Polynuclear Homo- or Heterometallic Palladium(II)−Platinum(II) Pentafluorophenyl Complexes Containing Bridging Diphenylphosphido Ligands. 8.[†] Syntheses and Reactivity of the Tetranuclear $[Pt_4(\mu_2\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P\}(C_6F_5)_4]$ Cluster

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The reaction of $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)\}_2]$ with $AgClO_4$ in CH_2Cl_2 (1:2 mol ratio) gives the neutral tetranuclear compound $[Pt_4(\mu\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P)\}(C_6F_5)_4]$ (**5**), a 58-electron cluster that displays three Pt−Pt bonds and a 1,2-η^2-Ph (of the PPh_2 ligand) Pt interaction. This complex reacts with bipy or phen (L−L), giving the tetranuclear clusters $[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(L\text{−}L)]$ (L−L = bipy **6**, phen **7**), while its reaction with CO in CH_2Cl_2 renders $[\{Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_2(CO)\}_2]$ (**8**). The molecular structures of complexes **5** and **6** have been established by X-ray crystallography, and the structure of **8** is inferred by ^{31}P NMR spectroscopy.

Introduction

Phosphido ligands have been widely used as building blocks in the synthesis of a great variety of polynuclear complexes,[1] mainly due to both (a) their flexibility which allows them to support a wide range of M−M′ distances and (b) the stability of the bridging system $M(\mu\text{-}PR_2)_xM'$ which permits in many cases the retention of the polynuclear framework during the chemical reactions.

The synthesis of the dinuclear phosphido complexes $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(C_6F_5)_2]$ (M = Pd(II), Pt(II)),[2] which do not contain metal−metal bonds, gave us the opportunity to prepare several types of polynuclear phosphido complexes with metal−metal bonds.[3] In some cases the adequate intermediates for such reactions are the tetranuclear complexes $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$, which can be formed easily by reacting the dinuclear compounds with aqueous HCl in methanol.[2] As expected, these tetranuclear complexes react with neutral monodentate ligands L such as PPh_3 with halide bridge cleavage and the formation of dinuclear complexes without metal−metal bonds. (Scheme 1a)

The elimination of the chloro ligand in the dinuclear complexes results in the formation of complexes of type **2** (Scheme 1), which display a Pt→M (M = Pd, Pt) donor−acceptor bond (total valence electron count 30).[3a] Surprisingly the use of CO as a monodentate ligand produces very different effects on the tetranuclear complexes, since when M = Pt, the expected dinuclear compound of type **1** is obtained, while for M = Pd no reaction takes place.[3b] In addition, the elimination of the chloro ligand in the dinuclear carbonyl derivative does not result in the formation of a dinuclear compound type **2**, but a tetranuclear dicarbonyl derivative **3** is obtained instead (Scheme 1c).

In an attempt to eliminate the chloro ligands in these tetranuclear complexes, we have studied the reaction of the mixed-metal tetranuclear compound (M = Pd) with $AgClO_4$, which yields the tetranuclear cluster $[Pt_2Pd_2(\mu\text{-}PPh_2)_3(C_6F_5)_3(PPh_2C_6F_5)]$ (Scheme 1d, **4**) with the metal atoms in mixed oxidation state, through a very unusual reductive coupling between PPh_2 and C_6F_5 to produce the phosphine $PPh_2C_6F_5$.[3b] The surprising formation of complex **4** prompted us to study the

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[†] Part 7. See ref 3d.

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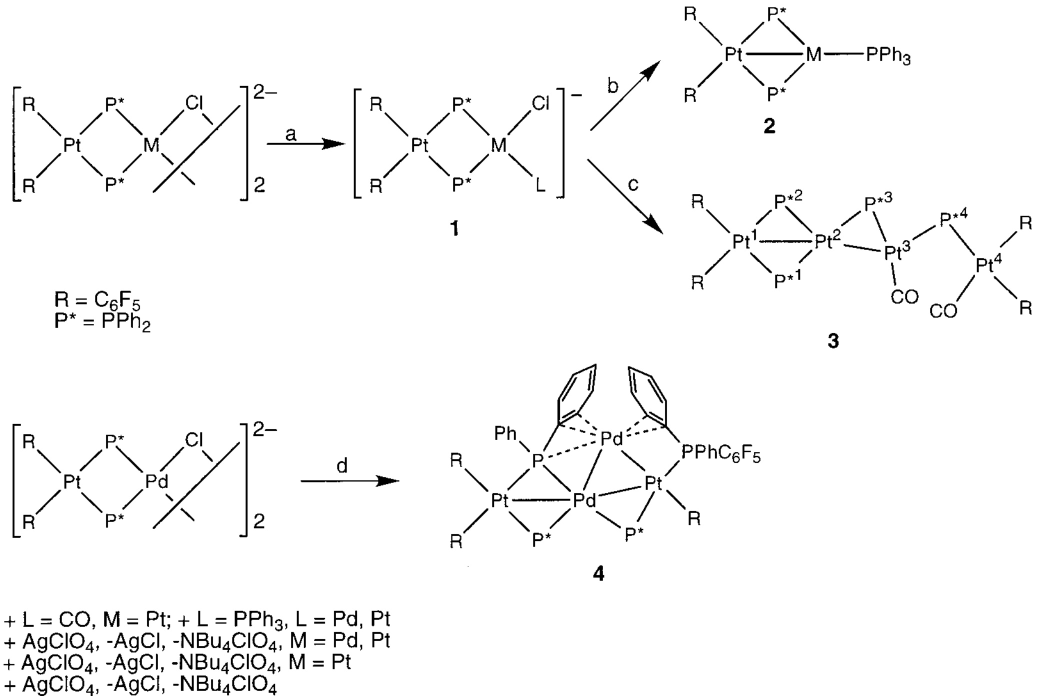
Scheme 1



reaction of the chloride elimination on the analogous homonuclear compound $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)\}_2]$, which results in the formation of a new Pt(II) tetranuclear compound **5** completely different from the tetranuclear compound **4** obtained from the mixed Pt/Pd compound.

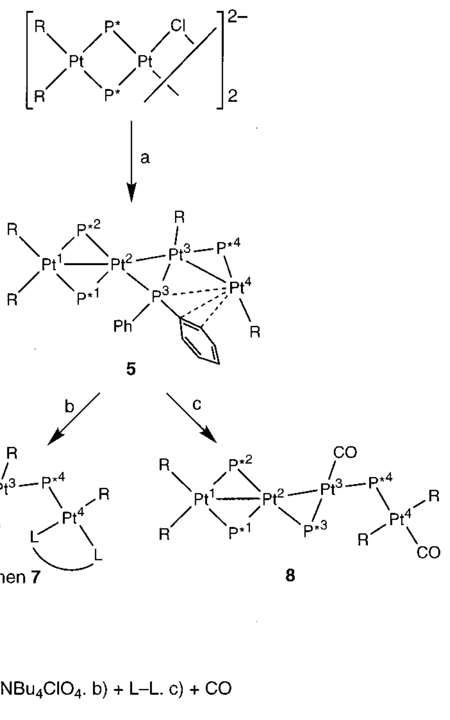
The synthesis of compound **5**, its structural characterization, and the study of some of its reactions are the subject of this paper.

Results and Discussion

Reaction of $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)\}_2]$ with $AgClO_4$. The reaction of $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)\}_2]$ with $AgClO_4$ (1:2 molar ratio) in CH_2Cl_2 results in the precipitation of AgCl, and from the mother liquors, after appropriate treatment, an orange solid, **5**, of general formulas $[Pt(PPh_2)(C_6F_5)]_x$ is obtained (Scheme 2a). The structure of **5** as a dichloromethane solvate has been established by an X-ray diffraction study.

Crystal Structure of $[Pt_4(\mu\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P)\}(C_6F_5)_4]\cdot CH_2Cl_2$. The structure of complex **5** together with the atom-labeling scheme is shown in Figure 1. Selected bond distances and angles are listed in Table 1. The compound is tetranuclear, the four platinum atoms being ordered in a nonlinear array and bridged by four diphenylphosphido ligands which display different structural features. The most significant interactions are shown in Figure 2. Pt(1) and Pt(2) atoms are bridged by two phosphido groups, the intermetallic distance (2.690(1) Å) being indicative of the existence of a Pt(1)–Pt(2) bond.[3,4] Consequently, the corresponding Pt–P–Pt angles are quite acute (Pt(1)–P(1)–Pt(2) = 72.56(5)°; Pt(1)–P(2)–Pt(2) = 71.50(5)°).

Scheme 2



Pt(2) and Pt(3) are bridged by only one phosphido ligand, the Pt(2)–Pt(3) distance being 2.767(1) Å, slightly longer than that previously mentioned, but in the range of distances found in other Pt–Pt bonded complexes. Both the Pt(2,3)–P(3) distances and the Pt(2)–P(3)–Pt(3) angle are very similar to the analogous parameters for the phosphido ligands at P(1) and P(2). A remarkable feature is that the P(3) diphenylphosphide is also connected to Pt(4), and there is at least an η^2 interaction between the *ipso* and *ortho* carbon atoms of one of the phenyl rings of this phosphido ligand and the Pt(4) atom (Pt(4)–C(43) and Pt(4)–C(44) distances are 2.387(6) and 2.579(6) Å, respectively). However this interaction does

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Pt_4(\mu\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P\}(C_6F_5)_4]\cdot CH_2Cl_2$ (5·CH$_2$Cl$_2$)

Pt(1)−C(1)	2.070(7)	Pt(1)−C(7)	2.079(7)	Pt(1)−P(1)	2.297(2)
Pt(1)−P(2)	2.349(2)	Pt(1)−Pt(2)	2.6897(4)	Pt(2)−P(3)	2.245(2)
Pt(2)−P(1)	2.248(2)	Pt(2)−P(2)	2.253(2)	Pt(2)−Pt(3)	2.7671(4)
Pt(3)−C(37)	2.036(7)	Pt(3)−P(4)	2.233(2)	Pt(3)−P(3)	2.314(2)
Pt(3)−Pt(4)	2.7331(5)	Pt(4)−C(67)	2.036(7)	Pt(4)−P(4)	2.207(2)
Pt(4)−C(43)	2.387(6)	Pt(4)−P(3)	2.454(2)	Pt(4)−C(44)	2.579(6)

C(1)−Pt(1)−C(7)	84.6(3)	C(1)−Pt(1)−P(1)	85.7(2)
C(7)−Pt(1)−P(1)	166.0(2)	C(1)−Pt(1)−P(2)	167.8(2)
C(7)−Pt(1)−P(2)	85.3(2)	P(1)−Pt(1)−P(2)	105.40(6)
P(3)−Pt(2)−P(1)	106.61(6)	P(3)−Pt(2)−P(2)	142.55(6)
P(1)−Pt(2)−P(2)	110.44(6)	Pt(1)−Pt(2)−Pt(3)	145.296(12)
C(37)−Pt(3)−P(4)	103.7(2)	C(37)−Pt(3)−P(3)	145.8(2)
P(4)−Pt(3)−P(3)	103.41(6)	Pt(2)−Pt(3)−Pt(4)	100.780(13)
C(67)−Pt(4)−P(4)	103.7(2)	C(67)−Pt(4)−C(43)	111.3(2)
P(4)−Pt(4)−C(43)	144.2(2)	C(67)−Pt(4)−P(3)	153.0(2)
P(4)−Pt(4)−P(3)	99.82(6)	C(43)−Pt(4)−P(3)	44.4(2)
Pt(2)−P(1)−Pt(1)	72.56(5)	Pt(2)−P(2)−Pt(1)	71.50(5)
Pt(2)−P(3)−Pt(3)	74.71(5)	Pt(2)−P(3)−Pt(4)	128.71(7)
Pt(3)−P(3)−Pt(4)	69.88(4)	Pt(4)−P(4)−Pt(3)	75.99(5)

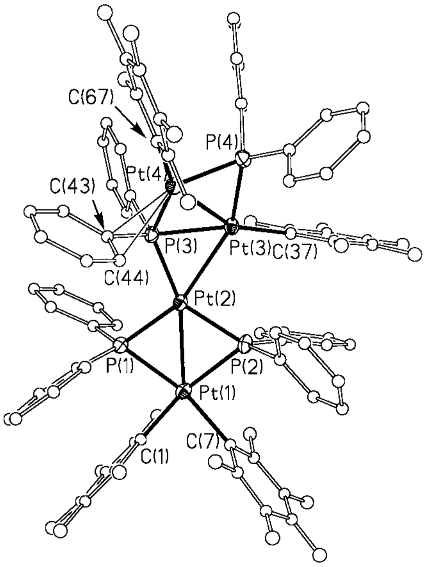

Figure 1. Structure of complex $[Pt_4(\mu\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P\}(C_6F_5)_4]$ (**5**).

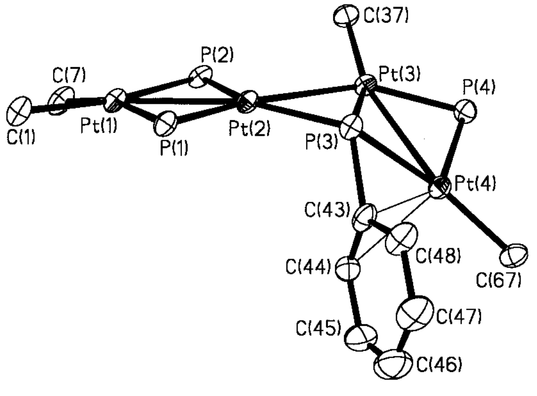

Figure 2. Schematic view of the central core of **5**.

not perceptibly affect the P−C and C−C distances within this group. In addition, the Pt(4)−P(3) distance is 2.454(2) Å, slightly longer than the other Pt−P distances in the complex. This may indicate the existence of a Pt(4)−P(3) bond. However, it seems more likely that this short Pt(4)···P(3) distance arises because of the η^2-phenyl−Pt(4) interaction, which constrains the P(3)···Pt(4) distance to be short. The μ_3-PPh(1,2-η^2-Ph)-κ^3P coordination of the formally anionic P(3) phosphido ligand, which donates six electrons to the complex through Pt−P interactions and the η^2-coordination of the phenyl group, is rather unusual, but has been found previously in two other compounds prepared by us, $[Pt_2Pd_2(\mu\text{-}PPh_2)_3(C_6F_5)_3(PPh_2C_6F_5)(CO)]$[3b] and $[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]$.[3c] Some other complexes in which the phosphorus of a phosphido ligand shows five-coordination are known.[5] Pt(3) and Pt(4) atoms are also bridged in a more "classical" way by another phosphido ligand (P(4)). The Pt(3)−Pt(4) distance (2.733(1) Å) is indicative of a metal−metal bond.[3,4] Compound **5** has a total valence electron count of 58, which is consistent with the presence of three Pt−Pt bonds between the Pt(II) centers. The coordination spheres of the Pt(1), Pt(3), and Pt(4) atoms are completed by pentafluorophenyl groups whose structural parameters are typical of this ligand in this kind of complex.[6]

This tetranuclear compound can be considered (See Figure 2) as formed by two dinuclear fragments, the one including Pt(1) and Pt(2) and $(C_6F_5)_2Pt(1)(\mu\text{-}PPh_2)_2Pt(2)$ and in which the Pt(1), P(1), P(2), and Pt(2) atoms are coplanar, and the other $(C_6F_5)Pt(3)(\mu\text{-}PPh_2)_2Pt(4)(C_6F_5)$, with the Pt_2P_2 skeleton not planar, the dihedral angle formed by the planes Pt(3), P(3), Pt(4) and Pt(3), P(4), Pt(4) being 31°. A plausible mechanism for the formation of **5** could be as follows: The reaction of the tetranuclear compound with $AgClO_4$ which results in the precipitation of AgCl could generate two unsaturated $(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt$ fragments (Scheme 3a) which in a nondonor solvent could establish donor−acceptor interactions between them (Scheme 3b). The migration of a C_6F_5 group from Pt(4) to Pt(3) leaves Pt(4) coordinatively unsaturated, favoring the establishment of a η^2phenyl−Pt(4) interaction (Scheme 3c) and resulting in **5**. The connection between the two binuclear fragments was finally carried out through the establishment of both the Pt(2)−Pt(3) and the Pt(2)−P(3) bonds.

As previously stated, the geometry of the unusual μ_3-PPh$_2$ ligand might serve as a model for an intermediate on the pathway for P−Ph cleavage at a polynuclear

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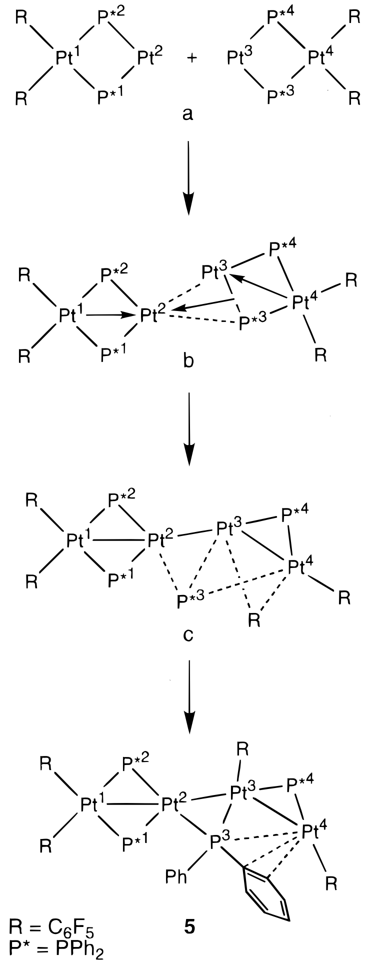
Scheme 3



metal center, a reaction often observed in cluster chemistry.[1e,4b,7] The η^2-phenyl interactions could favor as well the migration of the P donor ligand between the metal centers.[8] It is also interesting to point out the very different behavior of the homologous mixed Pt/Pd compound toward $AgClO_4$, which although precipitates AgCl, results in the formation of a mixed formal oxidation state Pt_2Pd_2 (+6) compound through a reductive coupling between a phosphido ligand and a C_6F_5 group[3b] (Scheme 1).

The ^{31}P NMR spectrum of **5** is in accord with the solid-state structure. It shows four signals at higher chemical shifts (δ from +283.3 to +116.4 ppm) than the signal observed in the ^{31}P NMR spectrum of the starting material (−139.4 ppm).[2] It is well documented that a deshielding of the ^{31}P resonances (typically in the range from +50 to +300 ppm) in phosphido-bridged complexes usually indicates the presence of metal−metal bonds supported by the phosphido ligand.[9] Signals appearing at 283.3 and 261.8 ppm can be assigned to P(2) and P(1) (atoms of PPh_2 groups that bridge two platinum centers joined by a metal−metal bond), respectively. Analogous chemical shifts have been found in other complexes that show the "$(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M$" fragment with short Pt−M (M = Pt, Pd) distances.[3a,b] The signal due to P(4) could be that appearing at 180.3 ppm, in the same region found for a structurally analogous PPh_2 in $[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]$ (179.5 ppm).[3c] Finally, the signal at 116.4 ppm can be assigned to P(3). Although the signals of the spectrum are very broad, the signal appearing at 116.4 ppm is a doublet (105 Hz) by coupling with P(2). The value of this coupling constant, $^2J_{P(2)-P(3)}$, is similar to that found for *trans*-$^2J_{P-P}$ in complex $[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(CO)_2]$, **3**.[3b] A relationship between the angular parameters at the phosphorus atom and the corresponding $\delta^{31}P$, the closing of the M−P−M′ angle, resulting in a deshielding of the P nucleus, has been previously observed.[10] In fact, all the Pt−P−Pt angles in **5** are small and the chemical shift values appear at a downfield region. Nevertheless, although the angles are in fact rather similar (71.50(5)° and 75.99(5)°), the values of δP(1) and δP(2) (double bridging skeleton) are very different from those of δP(3) and δP(4) (single bridging skeleton). The chemical shifts of P atoms in singly bridged diphenylphosphido complexes with a metal−metal bond appear at higher field than those of P atoms in dibridged bis(diphenylphosphido) complexes with a metal−metal bond. Thus, from these and other cases[3b] it can be concluded that the $\delta^{31}P$ values can yield important structural information not only about the presence of a metal−metal bond but also on whether the metal−metal bond is supported by one or two PPh_2 ligands. All signals show platinum satellites, and in each case two $^1J_{Pt-P}$ values can be calculated. The assignment of the $^1J_{Pt-P}$ values can be tentatively carried out by comparing the "$(C_6F_5)_2Pt(1)(\mu\text{-}PPh_2)_2Pt(2)$" fragment in complex **5** with the analogous one in complexes **2** and **3** (Scheme 1) and the "$Pt(2)(\mu\text{-}P(3)Ph_2)Pt(3)(\mu\text{-}P(4)Ph_2)Pt(4)$" fragment in **5** with the analogous one in $[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]$[3c] and taking into account the correlation[11] between Pt−Pμ bond lengths with $^1J_{Pt-P\mu}$ values found in closely related dinuclear systems (longer Pt−P bonds being associated with a decrease in the coupling constants). Nevertheless, as Powell et al. have pointed out,[11] $^1J_{Pt-P\mu}$ values are very sensitive to changes in ligands at Pt. In agreement with this we have observed that while the Pt(2)−P(3) distance (2.245(2) Å) is similar to that of Pt(2)−P(1) (2.248(2) Å), the $^1J_{Pt(2)-P(3)}$ value (3884.1 Hz) is much larger than $^1J_{Pt(2)-P(1)}$ (2151.2 Hz). It can be concluded that although δP values for μ-phosphido complexes give very important structural information, one has to be very careful when deducing structural information from J_{Pt-P} values.

The ^{19}F NMR spectrum of **5** shows four signals due to *o*-F atoms thus indicating the inequivalence of the four C_6F_5 groups. Two of these signals have similar chemical shifts and may be tentatively assigned to the C_6F_5 groups linked to Pt(1). Signals due to *m*- and *p*-F

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(2,2'\text{-bipy})]\cdot 2Me_2CO$ ($6\cdot 2Me_2CO$)

Pt(1)−C(1)	2.061(9)	Pt(1)−C(7)	2.065(9)	Pt(1)−P(1)	2.318(3)
Pt(1)−P(2)	2.368(3)	Pt(1)−Pt(2)	2.698(1)	Pt(2)−P(1)	2.231(3)
Pt(2)−P(2)	2.236(2)	Pt(2)−P(3)	2.270(2)	Pt(2)−Pt(3)	2.780(2)
Pt(3)−C(13)	2.078(8)	Pt(3)−P(3)	2.237(3)	Pt(3)−P(4)	2.292(3)
Pt(4)−C(19)	1.993(9)	Pt(4)−N(2)	2.094(7)	Pt(4)−N(1)	2.107(7)
Pt(4)−P(4)	2.281(3)				

C(1)−Pt(1)−C(7)	86.5(3)	C(1)−Pt(1)−P(1)	86.5(3)
C(7)−Pt(1)−P(1)	172.4(3)	C(1)−Pt(1)−P(2)	169.7(3)
C(7)−Pt(1)−P(2)	83.6(2)	P(1)−Pt(1)−P(2)	103.58(9)
P(1)−Pt(2)−P(2)	111.04(9)	P(1)−Pt(2)−P(3)	105.14(9)
P(2)−Pt(2)−P(3)	142.98(9)	Pt(1)−Pt(2)−Pt(3)	148.36(3)
C(13)−Pt(3)−P(3)	160.0(2)	C(13)−Pt(3)−P(4)	93.0(2)
P(3)−Pt(3)−P(4)	106.98(9)	C(19)−Pt(4)−N(2)	170.8(3)
C(19)−Pt(4)−N(1)	92.3(3)	N(2)−Pt(4)−N(1)	78.6(3)
C(19)−Pt(4)−P(4)	90.9(3)	N(2)−Pt(4)−P(4)	98.3(2)
N(1)−Pt(4)−P(4)	175.6(2)	Pt(2)−P(1)−Pt(1)	72.74(8)
Pt(2)−P(2)−Pt(1)	71.70(8)	Pt(3)−P(3)−Pt(2)	76.15(8)
Pt(4)−P(4)−Pt(3)	113.02(10)		

atoms appear overlapped at downfield and an unambiguous assignment for *m*-F and *p*-F cannot be made.

As expected the IR spectrum of **5** does not show any absorption assignable to *ν*(Pt−Cl). The X-sensitive modes of C_6F_5 groups[6] appear as a broad absorption with a shoulder.

The structure of cluster **5** indicates that in the reaction process (i) a C_6F_5 group migrates from one platinum center to another, (ii) one "$(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2$-Pt" unit is not maintained, and (iii) the coordinative unsaturation on a platinum center forces a C_6H_5 group in the PPh_2 ligand to act as a two-electron-donor ligand. Although it has been argued that the phosphido ligand is able to ensure the integrity of the polynuclear metal framework during chemical reactions, this is not the case in the formation of complex **5**. In this case the PPh_2 ligands cannot be considered as innocent. These observations cast doubt on the ability of phosphide ligands as metal framework stabilizing fragments.

Reaction of [$Pt_4(\mu\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P\}$-$(C_6F_5)_4$] with 2,2′-bipy or 1,10-phen. In complex **5** the coordination spheres of the metal centers reach saturation through the formation of metal−metal bonds and a η^2-arene−Pt interaction of one of the phenyl groups of a phosphido ligand. It is well known that both interactions are labile enough to be displaced easily by other ligands.[3a,12] For this reason we have studied the reactions of this compound with several ligands. When a CH_2Cl_2 solution of complex **5** is treated with an excess of bipy or phen, red solids of stoichiometry [$Pt_4(\mu\text{-}PPh_2)_4$-$(C_6F_5)_4$(L−L)] (L−L = 2, 2′-bipy, **6**; 1,10-phen, **7**) are isolated (Scheme 2b). The structures of these complexes have been established unambiguously by an X-ray diffraction study of complex **6** as an acetone solvate.

Its structure together with the atom labeling scheme is shown in Figure 3. Selected bond distances and angles are listed in Table 2. As can be seen, complex **6** is the result of the coordination of the bipy ligand (four-electron donor) to the most unsaturated part of complex **5** (see Figure 2). This produces the breaking of the η^2-phenyl−Pt(4) interaction, the Pt(3)−Pt(4) bond, and the P(3)−Pt(4) interaction (if any). Thus the fragment containing Pt(1), Pt(2), P(1), and P(2) is very similar to the analogous fragment in complex **5** (see Table 1 for comparison), with the atoms Pt(1) and Pt(2) double bridged by two PPh_2 ligands (Pt(1)−Pt(2) = 2.698(1) Å). This fragment is connected to that containing Pt(3) and Pt(4) through a Pt−Pt bond (Pt(2)−Pt(3) = 2.780(2) Å) and by a *μ*-phosphido ligand (P(3)) which supports the Pt(2)−Pt(3) bond. The Pt(4) center is bonded to the bipy ligand, one C_6F_5 group, and a *μ*-phosphido ligand and is therefore four-coordinated. As a consequence, neither the η^2-phenyl−Pt(4) nor the Pt(3)−Pt(4) bond that are present in complex **5** are required in complex **6**. The long Pt(3)···Pt(4) distance (3.814(2) Å) is obviously related to the large Pt(3)−P(4)−Pt(4) angle (113.02(10)°). The two pyridine rings of the bipy ligand are nearly coplanar, the dihedral angle between them being 4.3°. As stated before, Pt(1), Pt(2), P(1), and P(2) are coplanar, and the dihedral angle between this plane and the one formed by Pt(2), P(3), and Pt(3) is 5.6°. The best least-squares coordination plane of Pt(4) forms a dihedral angle of 107.4° with the plane formed by Pt(2), P(3), and Pt(3). This structure gives a total valence electron count of 60, which is consistent with the presence of only two Pt−Pt bonds between the Pt(II) centers in **6**.

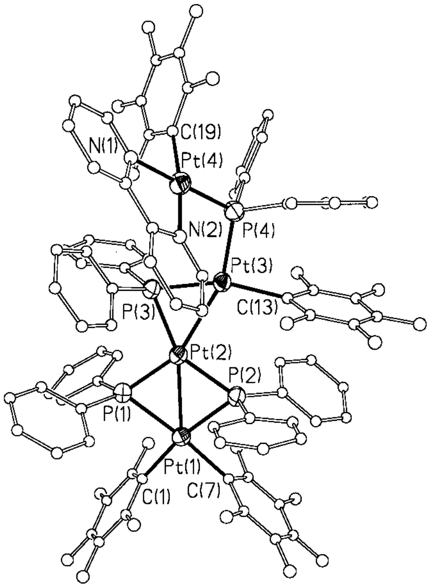

Figure 3. Structure of complex [$Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(2,2'\text{-bipy})$] (**6**).

Spectroscopic data are in accord with this structure being maintained in solution. The ^{31}P NMR spectrum

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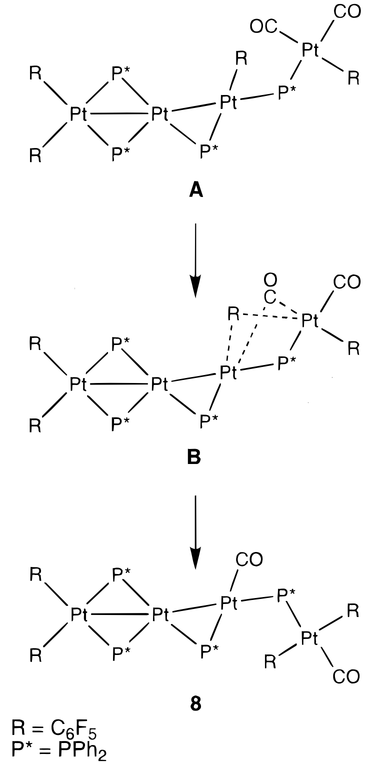
(12) (a) Casas, J. M.; Forniés, J.; Martín, A.; Menjón, B.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2949. (b) Forniés, J.; Menjón, B.; Gómez, N.; Tomás, M. *Organometallics* **1992**, *11*, 1187. (c) Casas, J. M.; Forniés, J.; Martín, A.; Menjón, B. *Organometallics* **1993**, *12*, 4376.

of **6** shows four signals, as does that of **7**. Downfield signals (278.2 and 249.5 ppm) are due to P(2) and P(1) (P atoms of two μ-PPh$_2$ ligands which are bridging two platinum centers linked by a metal−metal bond). The Pt(2) and Pt(3) centers (short distance, 2.780(2) Å) are bridged by the P(3)Ph$_2$ group alone, and the signal due to P(3) appears at lower frequency (122.1 ppm) than those due to P(1) and P(2). The signal due to P(4) appears at higher field (0.9 ppm), in accord with the long Pt(3)···Pt(4) distance and with the δ^{31}P found in other singly phosphido-bridged dinuclear complexes without metal−metal bonds.[13] As can be seen above, the Pt−P(4)−Pt angle in **6** is the largest, 113.02(10)°. Nevertheless we have reported previously complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$[2] and $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}OH)_2Pt(PPh_3)_2]$,[14] which show the "Pt(μ-PPh$_2$)$_2$M" fragment without a Pt−M bond and in which the Pt−P−M angles are smaller than 113° while their δP values appear at higher field. This once again indicates that one has to be careful in using the relationship[10] between M−P−M angles (or M···M distances) and δP in this type of complex. All the data that we have obtained from this and related work lead us to conclude that chemical shifts of single diphenylphosphido bridging ligands that are supporting nonbonded metal (Pt or Pd) centers appear at lower field than the signals due to bis(diphenylphosphido) ligands that are doubly bridging nonbonded metal centers. The signal at δ 0.9 ppm appears as a broad triplet (52.2 Hz), but the other three signals can be observed as broad multiplets, and therefore the fine structure was not studied. All of these signals show platinum satellites from which the corresponding $J_{\mathrm{Pt-P}}$ values can be extracted (see Experimental Section).

The ^{19}F NMR spectra of **6** and **7** show similar patterns. In the high-field region signals due to *m*- and *p*-F appear very overlapped and no structural information can be extracted from these signals. In the *o*-F region eight signals (of equal intensities) in **6** or seven signals (intensity ratio of 1:1:1:1:2:1:1, the largest being very broad) in **7** are observed. This pattern is in accord with the inequivalence of the four C$_6$F$_5$ groups in both complexes and with the inequivalence of the two *o*-F atoms of each C$_6$F$_5$ group.

Reaction of $[Pt_4(\mu\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P\}(C_6F_5)_4]$ with CO. As is to be expected, the tetranuclear complex **5**, which reacts with bidentate ligands such as bipy or phen, also reacts with CO. When CO is bubbled through a dichloromethane solution of **5** at room temperature, an orange solid **8** (49% yield) of stoichiometry $[\{Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_2(CO)\}_x]$ is obtained (Scheme 2c). Comparison of their spectroscopic data with those shown by related complexes allows a structural assignment as depicted in Scheme 2 to be carried out. Complex **8** is a stereoisomer of complex **3**,[3b] the only difference between them being the relative position of the two pentafluorophenyl rings bonded to Pt(4), which in **8** are in a *tran*s-arrangement, while in **3** they are in *cis* position. The IR spectrum of **8** shows two absorptions at 2096 and 2058 cm^{-1} due to the ν(C≡O) modes (the corresponding absorptions in **3** are 2082 and 2056 cm^{-1}) and two broad well-separated absorptions of similar intensity due to the X-sensitive modes of the C$_6$F$_5$ groups.[6]

Scheme 4



The ^{31}P NMR spectrum of **8** shows a pattern similar to that of **3**. The corresponding δP, $J_{\mathrm{P-P}}$, and $J_{\mathrm{Pt-P}}$ values (see Experimental Section) are similar to those found in **3** except for the $^1J_{\mathrm{Pt-P(4)}}$ values, which are very similar for the stereoisomer **8** (2648.0 and 2793.6 Hz) while rather different for the stereoisomer **3** (2653.3 and 1741.2 Hz). With all these data it is possible now to assign the 1741.2 Hz value in **3** to the coupling with the platinum center of the *cis*-"Pt(C$_6$F$_5$)$_2$(CO)" fragment. In addition, the values of both $^1J_{\mathrm{Pt-P(4)}}$ coupling constants in **8** (2648.0 or 2793.6 Hz) are larger than 1741.2 (**3**), this being in agreement with the high *trans* influence of the C$_6$F$_5$ group as previously observed.[15]

The ^{19}F NMR spectrum of **8** shows two downfield signals (4:4 intensity ratio) due to the *o*-F atoms of the pentafluorophenyl rings and three high-field signals (2:2:8 intensity ratio) due to *p*- and *m*-F atoms. This pattern shows that, unlike complex **3**, in compound **8** the two C$_6$F$_5$ groups of the fragment *trans*-"Pt^4(C$_6$F$_5$)$_2$-CO" are equivalent in solution. Moreover the *o*-F atoms, as well as the *m*-F and *p*-F atoms of the two C$_6$F$_5$ groups of the "(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$Pt" fragment, are, as in cluster **3**, isochronous.

As can be seen, in complex **5** the Pt(3) and Pt(4) atoms are each bonded to a C$_6$F$_5$ group, as they are in the bipy **6** and phen **7** derivatives, while in **8**, which is the result of the reaction between **5** and CO, both C$_6$F$_5$ groups are bonded to the same platinum atom (Pt(4)). The forma-

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[13] (a) Shyu, S.-G.; Lin, P.-J.; Lin, K.-J.; Chang, M.-C.; Wen, Y.-S. *Organometallics* **1995**, *14*, 2253. (b) Shyu, S.-G.; Hsiao, S.-M.; Lin, K.-J.; Gau, H.-M. *Organometallics* **1995**, *14*, 4300. (c) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Rosair, G. M.; Welch, A. J. *Inorg. Chem.* **1997**, *36*, 4426.

[14] Alonso, E.; Forniés, J.; Fortuño, C.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3777.

[15] Usón, R.; Forniés, J.; Espinet, P.; Fortuño, C. *J. Chem. Soc., Dalton Trans.* **1986**, 1849.

Table 3. Crystal Data and Structure Refinement for $[Pt_4(\mu\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P\}(C_6F_5)_4]\cdot CH_2Cl_2$ ($5\cdot CH_2Cl_2$) and $[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(2,2'\text{-bipy})]\cdot 2Me_2CO$ ($6\cdot 2Me_2CO$)

	5·CH_2Cl_2	**6**·$2Me_2CO$
empirical formula	$C_{72}H_{40}F_{20}P_4Pt_4\cdot CH_2Cl_2$	$C_{82}H_{48}F_{20}N_2P_4Pt_4\cdot 2Me_2CO$
unit cell dimens, *a* (Å)	12.5653(12)	14.134(5)
b (Å)	17.516(2)	15.142(5)
c (Å)	17.705(2)	21.405(7)
α (deg)	68.232(10)	86.16(3)
β (deg)	80.442(9)	75.59(3)
γ (deg)	81.676(10)	83.19(3)
volume (Å^3), *Z*	3553.8(7), 2	4397(4), 2
wavelength (Å)	0.71073	
temperature (K)	173(1)	293(1)
radiation	graphite-monochromated Mo Kα	
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
cryst dimens (mm)	0.50 × 0.25 × 0.10	0.60 × 0.50 × 0.20
abs coeff (mm^{-1})	8.109	6.506
transmn factors	1.000, 0.309	1.000, 0.567
abs corr	4313 equivalent reflections	*ψ* scans
diffractometer	Siemens SMART	Siemens P3m
2*θ* range for data collection (deg)	4.3−50.0 (±*h*, ±*k*, ±*l*)	3.2−50.0 (±*h*, ±*k*, +*l*)
no. of reflns collected	16607	15908
no. of ind reflns	12081 [*R*(int) = 0.0311]	15456 [*R*(int) = 0.0313]
refinement method	full-matrix least-squares on F^2	
goodness-of-fit on F^2	1.753	1.052
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0347 wR2 = 0.0981	R1 = 0.0413, wR2 = 0.0945
R indices (all data)	R1 = 0.0389 wR2 = 0.1038	R1 = 0.0699 wR2 = 0.1105

[a] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

tion of **8** instead of the expected tetranuclear derivative **A** (Scheme 4) could be a consequence of the ability of both CO and C_6F_5 ligands to act as bridging ligands,[16] giving the intermediate **B**, which rearranges to **8**.

Experimental Section

General Comments. C, H, and N analyses were performed with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 4000−200 cm^{-1}). NMR spectra were recorded on a Varian Unity 300 instrument with $CFCl_3$ and 85% H_3PO_4 as external references for ^{19}F and ^{31}P, respectively. Mass spectra were recorded on a VG-Autospec spectrometer operating at 30 kV, using the standard Cs-ion FAB gun and 3-nitrobenzyl alcohol (3-NOBA) as matrix. Literature methods were used to prepare the starting material $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)\}_2]$.[2]

Safety Note. Perchlorate salts are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Synthesis of $[Pt_4(\mu\text{-}PPh_2)_3\{\mu_3\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}\kappa^3P\}(C_6F_5)_4]$ (5). $AgClO_4$ (36 mg, 0.174 mmol) was added to a CH_2Cl_2 (20 mL) solution of $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)\}_2]$ (181 mg, 0.067 mmol). After 3.5 h stirring the suspension was filtered off, and the solvent was evaporated to ca. 1 mL. *i*-PrOH (8 mL) was added while stirring. An orange solid **5** crystallized and was filtered off and washed with 2 × 0.5 mL of *i*-PrOH (60 mg, 41%). Anal. Calcd for $C_{72}F_{20}H_{40}P_4Pt_4$: C, 39.5; H, 1.8. Found: C, 39.4; H, 1.65. IR (Nujol): 792, 781(sh) cm^{-1} (X-sensitive, C_6F_5). FAB-MS: *m/z* 2189 ([M]$^+$). ^{19}F NMR (20 °C, CD_2Cl_2, 282.4 MHz) δ: −115.4 (2 *o*-F, $^3J_{Pt-F} = 367.1$ Hz), −117.4 (2 *o*-F, $^3J_{Pt-F} = 412.3$ Hz), −118.5 (2 *o*-F, $^3J_{Pt-F} = 305.0$ Hz), −118.6 (2 *o*-F, $^3J_{Pt-F} = 278.4$ Hz), −160.7 (3 F), −162.7 (1 F), −163.9 (8 F). $^{31}P\{^1H\}$ NMR (20 °C, CD_2Cl_2, 121.4 MHz) δ: 283.3 (m, br, P(2), $^1J_{Pt(1)-P(2)} = 1017.6$ Hz, $^1J_{Pt(2)-P(2)} = 2283.1$ Hz), 261.8 (m, br, P(1), $^1J_{Pt(1)-P(1)} = 1359.0$ Hz, $^1J_{Pt(2)-P(1)} = 2151.2$ Hz), 180.3 (m, br, P(4), $^1J_{Pt(3)-P(4)} = 3039.7$, $^1J_{Pt(4)-P(4)} = 4104.1$ Hz), 116.4 (d, br, P(3), $^1J_{Pt(2)-P(3)} = 3884.1$, $^1J_{Pt(3)-P(3)} = 984.3$, $^2J_{P(2)-P(3)} = 105$ Hz).

Synthesis of $[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(L-L)]$, L−L = bipy (6). To a CH_2Cl_2 solution (10 mL) of **5** (100 mg, 0.045 mmol) was added bipy (28 mg, 0.180 mmol). After 3 h stirring, the red solution was evaporated to dryness. Addition of $CHCl_3$ (3 mL) caused the crystallization of a red solid **6**, which was filtered off and washed with small portions (2 × 0.5 mL) of cold $CHCl_3$ (83 mg, 79%). Anal. Calcd for $C_{82}F_{20}H_{48}N_2P_4Pt_4$: C, 42.0; H, 2.0; N, 1.2. Found: C, 41.7; H, 2.2; N, 1.2. IR (Nujol): 790, 778, 763 cm^{-1} (X-sensitive, C_6F_5). FAB-MS: *m/z* 2345 ([M]$^+$). ^{19}F NMR (20 °C, deuterioacetone, 282.4 MHz) δ: −111.7 (1 *o*-F, $^3J_{Pt-F} = 280.8$ Hz), −114.0 (1 *o*-F, $^3J_{Pt-F} = 248.1$ Hz), −115.1 (1 *o*-F, $^3J_{Pt-F} = 341.6$ Hz), −116.3 (1 *o*-F), −116.9 (1 *o*-F), −117.1 (1 *o*-F), −117.6 (1 *o*-F), −118.4 (1 *o*-F, $^3J_{Pt-F} = 455.5$ Hz), −162.1 (2 F), −162.6 (1 F), −163.5 (1 F), −163.8 (2 F), −164.5 (4 F), −165.4 (1 F), −166.0 (1 F). $^{31}P\{^1H\}$ NMR (20 °C, deuterioacetone, 121.4 MHz) δ: 278.2 (m, v br, P(2), $^1J_{Pt(2)-P(2)} \approx 2248$ Hz, $^1J_{Pt(1)-P(2)} \approx 983$ Hz), 249.5 (m, v br, P(1), $^1J_{Pt(2)-P(1)} \approx 2005$ Hz, $^1J_{Pt(1)-P(1)} \approx 1386$ Hz), 122.1 (m, v br, P(3) $^1J_{Pt(2)-P(3)} \approx {}^1J_{Pt(3)-P(3)} \approx 2535$ Hz), 0.9 (pseudo t, P(4), $^1J_{Pt-P(4)} = 3432.8$ and 3187.5 Hz, $^2J_{Pt(2)-P(4)} = 258.5$ Hz, $J_{P-P} = 52.2$ Hz).

L−L = phen (7). Complex **7** was prepared by the same procedure as that for **6**. The reaction of **5** (100 mg, 0.045 mmol) and 0.033 g (0.183 mmol) of phen gives a red solid (**7**, 0.090 g, 83%). Anal. Calcd for $C_{84}F_{20}H_{48}N_2P_4Pt_4$: C, 42.6; H, 2.0; N, 1.2. Found: C, 42.5; H, 2.1; N, 1.3. IR (Nujol): 807, 792, 780 cm^{-1} (X-sensitive, C_6F_5). FAB-MS: *m/z* 2369 ([M]$^+$). ^{19}F NMR (20 °C, deuterioacetone, 282.4 MHz) δ: −111.5 (1 *o*-F, $^3J_{Pt-F} \approx 346$ Hz), −114.1 (1 *o*-F, $^3J_{Pt-F} \approx 280$ Hz), −115.2 (1 *o*-F, $^3J_{Pt-F} \approx 360$ Hz), −116.3 (1 *o*-F), −116.9 (2 *o*-F), −117.6 (1 *o*-F), −117.9 (1 *o*-F, $^3J_{Pt-F} \approx 470$ Hz), −161.7 (2 F), −162.4 (1 F), −163.2 (3 F), −164.0 (4 F), −164.8 (1 F), −165.5 (1 F). $^{31}P\{^1H\}$ NMR (20 °C, deuterioacetone, 121.4 MHz) δ: 277.0 (m, v br, P(2), $^1J_{Pt(2)-P(2)} \approx 2195$ Hz, $^1J_{Pt(1)-P(2)} \approx 984$ Hz), 248.7 (m, v

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[16] (a) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R.; Llusar, R. *Organometallics* **1988**, *7*, 2279. (b) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R.; Feng, X. *J. Am. Chem. Soc.* **1993**, *115*, 4145. (c) Ara, I.; Casas, J. M.; Forniés, J.; Rueda, A. *Inorg. Chem.* **1996**, *35*, 7345.

br, P(1), $^1J_{\mathrm{Pt(2)-P(1)}} \approx 2440$ Hz, $^1J_{\mathrm{Pt(1)-P(1)}} \approx 1190$ Hz), 122.8 (m, v br, P(3) $^1J_{\mathrm{Pt(2)-P(3)}} \approx {}^1J_{\mathrm{Pt(3)-P(3)}} \approx 2568$ Hz), −3.3 (pseudo t, P(4), $^1J_{\mathrm{Pt-P(4)}} = 3413.3$ and 3300.7 Hz, $^2J_{\mathrm{Pt(2)-P(4)}} = 283.2$ Hz, $J_{\mathrm{P-P}} = 56.8$ Hz).

Synthesis of [Pt$_4$(*μ*-PPh$_2$)$_4$(C$_6$F$_5$)$_4$(CO)$_2$] (8). To a CH_2Cl_2 (8 mL) solution of **5** (95 mg, 0.043 mmol) was bubbled CO for 15 min. Hexane (50 mL) was added, and CO was bubbled until an orange solid, **8**, crystallized. The solid was filtered off and washed with 2 × 0.5 mL of hexane (48 mg, 49%). Anal. Calcd for $C_{74}F_{20}H_{40}O_2P_4Pt_4$: C, 39.6; H, 1.8. Found: C, 39.2; H, 1.7. IR (Nujol): 794, 779 cm^{-1} (X-sensitive, C_6F_5); 2096, 2058 cm^{-1} (ν(C≡O)). FAB-MS: *m*/*z* 2189 ([M − 2CO]$^+$). ^{19}F NMR (20 °C, $CDCl_3$, 282.4 MHz) δ: −115.7 (4 *o*-F, $^3J_{\mathrm{Pt-F}} = 257.7$ Hz), −119.3 (4 *o*-F, $^3J_{\mathrm{Pt-F}} = 297.6$ Hz), −159.7 (2 *p*-F),-160.4 (2 *p*-F), −163.2 (8 *m*-F). ^{31}P{^{1}H} NMR (20 °C, $CDCl_3$, 121.4 MHz) δ: 274.6 (ddd, P(2), $^1J_{\mathrm{Pt(1)-P(2)}} = 1126.7$ Hz, $^1J_{\mathrm{Pt(2)-P(2)}} = 1857.5$ Hz, $^2J_{\mathrm{P(2)-P(3)}} = 117.8$ Hz, $^2J_{\mathrm{P(1)-P(2)}} = 65.5$ Hz, $^3J_{\mathrm{P(2)-P(4)}} = 29.8$ Hz), 256.7 (pseudo t, br, P(1), $^1J_{\mathrm{Pt(1)-P(1)}} = 1281.6$ Hz, $^1J_{\mathrm{Pt(2)-P(1)}} = 2181.9$ Hz), 150.6 (d, P(3), $^1J_{\mathrm{Pt-P(3)}} = 2903.5$ and 2818.8 Hz, $^2J_{\mathrm{Pt(1)-P(3)}} = 81.4$ Hz, $^2J_{\mathrm{P(2)-P(3)}} = 117.8$ Hz), −3.3 (dd, P(4), $^1J_{\mathrm{Pt-P(4)}} = 2793.6$ and 2647.9 Hz, $^2J_{\mathrm{Pt(2)-P(4)}} = 233.0$ Hz, $^3J_{\mathrm{P(2)-P(4)}} = 29.8$ Hz, $^3J_{\mathrm{P(1)-P(4)}} = 49.6$ Hz).

Crystal Structure Analysis of [Pt$_4$(*μ*-PPh$_2$)$_3${*μ*$_3$-PPh-(1,2-*η*^{2}-Ph)-*κ*^{3}*P*}(C$_6$F$_5$)$_4$]·CH$_2$Cl$_2$ (5·CH$_2$Cl$_2$) and [Pt$_4$(*μ*-PPh$_2$)$_4$(C$_6$F$_5$)$_4$(2,2′-bipy)]·2Me$_2$CO (6·2Me$_2$CO). Crystal data and other details of the structure analysis are presented in Table 3. Suitable crystals of **5** and **6** were obtained by slow diffusion of *n*-hexane into a solution of 0.025 g of [Pt_4(μ-PPh_2)$_3$-{μ_3-PPh(1,2-η^2-Ph)-κ^3*P*}(C_6F_5)$_4$] in CH_2Cl_2 (3 mL) and [Pt_4(μ-PPh_2)$_4$(C_6F_5)$_4$(2,2′-bipy)] in acetone (3 mL) and were mounted at the end of a glass fiber. For **5**, unit cell dimensions were initially determined from the positions of 359 reflections in 90 intensity frames measured at 0.3° intervals in ω and subsequently refined on the basis of positions of 6812 reflections from the main dataset. An absorption correction was applied on the basis of 4313 symmetry equivalent reflection intensities. For **6**, unit cell dimensions were determined from 30 centered reflections in the range $25.8° < 2\theta < 44.6°$. An absorption correction was applied based on 576 azimuthal scan data. Lorentz and polarization corrections were applied for both structures.

The structures were solved by Patterson and Fourier methods. All refinements were carried out using the program SHELXL-93.[17] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. 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 **5**, the unit cell contains a CH_2Cl_2 solvent molecule disordered over two positions sharing a common Cl atom. The geometry of this CH_2Cl_2 solvent molecule was fixed. For **6**, one of the molecules of the acetone solvent was refined with full occupancy. Two more Me_2CO moieties are present in the structure, being refined with 0.5 of occupancy each. For all the acetone molecules present the C−C and C−O distances were restrained (1.20(2) and 1.50(2) Å, respectively). Full-matrix least-squares refinement of these models against F^2 converged to final residual indices. Final difference electron density maps showed 18 features above 1 e/Å^3 (max/min 1.78/−1.80 e/Å^3), with the largest peaks lying closer than 1 Å to the platinum and chlorine solvent atoms for **5**, and one feature above 1 e/Å^3 (max/min 1.14/-0.77 e/Å^3), being close to one of the platinum atoms for **6**.

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Supporting Information Available: Tables of full atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, full bond distances and bond angles, hydrogen coordinates, isotropic displacement parameters for the crystal structures, and full labeled figures of complexes **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Sheldrick, G. M. *SHELXL-93*, a program for crystal structure determination; University of Göttingen: Germany, 1993.