PPh}_2)_2ML_2]$ (2 L = phen, M = Pt **1**,[36] Pd **2**; 2 L = dppm, M = Pt **3**,[36] Pd **4**; 2 L = dppe, M = Pt **5**, Pd **6**) toward AgClO_4 and [AgClO_4(PPh_3)].

The heterodinuclear complexes **2**, **4**, and **6** were prepared from cis-$[Pt(R_F)_2(PPh_2)_2]^{2-}$ and [PdCl_2(phen)], [PdCl_2(dppm)], or [PdCl_2(dppe)], respectively, in a way similar to that followed for the synthesis of **3**.[36] Complex **5** was synthesized from $[(R_F)_2Pt(\mu\text{-PPh}_2)_2Pt(NCCH_3)_2]$[37] and dppe (1:1 molar ratio). The elimination of two acetonitrile ligands and coordination of the dppe gave **5** in very good yield. These new neutral complexes were characterized by elemental analysis and spectroscopic methods. All data are given in the Experimental Section, and they compare well with those found for related saturated dinuclear 32 VEC derivatives previously prepared by us.[22,36,38]

The reaction of **1** (Scheme 2) with AgClO_4 even in excess affords the type **B** trinuclear complex $[AgPt_2(\mu\text{-PPh}_2)_2(R_F)_2(OClO_3)(phen)]$ (**7a**), in which both Pt atoms of the starting material act as donors toward the silver center, forming two Pt−Ag bonds (Scheme 2).

The structure of this type **B** trinuclear complex has been established by an X-ray diffraction study. A noteworthy feature of this structure is that two different trinuclear complexes are copresent in the asymmetric part of the unit cell. Figure 1 shows these structures, **7a** and **7b**, and Table 2 lists the most relevant bond lengths and angles. Complexes **7a** and **7b** differ in the coordination environment of the silver center. In fact, while in **7a** the silver atom completes its coordination sphere with an O atom of the perchlorate counterion (Figure 1a), in **7b** the oxygen atom bonded to Ag belongs to a water molecule, presumably present in the crystallization solvents (Figure 1b). Moreover, this water moiety establishes a hydrogen bond with the "free" ClO_4^− anion. The existence of these two different coordination modes of the silver center in the same crystal is probably due to the weak coordinating ability of the OClO_3^− ligand, which is partially displaced from **7a** by traces of water in the crystallization process. Both complexes are trinuclear, with the Pt atoms in square planar environments, and display "open book" structures, characteristic of type **B** complexes. Thus, the two square planar environments of the platinum atoms are not coplanar but form an angle of 40.1(1)° for **7a** and 35.2(1)° for **7b**. The silver atoms lie in the "inner side of the book", forming two Pt−Ag donor−acceptor bonds and a Pt−Ag axis tending to perpendicularity with respect to its corresponding Pt plane. As has been observed in previous cases, the shorter Pt−Ag bonds correspond to the Pt centers which are bonded to the pentafluorophenyl ligands [Pt(1)−Ag(1) = 2.7684(6) Å, Pt(3)−Ag(2) = 2.8184(6) Å], while the Pt atoms bonded to the phenanthroline establish longer bond distances [Pt(2)−Ag(1) = 2.8773(7) Å, Pt(4)−Ag(2) = 2.9051(6) Å]. It can be noticed that the shorter distance is related to a stronger bond formed with the Pt atoms bearing C_6F_5 groups and thus is more basic in character.
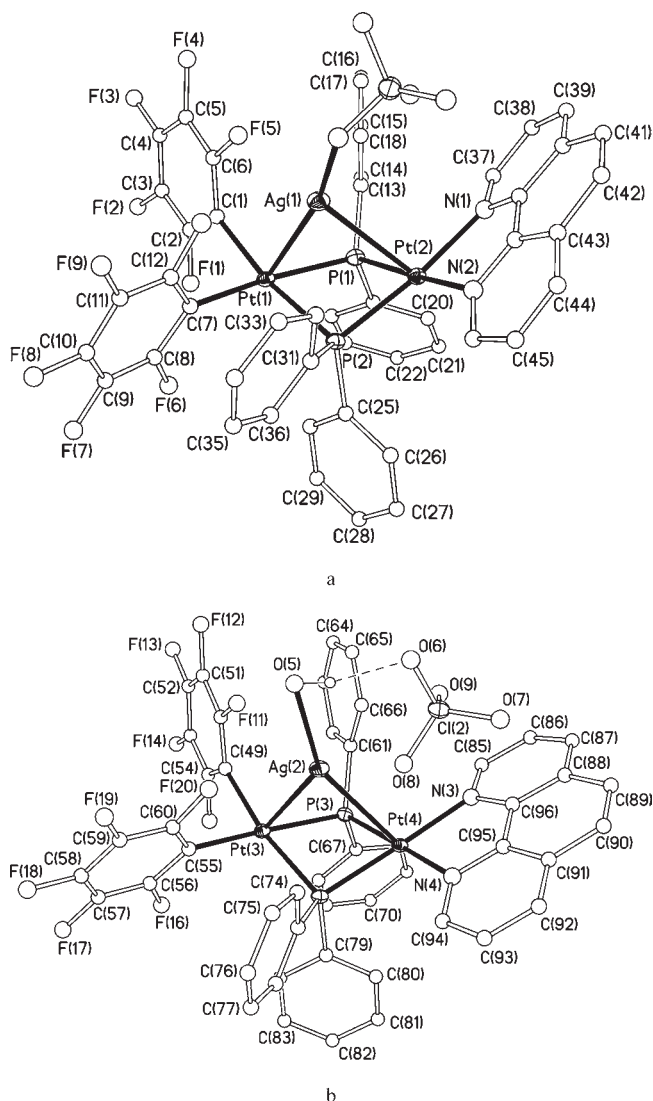
Scheme 2

$R_F = C_6F_5$
$P^* = PPh_2$

N-N = phen
M = Pt **1**, Pd **2**

AgClO$_4$ or [Ag(OClO$_3$)PPh$_3$]

7a → H$_2$O → **7b**

Type **B**
M = Pt **8**, Pd **9**

$[AgPt_2(\mu\text{-}PPh_2)_2(C_6F_5)_2(dppm)(PPh_3)](ClO_4)$ Type **B**
10

M = Pt **3**, Pd **4**

AgClO$_4$ or [Ag(OClO$_3$)PPh$_3$]

11

12

Type **C**

M = Pt **5**, Pd **6**

AgClO$_4$ or [Ag(OClO$_3$)PPh$_3$]

M = Pt **13**, Pd **14**

2 L = phen **15**
L = PPh$_3$ **16**

+ 2 AgClO$_4$
− 2 Ag^0

2 L = phen **17**
L = PPh$_3$ **18**

(ClO$_4$)$_2$ Type **A**

The geometries around the silver centers for **7a** and **7b** are also different. While in complex **7a** the Pt(1), Ag(1), and O(1) display a nearly linear disposition [Pt(1)−Ag(1)−O(1) angle = 162.32(11)°], and the Pt(2)−Ag(1)−O(1) angle [117.60(12)°] is significantly more acute, in **7b** these values are inverted for the analogous Pt atoms, being 132.26(9)° for the Pt(3)−Ag(2)−O(5) angle and 151.76(10)° for the Pt(4)−Ag(2)−O(5) one. In all likelihood, these differences are due to the copresence in **7b** of water and ClO$_4$ in the Pt(4)Ag(2)O(5) region.

The strong tendency of water to replace the perchlorate in the Ag coordination sphere of **7a** was confirmed by $^{31}P\{^1H\}$ NMR experiments. The $^{31}P\{^1H\}$ NMR spectrum of a CD$_2$Cl$_2$ solution of **7a** kept at 193 K showed only a signal at δ −140.6 broadened by the couplings with $^{107/109}$Ag and flanked by two sets of ^{195}Pt satellites ($^1J_{P,Pt}$ =1843 and 2342 Hz). Monitoring the solution at intervals of 5 min revealed the progressive decreasing of the

signal at δ −140.6, with a contemporary appearance of a signal at δ −108.1 ($^1J_{P,Pt}$ =1452 and 2091 Hz), which became the only signal after 30 min. On warming the solution up to 298 K, the chemical shift of this species did not significantly change (δ −106), but the signal became considerably broad ($\Delta\nu_{1/2}$ = 250 Hz). We interpret these results admitting that the species at δ −140.6 is the perchlorate adduct **7a**, which reacts with the water present in the CD$_2$Cl$_2$ to give the H$_2$O adduct of silver **7b**.

The ^{19}F NMR spectrum of **7b** (the stable form in commercial CD$_2$Cl$_2$) at 193 K showed five broad signals (see Experimental Section) of the same intensity, thus indicating that the two C$_6$F$_5$ groups are equivalent and the two halves of each C$_6$F$_5$ ring are unequivalent. This pattern is in agreement with the presence of the Pt−Ag bonds in solution and with a hindered rotation about the Pt−C bonds. Upon warming the solution up to room temperature, the C$_6$F$_5$ rings can freely rotate, and the ^{19}F

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Figure 1. Drawings of the two complexes found in the crystal structure of 7 (**7a** and **7b**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 7·0.50H$_2$O·1.25CH$_2$Cl$_2$

Pt(1)−C(1)	2.072(5)	Pt(3)−C(55)	2.080(5)
Pt(1)−C(7)	2.078(5)	Pt(3)−C(49)	2.082(5)
Pt(1)−P(2)	2.3084(13)	Pt(3)−P(3)	2.3044(14)
Pt(1)−P(1)	2.3093(14)	Pt(3)−P(4)	2.3053(12)
Pt(1)−Ag(1)	2.7684(6)	Pt(3)−Ag(2)	2.8184(6)
Pt(2)−N(1)	2.101(4)	Pt(4)−N(3)	2.106(4)
Pt(2)−N(2)	2.112(4)	Pt(4)−N(4)	2.121(4)
Pt(2)−P(2)	2.2871(13)	Pt(4)−P(4)	2.2970(14)
Pt(2)−P(1)	2.2930(13)	Pt(4)−P(3)	2.2987(12)
Pt(2)−Ag(1)	2.8773(7)	Pt(4)−Ag(2)	2.9051(6)
Ag(1)−O(1)	2.285(4)	Ag(2)−O(5)	2.323(4)
C(1)−Pt(1)−C(7)	91.84(19)	C(55)−Pt(3)−C(49)	90.44(19)
C(1)−Pt(1)−P(2)	170.88(14)	C(55)−Pt(3)−P(3)	172.58(13)
C(7)−Pt(1)−P(2)	95.12(14)	C(49)−Pt(3)−P(3)	95.19(15)
C(1)−Pt(1)−P(1)	97.80(15)	C(55)−Pt(3)−P(4)	99.49(13)
C(7)−Pt(1)−P(1)	169.27(14)	C(49)−Pt(3)−P(4)	169.74(15)
P(2)−Pt(1)−P(1)	74.83(5)	P(3)−Pt(3)−P(4)	74.70(5)
C(1)−Pt(1)−Ag(1)	97.55(14)	C(55)−Pt(3)−Ag(2)	98.91(14)
C(7)−Pt(1)−Ag(1)	96.22(14)	C(49)−Pt(3)−Ag(2)	99.09(14)
P(2)−Pt(1)−Ag(1)	75.87(3)	P(3)−Pt(3)−Ag(2)	75.46(3)
P(1)−Pt(1)−Ag(1)	77.91(3)	P(4)−Pt(3)−Ag(2)	76.96(3)
N(1)−Pt(2)−N(2)	78.78(16)	N(3)−Pt(4)−N(4)	78.72(16)
N(1)−Pt(2)−P(2)	173.71(11)	N(3)−Pt(4)−P(4)	177.90(11)
N(2)−Pt(2)−P(2)	103.08(12)	N(4)−Pt(4)−P(4)	103.36(13)
N(1)−Pt(2)−P(1)	101.99(12)	N(3)−Pt(4)−P(3)	102.94(11)
N(2)−Pt(2)−P(1)	174.21(11)	N(4)−Pt(4)−P(3)	177.71(12)
P(2)−Pt(2)−P(1)	75.55(5)	P(4)−Pt(4)−P(3)	74.97(5)
N(1)−Pt(2)−Ag(1)	99.88(11)	N(3)−Pt(4)−Ag(2)	104.07(10)
N(2)−Pt(2)−Ag(1)	98.32(11)	N(4)−Pt(4)−Ag(2)	104.35(10)
P(2)−Pt(2)−Ag(1)	73.95(3)	P(4)−Pt(4)−Ag(2)	75.29(3)
P(1)−Pt(2)−Ag(1)	75.89(3)	P(3)−Pt(4)−Ag(2)	73.78(3)
O(1)−Ag(1)−Pt(1)	162.32(11)	O(5)−Ag(2)−Pt(3)	132.26(9)
O(1)−Ag(1)−Pt(2)	117.60(12)	O(5)−Ag(2)−Pt(4)	151.76(10)
Pt(1)−Ag(1)−Pt(2)	74.895(11)	Pt(3)−Ag(2)−Pt(4)	74.446(11)
Pt(2)−P(1)−Pt(1)	96.51(5)	Pt(4)−P(3)−Pt(3)	97.58(5)
Pt(2)−P(2)−Pt(1)	96.70(5)	Pt(4)−P(4)−Pt(3)	97.60(5)

spectrum showed the expected three signals in 2:1:2 intensity ratio for the *o*-, *p*-, and *m*-F atoms of both rings. This behavior is analogous to that previously observed for the silver adduct of the $[(R_F)_2Pt(\mu\text{-}PPh_2)_2M(acac)]^-$ species.[17]

As to the ^{195}Pt NMR of **7b**, we were able to find the signals of Pt^3 (δ_{Pt3} −3340) and Pt^4 (δ_{Pt4} −3450) by recording the ^{1}H−^{195}Pt HMQC spectrum which showed the cross peaks between a phenanthroline proton and Pt^4 and between the *ortho* phenyl protons and Pt^3 (see Figure 1 for Pt atom numbering).

The treatment of CH$_2$Cl$_2$ solutions of **1** and **2** with [Ag(OClO$_3$)(PPh$_3$)] (1:1 molar ratio) afforded yellow solids which can be formulated as $[AgMPt(\mu\text{-}PPh_2)_2(R_F)_2(PPh_3)\text{-}(phen)][ClO_4]$ (M = Pt, **8**; M = Pd, **9**; Scheme 2). Despite several attempts, only low quality crystals could be obtained, and thus no complete X-ray studies could be performed. Nevertheless, the connectivity of the atoms could be established unambiguously, indicating that the complexes formed are of type **B**, but with only one of the metal centers (the platinum atom bonded to the two C$_6$F$_5$ groups) establishing a bond with the Ag center.

For cluster **8**, the ^{31}P{^{1}H} NMR spectrum at 293 K showed a broad signal at δ −129.2 ($^1J_{P,Pt}$ =1792 and 2240 Hz) attributable to the bridging phosphides and a couple of doublets centered at δ 8.8 attributable to the coordinated PPh$_3$ ($^1J_{P,107Ag}$ = 680 Hz; $^1J_{P,109Ag}$ = 760 Hz), while for cluster **9** the bridging phosphides and the coordinated PPh$_3$ gave signals at δ −111.0 ($^1J_{P,Pt}$ =1441 Hz) and at δ 12.3, respectively.

The ^{19}F NMR spectra of **8** and **9** (CD$_2$Cl$_2$ solution) at room temperature showed three signals in a 2:1:2 intensity ratio for the *o*-, *p*-, and *m*-F atoms of both rings. In contrast to the case of **7b**, at 193 K, only a signal broadening is observed, indicating that for **8** and **9** the C$_6$F$_5$ rings can freely rotate even at low *T*.

The ^{195}Pt signal of **9** was found at δ −3431 by means of a ^{19}F−^{195}Pt HMQC spectrum. Given that the projection of the 2D spectrum on F1 appears as a pseudoquartet (Figure 2), it can be affirmed that the direct ^{195}Pt−$^{107/109}$Ag coupling constants are of the same order of magnitude as the $^1J_{Pt,P}$ (1440 Hz).

The neutral dinuclear diphosphine complexes $[(R_F)_2Pt(\mu\text{-}PPh_2)_2M(P\text{-}P)]$ [P−P = dppm, M = Pt (**3**) or Pd (**4**);

P—P = dppe, M = Pt (**5**) or Pd (**6**)] displayed different behavior when reacted with silver derivatives. While a mixture of unidentified compounds was obtained from the reaction of **3** with AgClO$_4$, a single species formed by the reaction of **3** with an equimolar amount of [Ag(OClO$_3$)(PPh$_3$)]. Such a species displays dynamic behavior in solution, and good quality crystals for XRD analysis were not obtained. However, elemental analysis and spectroscopic features indicate the formula [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(dppm)Ag(PPh$_3$)][ClO$_4$] (**10**) and a structure of type **B**.

The ^{31}P{^{1}H}NMR in CDCl$_3$ at 213 K of **10** showed, besides a couple of doublets due to the Ag-bound PPh$_3$ (δ 10.0; $^1J_{107Ag,P}$ = 691 Hz; $^1J_{109Ag,P}$ = 795 Hz), two mutually coupled multiplets arising from an AA′XX′ system due to the μ-PPh$_2$ (δ −143.5) and to the dppm P atoms (δ −24.1, J_{AX} + $J_{AX'}$ = 315 Hz). The appearance of the μ-PPh$_2$ signals at a high field indicate that the bridging phosphides do not subtend a Pt—M bond,[34,35,39−41] thus excluding for **10** a structure of type **A** or **C**. The most remarkable feature of the ^{1}H NMR spectrum of **10** in CDCl$_3$ at 213 K is that the methylene protons gave two separate resonances at δ 5.0 and δ 4.5, indicating that the position of the Ag(PPh$_3$) moiety at low T renders inequivalent the two methylene protons. All of these data, along with the ^{195}Pt resonance of Pt^1, which was found at δ −3390 (^{19}F−^{195}Pt HMQC), a value comparable to that obtained for the analogous Pt^1 atoms of complexes **7b** (δ_{Pt3} −3340) or **9** (δ −3431), suggest for **10** at low T an "open book" structure with two Pt—Ag bonds.

The three ^{31}P{^{1}H} NMR signals of **10** are quite broad at room temperature (the broadest one being that of the μ-PPh$_2$) but maintain the multiplicity observed at low T, indicating the occurrence of a dynamic process that does not affect the mutual position of the P atoms. A plausible dynamic process which accounts for the experimental data is depicted in Scheme 3. While at low T the Ag(PPh$_3$) moiety bridges to both Pt atoms, on

increasing the temperature the Ag—Pt^2 bond is continuously broken and reformed, as depicted in Scheme 3. Since the room temperature ^{1}H NMR spectrum showed the methylene protons as a broad triplet, it can be assumed that dissociation-recoordination of the Ag(PPh$_3$) moiety may also occur in solution at room temperature, thus rendering equivalent the two methylene protons.

The heterodinuclear complex **4**, in which the dppm ligand is bonded to the palladium center, reacts with silver derivatives to afford type **C** species (Scheme 2). The reaction of **4** with AgClO$_4$ produces [AgPdPt(μ-PPh$_2$)$_2$(R$_F$)$_2$(OClO$_3$)(dppm)] (**11**). Two different crystals of **11** have been studied by X-ray diffraction, but in both cases their low quality prevented the measurement of good sets of diffraction data and thus a complete characterization of the crystal structure. Nevertheless, the connectivity of the atoms in complex **11** could be unambiguously established as that represented in Scheme 2. As can be observed, the "AgOClO$_3$" fragment is inserted into the Pd—PPh$_2$CH$_2$PPh$_2$ bond, and at the same time, the (μ-P)—Pd bond of the phosphido group behaves as a donor toward the silver center. The electronic requirements of the palladium center are fulfilled by a Pt—Pd bond.

The addition of [Ag(OClO$_3$)(PPh$_3$)] to **4** (1:1 molar ratio) afforded a solid made up of a 1:1 mixture of **11** and the previously reported [AgPdPt(μ-PPh$_2$)$_2$(R$_F$)$_2$(PPh$_3$)$_2$][ClO$_4$] (**12**;[35] Table 1, entry 5) along with minor amounts of other unidentified byproducts (NMR spectroscopy). The formation of the **11**/**12** mixture, together with the detection in solution of free dppm, can be explained, according to Scheme 4, by admitting that complex **4** reacts with [Ag(OClO$_3$)(PPh$_3$)], giving **11** and free PPh$_3$, which, in turn, can attack the not yet reacted **4** to give an intermediate in which the Pd atom is bonded to dppm (which behaves as a monodentate ligand) and to PPh$_3$. The reaction of fresh [Ag(OClO$_3$)(PPh$_3$)] with the latter intermediate can afford, upon a loss of dppm, the product **12**.

The ^{31}P{^{1}H} NMR spectrum of **11** shows four signals (see Scheme 2 for the atom numbering) and indicates that the structure proposed in the solid state is maintained in solution. The two signals due to the P atoms of the phosphido ligands appear at low fields, in agreement with the presence of the bridging phosphides subtending a Pd—Pt bond.[35,41−44] The presence of the Pt—Pd bond is also supported by the value of the coupling between Pt and P^3 atoms, 92 Hz.[45−51] Moreover, the chemical shift of the P^2 atom (phosphido group bridging two metal centers, μ^2-PPh$_2$) appears at δ 293.2, while the P^1 atom (phosphido group bridging three metal centers, μ^3-PPh$_2$) appears at δ 138.3. This decrease in the value of δ on going from a μ^2-PPh$_2$ coordination mode to a μ^3-PPh$_2$ one has been observed before,[35,42,52−55] and in complex **11**, this $\Delta\delta$ (155 ppm) is greater than in the previously reported complexes [MM′Pt(μ-PPh$_2$)$_2$(R$_F$)$_2$(PPh$_3$)$_2$][ClO$_4$] (M = Pt, Pd; M′ = Ag, Au).[35]
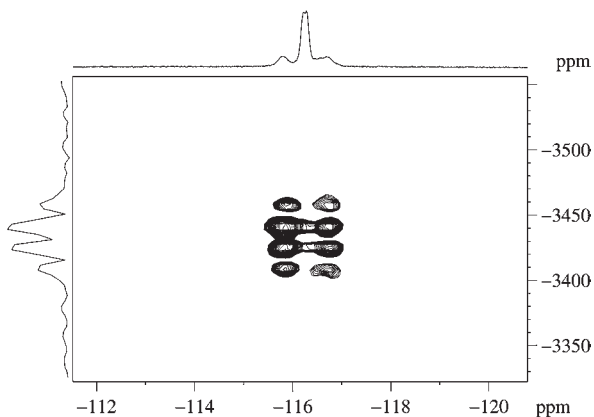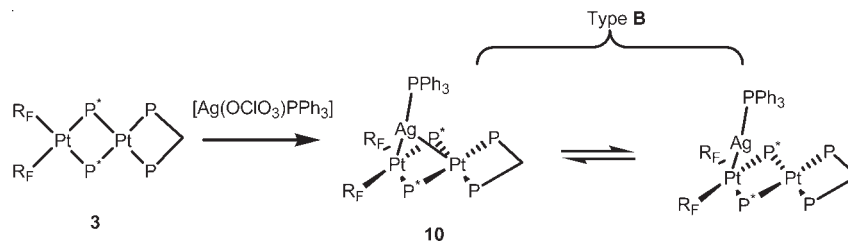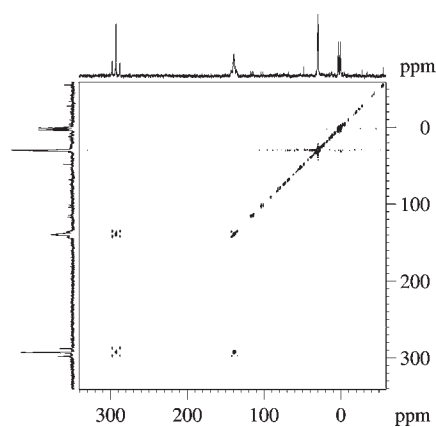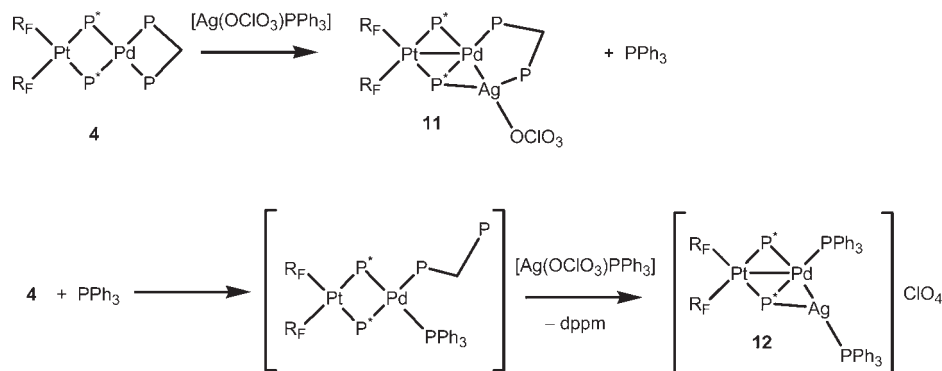

Figure 2. ^{19}F−^{195}Pt HMQC spectrum of **9** (CD$_2$Cl$_2$, 213 K).

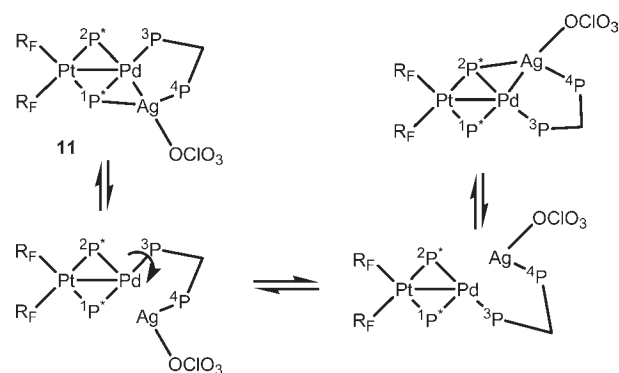**Scheme 3. Dynamic Behavior Observed for 10 in Solution at Room Temperature**

Scheme 4. Plausible Mechanism for the Reaction between 4 and [Ag(OClO₃)PPh₃]

Figure 3. $^{31}P\{^{1}H\}$ EXSY spectrum of **11** (CDCl₃, 255 K).

Scheme 5. The Dynamic Process Occurring for 11 in Solution

Assuming that this decrease of the chemical shift is related to the 2e–3c bonding mode, it can be concluded that the interaction of the $(\mu\text{-}P)$–Pd bond with the silver center in **11** is strong. This $P^1\cdots$Ag interaction is also supported by the coupling between P^1 and P^4, 123 Hz, while the coupling of P^1 with P^3 is smaller, 81 Hz.

The $^{31}P\{^{1}H\}$ and ^{19}F NMR features of **11** suggest the occurrence of dynamic processes in solution. In fact, while the ^{19}F NMR spectrum of **11** at 213 K showed the expected six signals with a 2:2:1:1:2:2 intensity ratio (o,o',p,p',m,m') due to two unequivalent C_6F_5 groups, at room temperature only one (averaged) signal is observed for the four o-F atoms, one signal for the four m-F atoms and one signal for the two p-F atoms. This behavior is analogous to that observed for the related cluster **12**[35] and indicates that a dynamic behavior rendering the two C_6F_5 groups equivalent at room temperature is operating.[35]

The broadness of the $^{31}P\{^{1}H\}$ NMR signals, especially those of P^1 and P^2, is also in accord with the fluxional behavior of **11**. In order to gain insight into the dynamic process occurring for **11**, we recorded a $^{31}P\{^{1}H\}$ EXSY spectrum at 255 K (Figure 3) which showed cross peaks between the P^1 (δ 139) and P^2 (δ 293) signals but not between P^3 (δ 30) and P^4 (δ 1.8). This evidence is compatible with the mechanism shown in Scheme 5 in which the Pd–Ag and P^1–Ag bonds are continuously broken and reformed, while the Pd and P^3 atoms remain bonded to each other. The mechanism envisages the breaking and reforming of the weakest bonds in the molecule, and it parallels the mechanism validated for the dynamic process occurring for **12** in solution,[35] which is depicted in Scheme 6.

Different results are observed when the starting materials are the dppe-containing derivatives **5** and **6**. Complexes **5** and **6** react with AgClO₄ or [Ag(OClO₃)(PPh₃)] (room temperature, 1:2 molar ratio) producing a silver mirror and the cationic complexes [(PPh₂C₆F₅)(C₆F₅)Pt(μ-PPh₂)(μ-OH)M(dppe)][ClO₄] (M = Pt, **13**; Pd, **14**). The formation of these 32-VEC Pt(II)/M(II) saturated complexes **13** and **14** which contain PPh₂C₆F₅ is a clear indication that the treatment of **5** and **6** with silver salts results in the oxidation of the dinuclear Pt(II)/Pd(II) derivatives (reduction to Ag⁰ is observed) probably to the dicationic Pt/Pd(III) intermediates $[(R_F)_2Pt^{III}(\mu\text{-}PPh_2)_2M^{III}(dppe)_2]^{2+}$ (although a mixed valence M(II),M(IV) cannot be discounted), which were neither isolated nor identified. Their very low stability could easily produce the reductive PPh₂/C₆F₅ coupling, favored by the presence of the nucleophile OH⁻ in the process, probably due to the presence of moisture in the system, and forming **13** and **14**. We have previously observed this type of process, and we have reported that polynuclear Pt(III)/Pd(III) derivatives are not very stable. These dinuclear derivatives evolve in the presence of nucleophiles such as I⁻ or Br⁻, and the trinuclear ones evolve even without the presence of nucleophiles, through a reductive PPh₂/C₆F₅ or PPh₂/PPh₂ coupling, with the formation of P–C (PPh₂C₆F₅) or P–P (PPh₂-PPh₂) bonds respectively and new platinum/palladium(II) derivatives.[28,29,38,47,56] In some cases, the M(III) intermediates are isolated, but in others the proposed M(III) intermediates are neither isolated nor identified.[28,29,39,56]

The structure of **14** has been established in an X-ray diffraction study. Figure 4 shows the structure of the complex cation, and
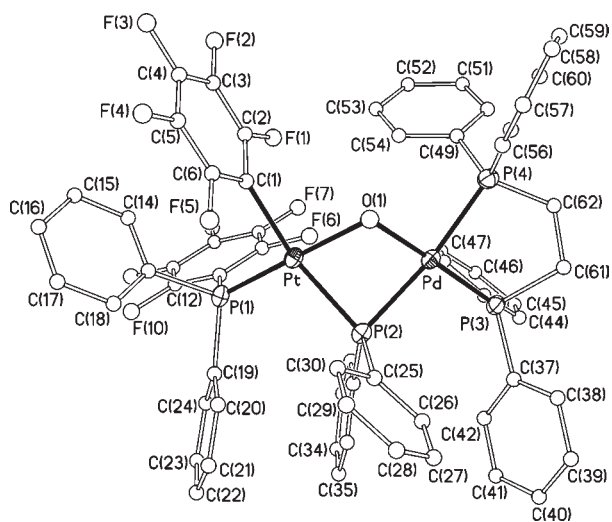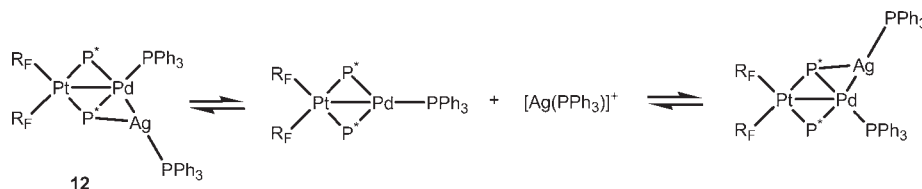
Scheme 6. The Dissociative Mechanism Occurring for 12 in Solution[35]

Figure 4. Drawing of the crystal structure of the complex cation of **14**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 14·2CH$_2$Cl$_2$

Pt−C(1)	2.065(7)	Pd−O(1)	2.158(5)
Pt−O(1)	2.116(5)	Pd−P(3)	2.221(2)
Pt−P(1)	2.199(2)	Pd−P(2)	2.335(2)
Pt−P(2)	2.3225(19)	Pd−P(4)	2.348(2)
C(1)−Pt−O(1)	89.5(2)	O(1)−Pd−P(3)	171.15(14)
C(1)−Pt−P(1)	91.3(2)	O(1)−Pd−P(2)	77.26(15)
O(1)−Pt−P(1)	178.09(14)	P(3)−Pd−P(2)	101.03(7)
C(1)−Pt−P(2)	167.8(2)	O(1)−Pd−P(4)	99.71(15)
O(1)−Pt−P(2)	78.33(15)	P(3)−Pd−P(4)	83.20(8)
P(1)−Pt−P(2)	100.92(7)	P(2)−Pd−P(4)	171.29(7)
C(1)−Pt−Pd	123.0(2)	O(1)−Pd−Pt	41.61(13)
O(1)−Pt−Pd	42.62(13)	P(3)−Pd−Pt	141.70(6)
P(1)−Pt−Pd	135.73(5)	P(2)−Pd−Pt	46.94(5)
P(2)−Pt−Pd	47.26(5)	P(4)−Pd−Pt	125.94(5)
Pt−P(2)−Pd	85.80(7)	Pt−O(1)−Pd	95.8(2)

Table 3 lists the most relevant bond lengths and angles. The cation of **14** is a dinuclear species in which both the platinum and palladium atoms have conventional square planar environments. They are not coplanar but form a dihedral angle of 46.4(1)°. The intermetallic distance is 3.170(1) Å. The formation of the PPh$_2$C$_6$F$_5$ ligand confirms the coupling of a terminal pentafluorophenyl group and a bridging diphenylphosphido ligand. The vacancy produced by the transformation of the PPh$_2$ group is occupied by a bridging hydroxo group. It is noteworthy that the new PPh$_2$C$_6$F$_5$ and OH ligands are coordinated mutually *trans*, which implies an isomerization process after the coupling of the PPh$_2$ and C$_6$F$_5$ groups, initially located mutually *cis*.

The ^{19}F NMR spectra of **13** and **14** at room temperature show six signals in a 2:2:1:1:2:2 intensity ratio (see the Experimental Section), in agreement with the presence of two kinds of pentafluorophenyl groups and the equivalence in solution of the two *o*-F atoms, as well as the *m*-F atoms, within each ring. The different chemical shifts of the F atoms of C$_6$F$_5$ groups bonded to the platinum or to the phosphorus atoms allow the assignment of these signals unequivocally.[28,38,40,54,56]

The ^{31}P{^{1}H} NMR spectra of the analogous complexes **13** and **14** are in full agreement with the presence of a "Pt(μ-PPh$_2$)(μ-X)M" fragment without a metal−metal bond[46,47,57−59] and with the solid-state structure of **14**, and all data are collected in the Experimental Section.

These results point out that the binuclear neutral [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$ML$_2$]$^{n−}$ complexes react with Ag$^+$ or Ag(PPh$_3$)$^+$, producing three different types of complexes. For L$_2$ = phen, adducts with one or two Pt−Ag bonds (complexes type **B**) are formed. For L$_2$ = dppe, Ag(PPh$_3$)$^+$ is not able to form stable adducts of

type **B**, but oxidation of Pt(III)−Pt(III) derivatives occurs. The oxidized complexes are very unstable, and **13** and **14** result from the reductive coupling of PPh$_2$/C$_6$F$_5$. For L$_2$ = dppm, two different situations are produced. When M = Pd, the higher lability of the Pd−P bonds and the low stability of the four-membered ring formed results in the opening of the Pd(dppm) ring and formation of the compound type **C**. Finally, for M = Pt, the higher stability of the Pt−P bonds precludes opening of the ring and formation of compound type **C**, and complex **10** (type **B**) is formed instead.

Behavior of Trinuclear Derivatives toward Ag(I). As far as the trinuclear derivatives are concerned, we have found that the anionic trinuclear platinum(II) complexes [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt-(μ-PPh$_2$)$_2$Pt(R$_F$)$_2$]$^{2−}$ and [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(μ-PPh$_2$)$_2$Pt-(acac)]$^−$ are oxidized by AgClO$_4$, affording the corresponding Pt(III)/Pt(III)/Pt(II) derivatives with a structure of type **A** (Table 1, entries 10 and 12).[39,40] We have completed this study by exploring the reactivity of the *neutral* trinuclear complexes of formula [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(μ-PPh$_2$)$_2$PtL$_2$] (L$_2$ = phen, **15**; L$_2$ = 2 PPh$_3$, **16**) bearing nitrogen or phosphorus donor ligands toward Ag derivatives.

The trinuclear complexes **15** and **16** were prepared by treating the hexanuclear species [NBu$_4$]$_2$[{(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt-(μ-PPh$_2$)$_2$Pt(μ-Cl)}$_2$] with an excess of the ligand L$_2$, which replaced the bridging chloro ligands. Complex **15** is slightly soluble in acetone, but **16** is sparingly soluble in all common organic solvents. Both precipitate from the reaction mixtures.

The reaction of suspensions of complexes **15** and **16** in CH$_2$Cl$_2$ with AgClO$_4$ results in the formation of Ag^0 and the cationic complexes [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(μ-PPh$_2$)$_2$PtL$_2$]-[ClO$_4$]$_2$, L$_2$ = phen, **17**; 2 PPh$_3$, **18** (46-VEC) endowed with a

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Pt—Pt bond between the central Pt atom and the Pt bonded to the C_6F_5 groups. Several batches of crystals of complex **18** with perchlorate or triflate as a counterion were grown, but again their poor quality prevented a satisfactory X-ray diffraction study. Nevertheless, it was possible to establish the connectivity of the atoms of the complex cation of **18**, which confirmed a structure of type **A**. The IR absorption in the 950 cm^{-1} region due to the C_6F_5 groups in **15** and **16** appears at 964 cm^{-1} in the oxidized complexes **17** and **18**. The blue-shift of this absorption is largely related to the increase in the formal oxidation state of the metal bonded to the C_6F_5 groups.[34,39,44,60]

The ^{19}F NMR spectra of **15** or **17** and **18** (the poor solubility of **16** in all common organic solvents precluded an NMR study) in a solution of $(CD_3)CO$, CD_2Cl_2, and CH_3Cl, respectively, showed three signals due to the *ortho*, *meta*, and *para* F atoms (2:2:1 intensity ratio, respectively), as a result of the symmetry of these molecules. The $^{31}P\{^1H\}$ NMR spectrum of **17** (**18**) showed a very low field signal at δ 272.9 (δ 268.8), in agreement with the presence of two bridging phosphides subtending a metal—metal bond.[39,40] The high field signal due to the P atoms of the μ-PPh$_2$ not subtending a Pt—Pt bond fell at δ −135.1 (δ −151.4).[39,40] In addition, a signal at δ 17.1 is observed in the spectrum of **18** for the P atoms of the PPh$_3$ ligands.

■ CONCLUDING REMARKS

The dinuclear phosphido complexes $[(R_F)_2Pt(\mu\text{-PPh}_2)_2PtL_2]^{n-}$ react with Ag$^+$ or Ag(PPh$_3$)$^+$, producing complexes of the type **A**, **B**, or **C**, the formation of which is essentially dependent on ligand L$_2$ (L$_2$ = 2 C_6F_5, acac, 2PPh$_3$, phen, dppm, dppe). For **C** type complexes, dynamic behavior consisting of the detachment and rebinding of the silver atom onto the M—μ-P bonds was invariably found.

On the other hand, anionic and neutral trinuclear phosphido derivatives of the general formula $[(R_F)_2Pt(\mu\text{-PPh}_2)_2Pt(\mu\text{-PPh}_2)_2PtL_2]^{n-}$ react with silver(I), giving in all cases complexes of the type **A** (Table 1, entries 10−13). In no case were the putative intermediates of type **B** or **C** observed. In addition, the Pt(III)—Pt(III) bond present in the 46 VEC derivatives is formed by the terminal Pt center bonded to the C_6F_5 groups and the central Pt atom, and in no case is the fragment bonded to the ligands L involved in the Pt—Pt bond.

■ EXPERIMENTAL SECTION

General Procedures and Materials. C, H, and N analyses were performed with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer (Nujol mulls between polyethylene plates in the range 4000−350 cm^{-1}). NMR spectra were recorded on Varian Unity 300, Bruker 300, and Bruker 400 spectrometers with SiMe$_4$, CFCl$_3$, 85% H$_3$PO$_4$, and H$_2$PtCl$_6$ as external references for ^{1}H, ^{19}F, ^{31}P, and ^{195}Pt, respectively. Literature methods were used to prepare the starting materials *cis*-[Pt(R$_F$)$_2$(PPh$_2$H)$_2$],[36] [PdCl$_2$-(L-L)] (L-L = phen, dppm, dppe),[61] [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(NCCH$_3$)$_2$],[37] [NBu$_4$]$_2$[{(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(μ-PPh$_2$)$_2$Pt(μ-Cl)}$_2$],[40] [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$-Pt(phen)],[36] and [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(dppm)].[36]

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and these should be handled with great caution.

Synthesis of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pd(phen)] (2). LiBu (0.44 mL of a hexane solution, 1.1 mmol) was added under an argon atmosphere to a colorless solution of *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] (0.500 g, 0.554 mmol) in THF (10 mL) at ca. −78 °C. The yellow solution was stirred

for 15 min, and then [PdCl$_2$(phen)] (0.198 g, 0.554 mmol) was added and allowed to react at room temperature for 16 h. The resulting yellow suspension was evaporated to dryness. CH$_2$Cl$_2$ (40 mL) was added to the residue. The mixture was filtered through Celite, and the resulting solution was evaporated to ca. 1 mL. The addition of methanol (10 mL) causes the crystallization of **2** as a yellow solid, which was filtered off and washed with methanol (2 × 0.5 mL). Yield: 0.466 g, 71%. Anal. Found (calcd for C$_{48}$F$_{10}$H$_{28}$N$_2$P$_2$PdPt): C, 48.36 (48.60); H, 2.35 (2.38); N, 2.37 (2.36). IR (cm^{-1}): 841 (phen); 782 and 774 (X-sensitive C$_6$F$_5$). ^{19}F NMR (CD$_2$Cl$_2$, 293 K, 282.4 MHz): δ −115.7 (4 *o*-F, ^3J(Pt,F) = 334 Hz), −165.3 (2 *p*-F), −165.5 (4 *m*-F). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, 121.5 MHz): δ −109.6 ppm, ^1J(Pt,P) = 1710 Hz.

Synthesis of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pd(dppm)] (4). LiBu (0.44 mL of a hexane solution, 1.1 mmol) was added under an argon atmosphere to a colorless solution of *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] (0.500 g, 0.554 mmol) in THF (10 mL) at ca. −78 °C. The yellow solution was stirred for 15 min, and then [PdCl$_2$(dppm)] (0.311 g, 0.554 mmol) was added and allowed to react at room temperature for 16 h. The resulting orange suspension was evaporated to dryness. CH$_2$Cl$_2$ (40 mL) was added to the residue. The mixture was filtered through Celite, and the resulting solution was evaporated to ca. 1 mL. The addition of CHCl$_3$ (10 mL) causes the crystallization of **4** as an orange solid, which was filtered off and washed with CHCl$_3$ (2 × 0.5 mL). Yield: 0.498 g, 65%. Anal. Found (calcd for C$_{61}$F$_{10}$H$_{42}$P$_4$PdPt): C, 52.51 (52.65); H, 2.91 (3.04). IR (cm^{-1}): 782 and 773 (X-sensitive C$_6$F$_5$). ^{19}F NMR (acetone-*d$_6$*, 293 K, 282.4 MHz): δ −113.7 (4 *o*-F, ^3J(Pt,F) = 313 Hz), −166.0 (4 *m*-F), −166.2 (2 *p*-F). ^{31}P{^{1}H} NMR (acetone-*d$_6$*, 293 K, 121.5 MHz): δ −22.0 (dppm), −124.9 (PPh$_2$, ^1J(Pt−P) = 1714 Hz) ppm. N = J_{AX} + $J_{AX'}$ = 330 Hz.

Synthesis of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(dppe)] (5). To a colorless solution of [(C$_6$F$_5$)$_2$Pt(μPPh$_2$)$_2$Pt(NCMe)$_2$] (0.350 g, 0.298 mmol) in acetone (10 mL) was added dppe (0.119 g, 0.298 mmol). The resulting yellow solution was stirred at room temperature for 4 h and then evaporated to 2 mL. Complex **5** crystallized as a yellow solid, which was filtered and washed with cold acetone (2 × 0.5 mL). Yield: 0.187 g, 42%. Anal. Found (calcd for C$_{62}$F$_{10}$H$_{44}$P$_4$Pt$_2$): C, 49.66 (49.85); H, 2.93 (2.97). IR (cm^{-1}): 782 and 773 (X-sensitive C$_6$F$_5$). ^{19}F NMR (CD$_2$Cl$_2$, 293 K, 282.4 MHz): δ −116.2 (4 *o*-F, ^3J(Pt,F) = 320 Hz), −166.3 (4 *m*-F), −166.5 (2 *p*-F). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, 121.5 MHz): δ 45.6 (dppe, ^1J(Pt−P) = 1988 Hz), −141.1 (PPh$_2$, the platinum satellites appears overlapped and the two values of ^1J(Pt−P) are ca. 1740 Hz) ppm. N = J_{AX} + $J_{AX'}$ = 259 Hz.

Synthesis of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pd(dppe)] (6). Complex **6** was prepared similarly to **4** (from LiBu (1.1 mmol), *cis*-[Pt(C$_6$F$_5$)$_2$-(PPh$_2$H)$_2$] (0.500 g, 0.554 mmol) and [PdCl$_2$(dppm)] (0.319 g, 0.554 mmol)) as an orange solid. Yield: 0.478 g, 62%. Anal. Found (calcd for C$_{62}$F$_{10}$H$_{44}$P$_4$PdPt): C, 52.96 (52.99); H, 3.13 (3.16). IR (cm^{-1}): 782 and 773 (X-sensitive C$_6$F$_5$). ^{19}F NMR (acetone-*d$_6$*, 293 K, 282.4 MHz): δ −114.2 (4 *o*-F, ^3J(Pt,F) = 308 Hz), −166.1 (4 *m*-F), −166.7 (2 *p*-F). ^{31}P{^{1}H} NMR (acetone-*d$_6$*, 293 K, 121.5 MHz): δ 43.9 (dppe), −134.9 (PPh$_2$, ^1J(Pt−P) = 1677 Hz) ppm. N = J_{AX} + $J_{AX'}$ = 282 Hz.

Reaction of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(phen)] with AgClO$_4$. Ag-ClO$_4$ (0.055 g, 0.265 mmol) was added to a yellow solution of [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(phen)] (**1**; 0.150 g, 0.117 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred at room temperature for 2 h with the exclusion of light and filtered through Celite. The yellow solution was evaporated to ca. 1 mL, and [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(phen)Ag-(OClO$_3$)] (**7a+7b**) crystallized as a yellow solid, which was filtered and washed with cold CH$_2$Cl$_2$ (2 × 0.5 mL). Yield: 0.082 g, 47%. Anal. Found (calcd for AgC$_{48}$ClF$_{10}$H$_{28}$N$_2$O$_4$P$_2$Pt$_2$): C, 38.83 (38.89); H, 1.93 (1.90); N 1.86 (1.89). IR of **7a** (cm^{-1}): 1092, 623 (broad) (ClO$_4$); 844 (phen); 784 and 779 (X-sensitive C$_6$F$_5$). **7b**. ^{19}F NMR (CD$_2$Cl$_2$, 293 K, 282.4 MHz): δ −116.9 (4 *o*-F, ^3J(Pt,F) = 389 Hz), −163.3

(2 p-F), −163.8 (4 m-F) ppm. ^{19}F NMR (CD$_2$Cl$_2$, 193 K, 282.4 MHz): δ −115.7 (2 o-F), −117.8 (2 o-F), −162.4 (2 p-F), −162.8 (2 m-F), −163.4 (2 m-F) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 193 K, 121.5 MHz): δ −108.1 ([1]J(Pt,P) = 1452 and 2091 Hz) ppm. [195]Pt NMR (CD$_2$Cl$_2$, 273 K, 86 MHz): δ −3340, Pt[3]; −3450 Pt[4].

Reaction of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$M(phen)] with [Ag(OClO$_3$)PPh$_3$]. $M = Pt$. [Ag(OClO$_3$)PPh$_3$] (0.055 g, 0.117 mmol) was added to a yellow solution of [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(phen)] (**1**; 0.150 g, 0.117 mmol) in CH$_2$Cl$_2$ (15 mL). The solution was stirred at room temperature for 30 min with the exclusion of light. The yellow solution was evaporated to ca. 1 mL. Hexane (2 mL) was added, and [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(phen)Ag(PPh$_3$)][ClO$_4$)] (**8**) crystallized as a yellow solid, which was filtered and washed with hexane (2 × 0.5 mL). Yield: 0.157 g, 89%. Anal. Found (calcd for AgC$_{66}$ClF$_{10}$H$_{43}$N$_2$O$_4$P$_3$Pt$_2$): C, 45.22 (45.44); H, 2.82 (2.48); N 1.60 (1.60). IR (cm^{-1}): 1092, 623 (ClO$_4$); 784 and 776 (X-sensitive C$_6$F$_5$). ^{19}F NMR (CD$_2$Cl$_2$, 293 K, 282.4 MHz): δ −116.0 (4 o-F, [3]J(Pt,F) = 333 Hz), −165.8 (2 p-F + 4 m-F). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, 121.5 MHz): δ 8.8 (PPh$_3$, two d, [1]J([109,107]Ag,P) ≈ 760 and 680 Hz), −129.2 (PPh$_2$, [1]J(Pt,P) = 1792 and 2240 Hz) ppm.

$M = Pd$. A similar procedure was used: [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pd(phen)] (**2**; 0.150 g, 0.126 mmol) and [Ag(OClO$_3$)(PPh$_3$)] (0.059 g, 0.126 mmol) give [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pd(phen)Ag(PPh$_3$)][ClO$_4$)] (**9**) as a yellow solid. Yield: 0.186 g, 89%. Anal. Found (calcd for AgC$_{66}$ClF$_{10}$H$_{43}$N$_2$O$_4$P$_3$PdPt): C, 48.10 (47.87); H, 2.91 (2.62); N 1.77 (1.69). IR (cm^{-1}): 1092, 623 (ClO$_4$); 784 and 776 (X-sensitive C$_6$F$_5$). ^{19}F NMR (CD$_2$Cl$_2$, 293 K, 282.4 MHz): δ −116.0 (4 o-F, [3]J(Pt,F) = 339 Hz), −162.2 (2 p-F), −163.8 (4 m-F). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 183 K, 121.5 MHz): δ 9.4 (PPh$_3$, broad d), −120.2 (PPh$_2$, [1]J(Pt,P) = 1302 Hz) ppm. [195]Pt NMR (CD$_2$Cl$_2$, 213 K, 86 MHz): δ −3431.

Reaction of [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(dppm)] with [Ag(OClO$_3$)(PPh$_3$)]. [Ag(OClO$_3$)PPh$_3$] (0.038 g, 0.081 mmol) was added to a yellow solution of [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(dppm)] (**3**; 0.120 g, 0.081 mmol) in CH$_2$Cl$_2$ (15 mL). The solution was stirred at room temperature for 30 min with the exclusion of light. The yellow solution was evaporated to ca. 1 mL. n-Hexane (5 mL) was added, and [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(dppm)Ag(PPh$_3$)][ClO$_4$)] (**10**) crystallized as a yellow solid, which was filtered and washed with hexane (2 × 0.5 mL). Yield: 0.136 g, 86%. Anal. Found (calcd for AgC$_{79}$ClF$_{10}$H$_{57}$O$_4$P$_5$Pt$_2$): C, 48.54 (48.69); H, 2.62 (2.95). IR (cm^{-1}): 1096, 622 (ClO$_4$); 782 and 773 (X-sensitive C$_6$F$_5$). ^{1}H NMR (CDCl$_3$, 293 K, 300 MHz): δ 7.5−6.8 (m, 55 H, C$_6$H$_5$), 4.8 (t, 2 H, CH$_2$, [2]J(P−H) = 10.5 Hz) ppm. ^{1}H NMR (CDCl$_3$, 213 K, 300 MHz): δ 7.6−6.8 (m, 55 H, C$_6$H$_5$), 5.0 (very broad signal, 1 H, CH$_2$), 4.5 (very broad signal, 1 H, CH$_2$) ppm. ^{19}F NMR (CDCl$_3$, 293 K, 282.4 MHz): δ −115.4 (4 o-F, [3]J(Pt,F) = 350 Hz), −162.9 (2 p-F), −164.3 (4 m-F). ^{19}F NMR (CDCl$_3$, 213 K, 282.4 MHz): δ −114.9 (2 o-F, very broad signal) −116.5 (2 o-F, [3]J(Pt,F) = 484 Hz), −161.8 (2 p-F), −163.2 (4 m-F). ^{31}P{^{1}H} NMR (CDCl$_3$, 213 K, 121.5 MHz): δ 10.0 (broad doublet, PPh$_3$, [1]J([109]Ag,P) = 795 Hz, [1]J([107]Ag,P) = 691 Hz) −24.1 ([1]J([195]Pt−P) = 1860 Hz), −143.5 (platinum satellites appear overlapped and the two values [1]J([195]Pt−P) can not be measured) ppm. N = J_{AX} + $J_{AX'}$ = 315 Hz. [195]Pt NMR (CDCl$_3$, 275 K, 86 MHz),: −3390, Pt[1].

Reaction of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pd(dppm)] with AgClO$_4$. Ag-ClO$_4$ (0.048 g, 0.231 mmol) was added to an orange solution of [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pd(dppm)] (**4**; 0.150 g, 0.107 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred at room temperature for 5 h with the exclusion of light and filtered through Celite. The resulting red solution was evaporated to ca. 1 mL, and n-hexane (3 mL) was added. [AgPdPt(μ-PPh$_2$)$_2$(R$_F$)$_2$(OClO$_3$)(dppm)], **11**, crystallized as a red solid, which was filtered and washed with hexane (2 × 0.5 mL). Yield: 0.132 g, 77%. Anal. Found (calcd for AgC$_{61}$ClF$_{10}$H$_{42}$O$_4$P$_4$PdPt): C, 45.61 (45.78); H, 2.56 (2.63). IR (cm^{-1}): 1098, 623 (broad) (ClO$_4$); 791 and 780 (X-sensitive C$_6$F$_5$). ^{19}F NMR (CDCl$_3$, 293 K, 282.4 MHz): δ −118.7 (4 o-F, [3]J(Pt,F) = 294 Hz), −160.6 (2 p-F), −163.2 (4 m-F)

ppm. ^{19}F NMR (CDCl$_3$, 213 K, 282.4 MHz): δ −118.9 (2 o-F, [3]J(Pt,F) = 300 Hz), −119.6 (2 o-F, [3]J(Pt,F) = 304 Hz), −159.1 (1 p-F), −160.9 (1 p-F), −162.4 (2 m-F), −163.0 (2 m-F) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 213 K, 121.5 MHz): δ 293.2 (m, P2, [1]J(Pt,P2) = 1659 Hz), 138.3 (very broad m, P1, platinum satellites are very broad and [1]J(Pt,P1) can not be measured), 28.9 (ddd, P3, [2]J(P3,P2) = 22 Hz, [2]J(P3,P1) = 81 Hz, [2]J(P3, P4) = 148 Hz, [2]J(Pt,P3) = 92 Hz), 1.7 (two ddd, P4, [1]J([109]Ag,P4) = 422 Hz), [1]J([107]Ag,P4) = 365 Hz), [2]J(P3,P4) = 148 Hz, [2]J(P1,P4) = 123 Hz) ppm.

Reaction of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$M(dppe)] with AgClO$_4$. $M = Pt$. AgClO$_4$ (0.049 g, 0.235 mmol) was added to a yellow solution of [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(dppe)] (**5**; 0.150 g, 0.100 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred at room temperature for 4 h with the exclusion of light and filtered through Celite. The yellow solution was evaporated to ca. 1 mL, and Et$_2$O (2 mL) was added. [(PPh$_2$C$_6$F$_5$)(C$_6$F$_5$)Pt(μ-PPh$_2$)(μ-OH)Pt(dppe)][ClO$_4$], **13**, crystallized as a yellow solid, which was filtered and washed with Et$_2$O (2 × 0.5 mL). Yield: 0.129 g, 75%. Anal. Found (calcd for C$_{62}$ClF$_{10}$H$_{45}$O$_5$P$_4$Pt$_2$): C, 46.18 (46.26); H, 2.80 (2.82.). IR (cm^{-1}): 3603 (OH); 1094, 623 (ClO$_4$); 1520, 981 (PPh$_2$C$_6$F$_5$); 786 (X-sensitive C$_6$F$_5$). ^{1}H NMR (CD$_2$Cl$_2$, 293 K, 300 MHz): δ from 7.7 to 6.8 (m, 40 H, C$_6$H$_5$), 2.4 (broad m, 2H, CH$_2$), 2.3 (broad m, 2H, CH$_2$), 0.3 (s, 1H, OH) ppm. ^{19}F NMR (CD$_2$Cl$_2$, 293 K, 282.4 MHz): δ −118.9 (2 o-F, [3]J(Pt,F) = 244 Hz), −122.7 (2 o-F, PPh$_2$C$_6$F$_5$), −146.7 (1 p-F, PPh$_2$C$_6$F$_5$), −159.5 (1 p-F), −159.7 (2 m-F, PPh$_2$C$_6$F$_5$), −162.9 (2 m-F). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, 121.5 MHz): δ 50.3 (d, P4, [2]J(P2,P4) = 282 Hz, [1]J(Pt2, P4) = 2206 Hz), 28.9 (d, P3, [2]J(P3,P2) = 14 Hz, [1]J(Pt2,P3) = 3810 Hz), −13.4 (d, P1, [2]J(P1,P2) = 13 Hz, [1]J(Pt1,P1) = 4352 Hz), −29.3 (broad d, P2, [2]J(P2,P4) = 282 Hz, [1]J(Pt1,P2) ≈ [1]J(Pt2,P2) ≈ 1820 Hz) ppm.

$M = Pd$. AgClO$_4$ (0.049 g, 0.235 mmol) was added to a yellow solution of [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pd(dppe)] (**6**; 0.150 g, 0.107 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred at room temperature for 7 h with the exclusion of light and filtered through Celite. The yellow solution was evaporated to ca. 1 mL, and a mixture of MeOH/^{i}PrOH (3/ 3 mL) was added. [(PPh$_2$C$_6$F$_5$)(C$_6$F$_5$)Pt(μ-PPh$_2$)(μ-OH)Pd(dppe)]-[ClO$_4$], **14**, crystallized as a yellow solid, which was filtered and washed with ^{i}PrOH (2 × 0.5 mL). Yield: 0.109 g, 67%. Anal. Found (calcd for C$_{62}$ClF$_{10}$H$_{45}$O$_5$P$_4$PdPt): C, 48.55 (48.94); H, 3.01 (2.98). IR (cm^{-1}): 3578 (OH); 1094, 623 (ClO$_4$); 1520, 981 (PPh$_2$C$_6$F$_5$); 787 (X-sensitive C$_6$F$_5$). ^{1}H NMR (CDCl$_3$, 293 K, 300 MHz): δ 7.6−6.9 (m, 40 H, C$_6$H$_5$), 2.7 (dm, 2H, CH$_2$, [2]J(P,H) = 33 Hz), 2.5 (dm, 2H, CH$_2$, [2]J(P,H) = 30 Hz),), −0.6 (m, 1H, OH) ppm. ^{19}F NMR (CDCl$_3$, 293 K, 282.4 MHz): δ −118.5 (2 o-F, [3]J(Pt,F) = 275 Hz), −122.2 (2 o-F, PPh$_2$C$_6$F$_5$), −145.9 (1 p-F, PPh$_2$C$_6$F$_5$), −158.6 (1 p-F), −159.0 (2 m-F, PPh$_2$C$_6$F$_5$), −161.9 (2 m-F). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K, 121.5 MHz): δ 55.9 (d, P3, [2]J(P3,P4) = 20 Hz), 52.3 (d, P4, [2]J(P2,P4) = 300 Hz), −11.5 (s, P1, [1]J(Pt,P1) = 4208 Hz), −19.9 (d, P2, [2]J(P2,P4) = 300 Hz, [1]J(Pt,P2) = 1810 Hz) ppm.

Synthesis of [(R$_F$)$_2$Pt(μ-PPh$_2$)$_2$Pt(μ-PPh$_2$)$_2$Pt(phen)] (15). To a yellow solution of [NBu$_4$]$_2$[{(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(μ-PPh$_2$)$_2$Pt-(μ-Cl)}$_2$] (0.500 g, 0.129 mmol) in acetone (20 mL) was added 1,10-phen·H$_2$0 (0.058 g, 0.290 mmol). The solution was stirred for 7 h at room temperature and evaporated to ca. 2 mL. CHCl$_3$ (6 mL) was added, and [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt(μ-PPh$_2$)$_2$Pt(phen)] (**15**) crystallized as a yellow solid, which was filtered and washed with CHCl$_3$ (2 × 0.5 mL). Yield: 0.285 g, 60%. Anal. Found (calcd for C$_{72}$F$_{10}$H$_{48}$ N$_2$P$_4$Pt$_3$): C, 46.60 (46.99); H, 2.42 (2.63.); N 1.40 (1.52). IR (cm^{-1}): 843 (phen); 778 and 769 (X-sensitive C$_6$F$_5$). ^{19}F NMR (acetone-d$_6$, 293 K, 282.4 MHz): δ −114.2 (4 o-F, [3]J(Pt,F) = 344 Hz), −167.6 (4 m-F), −168.6 (2 p-F) ppm. ^{31}P{^{1}H} NMR (acetone-d$_6$, 293 K, 121.5 MHz): δ −115.7 (P^A, PPh$_2$ groups in trans position to the C$_6$F$_5$ groups, [1]J(Pt,P) = 1775 and 1687 Hz), −130.3 (P^X, [1]J(Pt,P) = 2268 Hz, [1]J(Pt,P) = 1649 Hz) ppm; N = J_{AX} + $J_{A\dot{X}}$ = 309 Hz.

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Table 4. Crystal Data and Structure Refinement for $7 \cdot 0.50H_2O \cdot 1.25CH_2Cl_2$ and $14 \cdot 2CH_2Cl_2$

	$7 \cdot 0.50H_2O \cdot 1.25CH_2Cl_2$	$14 \cdot 2CH_2Cl_2$
empirical formula	$C_{48}H_{29}ClF_{10}P_2O_4Pt_2Ag$ $\cdot 0.50H_2O \cdot 1.25CH_2Cl_2$	$C_{62}H_{108}ClF_{10}N_2O_5P_4PdPt$ $\cdot 2CH_2Cl_2$
fw	3194.66	1690.65
unit cell dimensions		
a (Å)	12.109(2)	13.3787(16)
b (Å)	18.910(3)	19.201(2)
c (Å)	23.260(4)	24.777(3)
α (deg)	68.679(3)	90
β (deg)	88.867(3)	94.573(2
γ (deg)	88.136(3)	90
V (Å^3), Z	4958.5(15), 4	6344.7(13), 4
calc dens (g cm^{-1})	2.140	1.770
wavelength (Å)	0.71073	0.71073
temp (K)	100(1)	100(1)
radiation	graphite monochromated Mo Kα	
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
cryst dimens (mm)	$0.41 \times 0.22 \times 0.19$	$0.26 \times 0.34 \times 0.37$
color/habit	yellow/prismatic	yellow/prismatic
abs coeff (mm^{-1})	6.360	2.877
abs cor	SADABS[63]	SADABS[63]
2θ range for data collect. (deg)	3.36−50.06	3.06−50.08
no. rflns collected	27205	34463
no. indep rflns	17275 [R(int) = 0.0296]	11190 [R(int) = 0.0589]
refinement method	full-matrix least-squares on F^2	
goodness-of-fit on F^{2a}	1.011	1.006
final R indices $(I > 2\sigma(I))^b$	R1 = 0.0326	R1 = 0.0508
	wR2 = 0.0821	wR2 = 0.1220
R indices (all data)	R1 = 0.0367	R1 = 0.0727
	wR2 = 0.0849	wR2 = 0.1328

^{a} Goodness-of-fit = $[\Sigma\, w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$. ^{b} $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma\,|F_o|$. $wR_2 = [\Sigma w\,(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\,]^{1/2}$.

Synthesis of $[(R_F)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)_2]$ 16. To a yellow solution of $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)\}_2]$ (0.500 g, 0.129 mmol) in a mixture of $CH_2Cl_2/MeOH$ (80/20 mL) was added PPh_3 (0.203 g, 0.774 mmol). The mixture was stirred for 24 h at room temperature, while $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)_2]$ (16) precipitates as a yellow solid, which was filtered and washed with MeOH (2 × 1 mL). Yield: 0.442 g, 78%. Anal. Found (calcd for $C_{96}F_{10}H_{70}P_6Pt_3$): C, 52.49 (52.77); H, 3.17 (3.23). IR (cm^{-1}): 778 and 771 (X-sensitive C_6F_5).

Reaction of $[(R_F)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$ (15) with AgClO$_4$. To a yellow suspension of 15 (0.250 g, 0.136 mmol) in CH_2Cl_2 (20 mL) was added $AgClO_4$ (0.058 g, 0.280 mmol). The mixture was stirred at room temperature for 2 h with the exclusion of light and filtered through Celite. The orange solution was evaporated to ca. 2 mL and kept in the freezer at 253 K for 14 h. The complex $[(R_F)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)][ClO_4]_2$ (17) crystallized as an orange solid, which was filtered and washed with cold CH_2Cl_2 (2 × 0.5 mL). Yield: 0.145 g, 52%. Anal. Found (calcd for $C_{72}Cl_2F_{10}H_{48}N_2O_8P_4Pt_3$): C, 42.18 (42.38); H, 2.27 (2.35.); 1.30 (1.37). IR (cm^{-1}): 1093, 624 (ClO$_4$); 851 (phen); 793 and 783 (X-sensitive C_6F_5). ^{19}F NMR (CD_2Cl_2, 293 K, 282.4 MHz): δ −119.3 (4 o-F, ^3J(Pt,F) = 286 Hz), −156.8 (2 p-F,), −161.4 (4 m-F) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K, 121.5 MHz): δ 272.9 (P^A, PPh$_2$ groups in trans position to the C_6F_5 groups, ^1J(Pt,P) = 1290 and 1174 Hz), −135.1 (P^X, ^1J(Pt,P) = 2688 and 1906 Hz) ppm; N = $J_{AX} + J_{A\hat{X}}$ = 148 Hz.

Reaction of $[(R_F)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)_2]$ (16) with AgClO$_4$. To a yellow suspension of 16 (0.500 g, 0.229 mmol) in acetone (20 mL) was added $AgClO_4$ (0.005 g, 0.458 mmol). The mixture was stirred at room temperature for 1 h with the exclusion of light and filtered through Celite. The orange solution was evaporated to ca. 2 mL, and the complex $[(R_F)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)_2][ClO_4]_2$ (18) crystallized as an orange solid, which was filtered and washed with a mixture (1:1) of acetone/hexane (2 × 1 mL). Yield: 0.306 g, 56%. Anal. Found (calcd for $C_{96}Cl_2F_{10}H_{70}O_8P_6Pt_3$): C, 48.65 (48.35); H, 2.94 (2.94.). IR (cm^{-1}): 1091, 624 (ClO$_4$); 793 and 780 (X-sensitive C_6F_5). ^{19}F NMR (CDCl$_3$, 293 K, 282.4 MHz): δ −120.8 (4 o-F, ^3J(Pt,F) = 285 Hz), −157.0 (2 p-F,), −161.9 (4 m-F) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K, 121.5 MHz): δ 268.8 (PPh$_2$ groups in trans position to the C_6F_5 groups, ^1J(Pt,P) $\approx$ 1300 Hz for both values), 17.1 (PPh$_3$, ^1J(Pt,P) = 2258 Hz), −151.4 (^1J(Pt,P) $\approx$ 1800 Hz, ^{195}Pt satellites appear overlapped) ppm.

X-Ray Structure Determination. Crystal data and other details of the structure analysis are presented in Table 4. Suitable crystals of $7 \cdot 0.50H_2O \cdot 1.25CH_2Cl_2$ and $14 \cdot 2CH_2Cl_2$ were obtained by slow diffusion of n-hexane into CH_2Cl_2 solutions of the complexes. Crystals were mounted at the end of quartz fibers. Data collections were performed at 100 K temperature on a Bruker Smart CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 6.0 cm. Unit cell dimensions were initially determined from the positions of 346 reflections for

$7 \cdot 0.50H_2O \cdot 1.25CH_2Cl_2$ and 47 reflections for $14 \cdot 2CH_2Cl_2$ in 60 intensity frames measured at 0.3° intervals in ω and subsequently refined on the basis of positions of 1004 reflections for $7 \cdot 0.50H_2O \cdot 1.25CH_2Cl_2$ and 1024 reflections for $14 \cdot 2CH_2Cl_2$ from the main data set. The diffraction frames were integrated using the SAINT package[62] and corrected for absorption with SADABS.[63] Lorentz and polarization corrections were applied.

The structures were solved by Patterson and Fourier methods. All refinements were carried out using the program SHELXL-97.[64] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon atoms (1.5 times for methyl hydrogen atoms). For $7 \cdot 0.50H_2O \cdot 1.25CH_2Cl_2$, the position of one of the hydrogen atoms of the water ligand (H(5)) was found from the density maps and refined with the O—H constrained to a sensible value. The other hydrogen atom of the water was not found in the density map nor geometrically added to the model. The C—Cl distance for the half present CH_2Cl_2 molecule was constrained to a sensible value. For $14 \cdot 2CH_2Cl_2$, one very diffuse solvent molecule of CH_2Cl_2 was found during the last stages of the refinement. It was modeled as two disordered moieties (occupancy 0.6/0.4) sharing the same C atom. Geometrical constraints were used in this solvent molecule, and all of the anisotropic thermal parameters of the Cl atoms were constrained to be the same. No hydrogen atoms were included in this molecule. Also, no H atom was added to the bridging OH group either. Full-matrix least-squares refinement of these model against F^2 converged to final residual indices given in Table 4.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information.   Further details of the structure determinations of $7 \cdot 0.50H_2O \cdot 1.25CH_2Cl_2$ and $14 \cdot 2CH_2Cl_2$ including atomic coordinates, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes
[§]Polynuclear Homo- or Heterometallic Palladium(II)—Platinum (II) Pentafluorophenyl Complexes Containing Bridging Diphenylphosphido Ligands. 28. For part 27, see ref 65.

■ ACKNOWLEDGMENT

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