Reactivity of a Secondary Phosphine Platinum(II) Complex with [Pt(norbornene)$_3$] and PPh$_3$. Synthesis of New Single Phosphido-Bridged Derivatives of Platinum(I) and Phosphido-Bridged Platinum(II) Hydrides[†,‡]

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The reaction between *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$], [Pt(norbornene)$_3$], and PPh$_3$ (1:1:1) results in the formation of the Pt(II) derivatives [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)(μ-H)Pt(PPh$_2$H)(PPh$_3$)] (**1**) and [{(C$_6$F$_5$)(PPh$_3$)Pt(μ-PPh$_2$)(μ-H)}$_2$Pt] (**2**). For the molar ratio 1:1:2 the reaction proceeds with formation of the Pt(I) derivative [(C$_6$F$_5$)(PPh$_3$)Pt(μ-PPh$_2$)Pt(PPh$_3$)$_2$] (**3**) and the Pt(II) derivatives [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)(μ-H)Pt(PPh$_3$)$_2$] (**4**) and [(C$_6$F$_5$)(PPh$_3$)Pt(μ-PPh$_2$)$_2$Pt(H)(PPh$_3$)] (**5**). The structures of complexes **2**, **3**, and **5** have been established by X-ray diffraction. Spectroscopic (IR and NMR) data are also given.

Introduction

The dinuclear Pd(I) complexes [Pd$_2$(μ-PR$_2$)$_2$(PR$_2$H)$_2$] (R = Bu^t, Cy) have been synthesized[1] by reacting PdCp(η^3-C$_3$H$_5$) with PR$_2$H. For R = Bu^t the reaction is carried out through the intermediate formation of the Pd(0) complex Pd(PBu$^t_2$H)$_2$ and oxidative addition of a P−H bond. When the secondary phosphine is PPh$_2$H, the complex [Pd$_2$(μ-PPh$_2$)$_2$(PPh$_2$H)$_3$] is obtained, and this dinuclear complex cannot be obtained from [Pd(PPh$_2$H)$_4$].[2] Some heterometallic platinum μ-phosphido complexes in which the bridging phosphido moiety M(μ-PR$_2$)Pt is formed by reacting a transition-metal complex containing PR$_2$H with zerovalent complexes of platinum have been reported.[3] The synthesis of palladium or platinum trinuclear clusters in mixed formal oxidation state and displaying the M$_3$(μ-PR$_2$)$_3$ core has been carried out in some cases[4] by reacting dinuclear derivatives of the type [M$_2$(μ-PR$_2$)$_2$L$_2$(PR$_2$H)$_2$] with palladium(0) or platinum(0) complexes. Thus, the oxidative addition of the P−H bond of a secondary phosphine to zerovalent complexes of platinum or palladium provides easy access to polynuclear phosphido-bridged complexes.

In the past few years we have been involved in the synthesis of palladium and/or platinum polynuclear derivatives with bridging diphenylphosphido ligands. The precursors of this type of phosphido complexes were often Li$_2$[*cis*-Pt(C$_6$F$_5$)$_2$(PPh$_2$)$_2$] (M = Pd, Pt), prepared in situ by deprotonation of metal-coordinated secondary phosphines in *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$],[5] which by reacting with several Pt(II) derivatives are able to produce an interesting family of polynuclear phosphido palladium(II) or platinum(II) derivatives. In this paper we describe the reactions between *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] and the platinum(0) complex [Pt(norbornene)$_3$] in the presence of different molar ratios of PPh$_3$, which give different types of phosphido- or phosphido/hydrido-bridged platinum(I) or -(II) complexes.

Results and Discussion

Reaction of *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] with [Pt(C$_7$H$_{10}$)$_3$] (C$_7$H$_{10}$ = η^2-norbornene) and PPh$_3$ in a 1:1:1 Molar Ratio. The results of the reaction between *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] and [Pt(C$_7$H$_{10}$)$_3$] (1:1 molar ratio) in the presence of PPh$_3$ depend on the amount of PPh$_3$ used. When *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$] is added at room temperature to a toluene solution of [Pt(C$_7$H$_{10}$)$_3$] and PPh$_3$ in a 1:1:1 molar ratio, the dinuclear hydride-bridged Pt(II) complex [(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)(μ-H)Pt(PPh$_2$H)(PPh$_3$)] (**1**; 36% yield) is obtained (Scheme 1). In

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[†] Polynuclear Homo- or Heterometallic Palladium(II)−Platinum(II) Pentafluorophenyl Complexes Containing Bridging Diphenylphosphido Ligands. 9. Part 8: ref 13b.

[‡] Dedicated to Prof. Rafael Usón on the occasion of his 75th birthday.

[§] Universidad de Zaragoza-CSIC.

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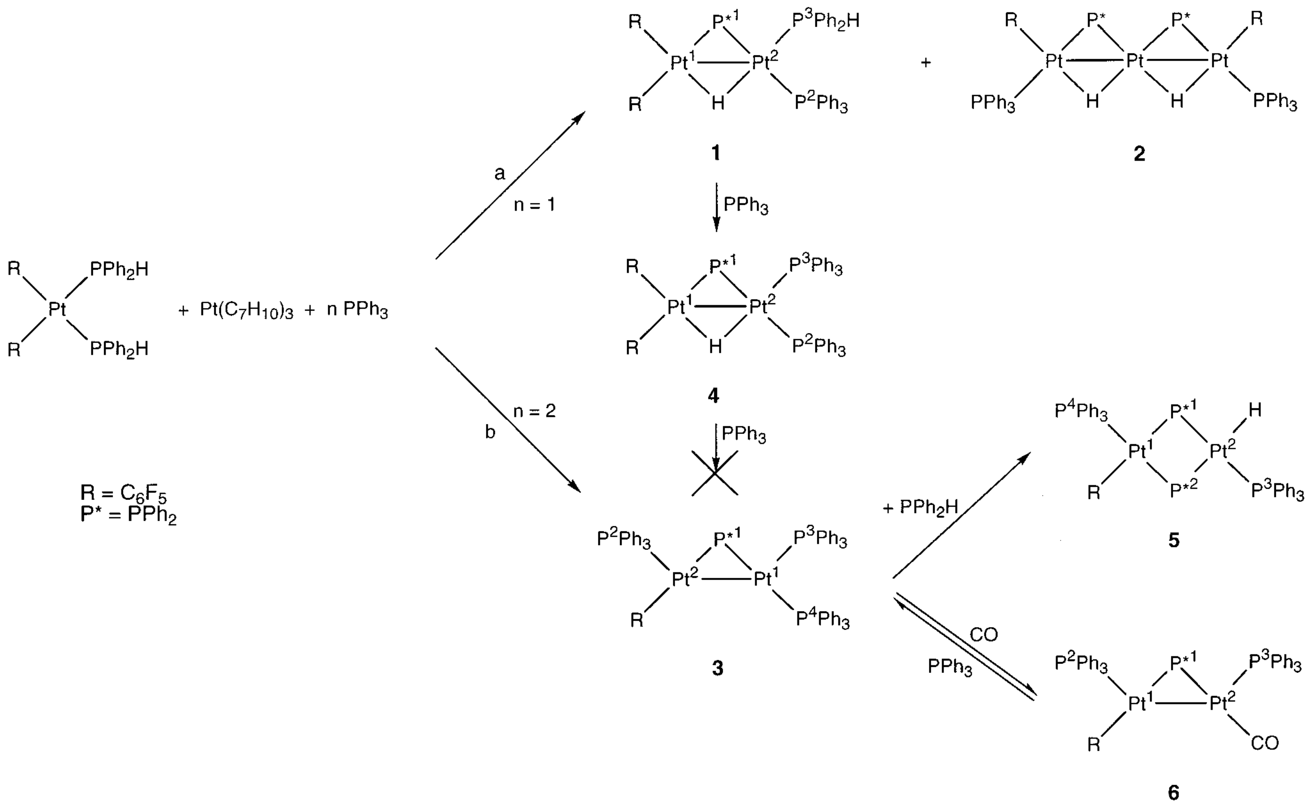
Scheme 1



addition, as we will see later, by workup of the mother liquors a trinuclear platinum(II) derivative, [{(C_6F_5)(PPh_3)Pt(μ-PPh_2)(μ-H)}$_2$Pt] (**2**; 21% yield), is obtained.

The structure of **1** (Scheme 1) has been established on the basis of NMR and IR data and results from the oxidative addition of one P−H bond to the Pt(0) center and migration of the PPh_2H ligand. Since complex **1** has a valence electron count of 30, a metal−metal bond between the two Pt(II) centers should be present. Hydride-bridged complexes containing other bridging ligands which contribute to the stability of the dinuclear unit are known.[6−8] The most representative are the cationic bis(diphenylphosphino)methane-bridged A-frame species of the type [$Pt_2X_2(\mu\text{-H})(\mu\text{-dppm})_2$]$^+$.[6] Mixed-bridge systems of the type Pt(μ-H)(μ-X)Pt (X being a monodentate ligand) are relatively scarce,[7] and only a few derivatives of Pt(II) with a mixed hydride/phosphide bridging system have been reported.[8]

The IR spectrum of **1** shows two absorptions of similar intensity in the 800 cm^{-1} region. This is in accord with the presence of two C_6F_5 groups bonded to the platinum center in a cis fashion.[9] The absorption due to the stretching mode of the P−H bond of the secondary phosphine is observed at 2320 cm^{-1}.[10] We have not located the IR absorption of the bridging hydride, although, as is well-known, such absorptions (ca. 1600 cm^{-1}) are usually weak and often difficult to assign.[11] The ^{1}H NMR spectrum unequivocally shows the presence of a bridging hydrido ligand. The hydrido resonance is a broad doublet ($^2J_{\mathrm{P(3),H}}$ = 81 Hz) centered at −6.0 ppm, the splitting being due to the phosphorus atom of the trans PPh_2H ligand (see Scheme 1 for nuclei labeling). The $^2J_{\mathrm{P(trans\ to\ H),H}}$ values for the hydride ligand are diagnostic of the bonding mode. Usually the $^2J_{\mathrm{P(trans\ to\ H),H}}$ values for the hydride ligand are ca. 55−80 Hz for bridged hydrides, while this coupling is much larger for terminal hydrides.[3c,8d,12] The signal is flanked by platinum satellites due to the coupling with the two inequivalent platinum atoms, $^1J_{\mathrm{Pt(1,2),H}}$ = 430 and 537

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Hz. In known diplatinum hydrido complexes, bridging hydrides display $^{1}J_{\mathrm{Pt,H}}$ values in the range 300−600 Hz, while terminal hydrides give signals with $^{1}J_{\mathrm{Pt,H}}$ values in the range 800−1400 Hz.[3c,8d,12] Since the C_6F_5 group has a high trans influence,[9] the value of 430 Hz can be assigned to the coupling with the platinum center bonded to the two C_6F_5 groups. The signal due to the P−H proton of the secondary phosphine must appear as a doublet by coupling with P(3). Nevertheless, the low-field part of this doublet is hidden by signals due to hydrogen atoms of phenyl groups in this part of the spectrum. The higher field part of the doublet is observed as a doublet centered at 6.2 ppm ($^{3}J_{\mathrm{P(1),H}} = 9$ Hz) with platinum satellites ($^{2}J_{\mathrm{Pt(2),H}} = 41$ Hz) that barely emerge from the baseline. Phosphorus-decoupled ^{1}H NMR experiments have been carried out. In the ^{1}H-{^{31}P} NMR experiment with irradiation in the P(2) resonance region (18 ppm, PPh_3 region, see below), the observed spectrum is unchanged. Thus, the observed splittings in the hydride and P−H signals cannot be due to coupling with P(2) (PPh_3 group). When the irradiation is carried out in the P(3) resonance region (−8 ppm, PPh_2H region, see below), both the signal due to the bridging hydride and that due to the P−H proton of the PPh_2H ligand change dramatically. This spectrum shows the signal for the hydride ligand (−6.0 ppm) as a broad singlet, thus confirming that the coupling of 81 Hz is due to P(3) of the PPh_2H ligand. The signal due to the hydrogen atom of the PPh_2H ligand appears as a doublet (9 Hz) at 6.8 ppm, whereas the high-field signal observed in the ^{1}H NMR spectrum was a doublet (9 Hz) at 6.2 ppm. Moreover, the spectrum with irradiation in the P(1) resonance region (111.5 ppm, see below) shows a singlet at 6.2 ppm due to the P−H proton. Therefore, the $^{1}J_{\mathrm{P(3),H}}$ value can be calculated (360 Hz), and the 9 Hz splitting is due to coupling with P(1).

The ^{19}F NMR spectrum of **1** shows six signals. Two of them (2:2 intensity ratio) appear at low field (*o*-F atoms) and show platinum satellites, while those appearing at higher field (1:1:2:2 intensity ratio) are assigned to the two *p*-F atoms and to the *m*-F atoms of the two C_6F_5 groups, respectively. This pattern confirms that the C_6F_5 groups are inequivalent.

The ^{31}P{^{1}H} NMR spectrum shows three signals. The signal due to the P atom of the phosphido group (P(1)) appears at 111.5 ppm, in the expected region for PPh_2-bridged metal−metal-bonded complexes.[13] The signal appears as a doublet ($^{2}J_{\mathrm{P(1),P(2)}} = 305$ Hz) flanked by ^{195}Pt satellites ($^{1}J_{\mathrm{Pt(1,2),P(1)}} = 1734, 2068$ Hz). The signal due to P(2) (PPh_3 group) appears at 18.1 ppm as a doublet (305 Hz) with one pair of platinum satellites, $^{1}J_{\mathrm{Pt(2),P(2)}} = 2636$ Hz, coupling with Pt(1) not being observed. The signal due to the P atom of the PPh_2H group (P(3)) appears as a singlet at −8.0 ppm. This signal shows two pairs of platinum satellites (splittings of 207 and 3996 Hz) due to coupling with Pt(1) and Pt(2), respectively.

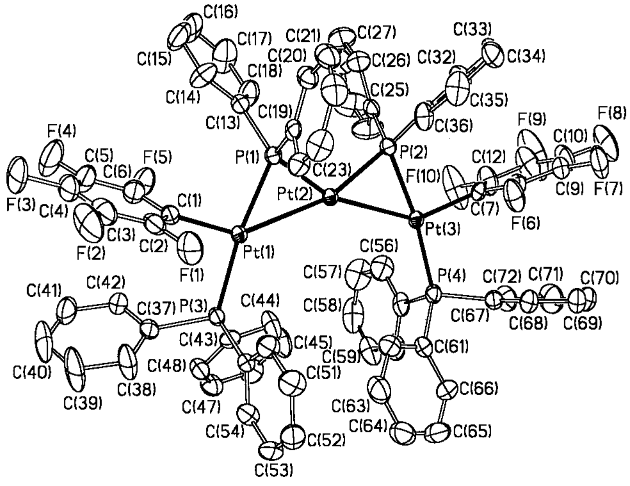

Figure 1. Structure of the complex [{(C_6F_5)(PPh_3)Pt(μ-PPh_2)(μ-H)}$_2$Pt] (**2**). Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [{(C_6F_5)(PPh_3)Pt(μ-PPh_2)(μ-H)}$_2$Pt]·C_6H_{12}·$^3/_8C_6H_{14}$ (2·C_6H_{12}·$^3/_8C_6H_{14}$)

Pt(1)−C(1)	2.051(6)	Pt(2)−P(1)	2.2249(14)
Pt(1)−Pt(2)	2.8474(3)	Pt(3)−C(7)	2.058(5)
Pt(2)−Pt(3)	2.8523(3)	Pt(1)−P(3)	2.3137(14)
Pt(3)−P(4)	2.3074(15)	Pt(2)−P(2)	2.2279(14)
Pt(1)−P(1)	2.2638(14)	Pt(3)−P(2)	2.2667(14)
C(1)−Pt(1)−P(1)	94.96(15)	C(1)−Pt(1)−P(3)	94.22(16)
P(1)−Pt(1)−P(3)	170.81(5)	C(1)−Pt(1)−Pt(2)	144.64(15)
P(1)−Pt(1)−Pt(2)	50.03(3)	P(3)−Pt(1)−Pt(2)	120.79(4)
P(1)−Pt(2)−P(2)	111.01(5)	P(1)−Pt(2)−Pt(1)	51.23(4)
P(2)−Pt(2)−Pt(1)	161.93(4)	P(1)−Pt(2)−Pt(3)	161.08(4)
P(2)−Pt(2)−Pt(3)	51.21(4)	Pt(1)−Pt(2)−Pt(3)	146.837(10)
C(7)−Pt(3)−P(2)	93.48(16)	C(7)−Pt(3)−P(4)	93.84(16)
P(2)−Pt(3)−P(4)	172.04(5)	C(7)−Pt(3)−Pt(2)	142.71(15)
P(2)−Pt(3)−Pt(2)	50.01(4)	P(4)−Pt(3)−Pt(2)	123.10(4)
Pt(2)−P(1)−Pt(1)	78.74(4)	Pt(2)−P(2)−Pt(3)	78.78(4)

The structure of **2** has been established by an X-ray diffraction study (see Figure 1). Selected bond distances and angles are listed in Table 1. The compound is a trinuclear complex in which the three platinum atoms are in a nonlinear array. As can be seen, two “(C_6F_5)(PPh_3)Pt(PPh_2)(H)” units are joined to another platinum atom through the diphenylphosphido and hydride groups that are acting as bridging ligands. The core of this complex is essentially planar, since the three platinum atoms, and the atoms directly bonded to them, lie in the same plane. The total valence electron count for this complex is 44, implying the presence of two metal−metal bonds. This is confirmed by the X-ray study, which shows Pt−Pt distances of 2.874(1) Å (Pt(1)−Pt(2)) and 2.852(1) Å (Pt(2)−Pt(3)), compatible with the existence of intermetallic bonds. Both Pt(1) and Pt(3) have the same four ligands completing a square-planar coordination around the metal centers. Unfortunately, the X-ray study did not give reliable information about the position of the hydride ligands, but their presence and structural role can be inferred from the ^{1}H NMR spectrum of **2** (see below). The available angles around Pt(1) and Pt(3) reveal a typical square-planar configuration for the metals. The P(1)−Pt(2)−P(2) angle has a somewhat high value, 111.01(5)°. This fact is probably related to the bent (146.84(1)°) Pt(1)−Pt(2)−Pt(3) unit and may be due to the small size of the hydride ligands located trans to the phosphido groups at Pt(2) and the steric repulsion caused by the phosphido phenyl rings. The Pt−P−Pt angles are small, Pt(1)−P(1)−Pt(2) = 78.74(4)° and Pt(2)−P(2)−Pt(3) = 78.78(4)°, as previ-

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ously observed in systems in which the phosphorus atom bridges two metal centers joined by an intermetallic bond.

The ^{1}H NMR spectrum of **2** confirms the presence of bridging hydride ligands. It contains a high-field resonance centered at −5.6 ppm as a broad doublet (45 Hz). The $^{1}H\{^{31}P\}$ NMR experiments show for this signal the same broad doublet when the spectrum is measured with P irradiation in the PPh_3 region (ca. 20 ppm, see below), while it shows a broad singlet when the spectrum is measured with P irradiation in the μ-PPh_2 region (ca. 107 ppm, see below). Thus, the splitting of the μ-hydride signal in the ^{1}H NMR spectrum is due to coupling with the P atom of the PPh_2 group trans to the hydride at Pt(2) ($^{2}J_{P,H} = 45$ Hz). This value is smaller than typical P−H couplings for tertiary phosphine complexes, but it is similar to that found in the μ-phosphido complex $[PtW_2(\mu\text{-}PPh_2)_2(\mu\text{-}H)(\mu\text{-}CO)Cp_2(CO)_4]^+$.[14] The signal shows platinum satellites from which two values of $^{1}J_{Pt,H}$ can be measured, 442 and 508 Hz, in accord with the presence of a bridging hydride.[3c,8d,12]

The ^{19}F NMR spectrum of **2** exhibits only three signals in a 2:1:2 intensity ratio, in agreement with the presence of two equivalent C_6F_5 groups.

The $^{31}P\{^{1}H\}$ NMR spectrum of **2** is in agreement with the trinuclear nature of the cluster. It shows signals due to all six subspectra arising from the six different isotopomeric combinations of platinum nuclei having different nuclear spins (Pt/Pt/Pt 29.1%, $^{195}Pt/Pt/Pt$ 29.6%, $Pt/^{195}Pt/Pt$ 14.8%, $^{195}Pt/^{195}Pt/Pt$ 15.1%, $^{195}Pt/Pt/^{195}Pt$ 7.5%, and $^{195}Pt/^{195}Pt/^{195}Pt$ 3.8%). The spectrum has two sharp doublets (308 Hz) at 106.8 (μ-P) and 19.9 (PPh_3) ppm. From the platinum satellites two values of $^{1}J_{Pt,P}$ (3195 and 1918 Hz) and one value of $^{2}J_{Pt,P}$ (132 Hz) can be extracted for the μ-PPh_2 groups and one value of $^{1}J_{Pt,P}$ and one of $^{2}J_{Pt,P}$ (2708 and 63 Hz, respectively) for the PPh_3 ligands.

As we have seen before, some dinuclear platinum complexes with the $Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt$ bridging system have been reported but, as far as we know, complex **2** is the first trinuclear platinum complex in which the three metal centers are linked by "$Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt$" units. The formation of complex **2** seems to be the result of the oxidative addition of the P−H bonds of the two PPh_2H ligands of the mononuclear starting material to one Pt(0) center and the migration of the C_6F_5 groups (see Scheme 2). In accord with this proposal, a similar reaction using *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]/[Pt(C_7H_{10})_3]/PPh_3$ in a 1:2:2 molar ratio gives **2** in a better yield (48%).

Reaction of *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ with $[Pt(C_7H_{10})_3]$ and PPh_3 in a 1:1:2 Molar Ratio. When *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ is added to a toluene solution of $[Pt(C_7H_{10})_3]$ and PPh_3 in a 1:1:2 molar ratio (Scheme 1), the neutral dinuclear Pt(I) derivative $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ (**3**) is isolated in 20% yield (based on platinum) from the reaction mixture.

The structure of **3** has been established by a X-ray diffraction study (see Figure 2). Selected bond distances and angles are listed in Table 2. Compound **3** is a dinuclear Pt(I) complex in which the platinum atoms are bridged only by a diphenylphosphido ligand which is trans to the only pentafluorophenyl group present in the complex. The central core of the complex, formed by the platinum and phosphorus atoms and C(1), is almost perfectly planar. The Pt−Pt distance (2.781(1) Å), which is slightly longer than those in complex **2**,

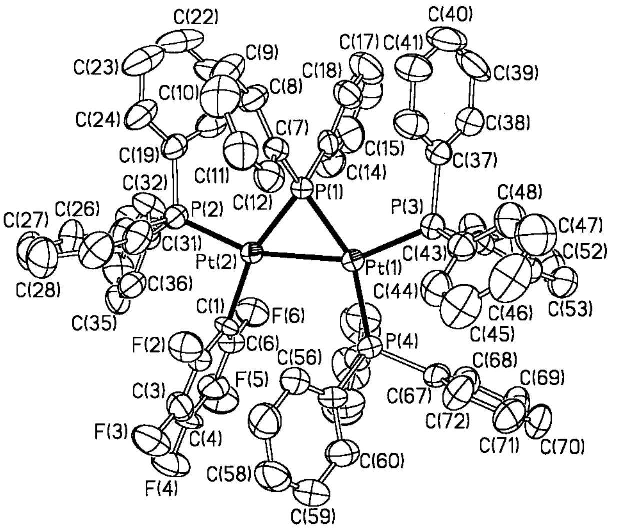

Figure 2. Structure of the complex $[Pt_2(\mu\text{-}PPh_2)(C_6F_5)(PPh_3)_3]$ (**3**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 2

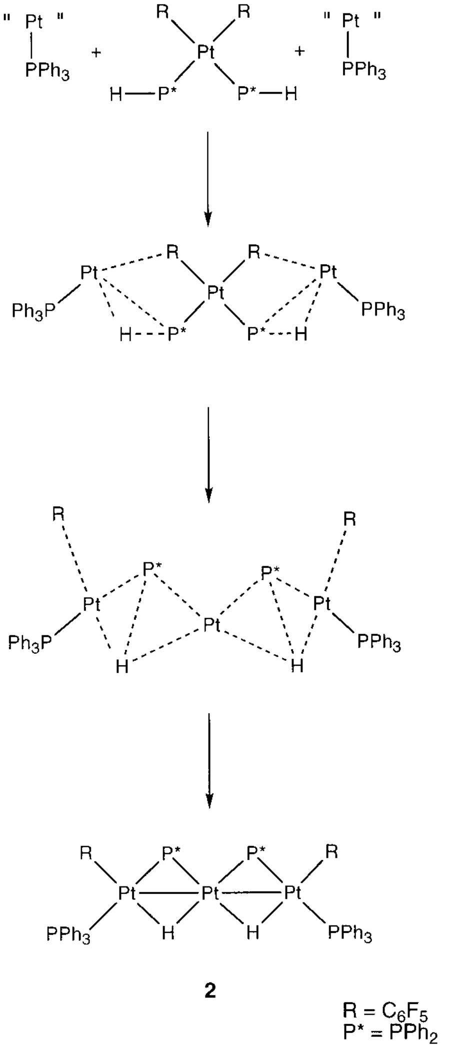

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Pt_2(\mu\text{-}PPh_2)(C_6F_5)(PPh_3)_3]\cdot{}^1/_2CH_3C_6H_5$ ($3\cdot{}^1/_2CH_3C_6H_5$)

Pt(1)−P(1)	2.262(2)	Pt(2)−C(1)	2.098(8)
Pt(1)−Pt(2)	2.7813(7)	Pt(1)−P(4)	2.311(2)
Pt(2)−P(2)	2.260(3)	Pt(2)−P(1)	2.223(2)
Pt(1)−P(3)	2.286(3)		
P(1)−Pt(1)−P(3)	103.21(9)	P(1)−Pt(1)−P(4)	150.47(9)
P(3)−Pt(1)−P(4)	105.09(10)	P(1)−Pt(1)−Pt(2)	51.04(6)
P(3)−Pt(1)−Pt(2)	154.20(7)	P(4)−Pt(1)−Pt(2)	100.19(7)
C(1)−Pt(2)−P(1)	160.8(3)	C(1)−Pt(2)−P(2)	93.0(3)
P(1)−Pt(2)−P(2)	106.00(9)	C(1)−Pt(2)−Pt(1)	108.5(3)
P(1)−Pt(2)−Pt(1)	52.31(6)	P(2)−Pt(2)−Pt(1)	157.87(7)
Pt(2)−P(1)−Pt(1)	76.65(7)		

confirms the existence of the expected intermetallic bond. The environment of the platinum atoms deviates strongly from square planar. Thus, the angles around platinum are as follows: around Pt(1), P(1)−Pt(1)−P(3) = 103.21(9)°, P(3)−Pt(1)−P(4) = 105.09(10)°, and P(1)−Pt(1)−P(4) = 150.47(9)°; around Pt(2), P(1)−Pt(2)−P(2) = 106.00(9)°, P(2)−Pt(2)−C(1) = 93.0(3)°, and P(1)−Pt(2)−C(1) = 160.8(3)°. These values are likely due to the steric effects introduced by the presence of several bulky PPh_3 ligands around the platinum atoms and the absence of a second bridging ligand. As for complex **2**, the Pt(1)−P(1)−Pt(2) angle has a small value, 76.65(7)°, in agreement with the existence of a Pt−Pt bond.

Complex **3** contains one phosphido ligand and only one C_6F_5 group and may be the result of two oxidative additions of P−H bonds to the Pt(0) derivative and reductive elimination of C_6F_5H. The total valence electron count of 30 is consistent with the presence of a platinum−platinum single bond, as confirmed by the X-ray study. Dinuclear cationic complexes of Pd(I) of the type $[Pd_2(\mu\text{-}PR_2)(PR'_3)_2LL']^+$ in which the two metal atoms are linked by both a metal−metal bond and a single PR_2 bridging ligand and in which a nearly linear P−Pd−Pd−P arrangement is present have been described.[15] The syntheses of these complexes is achieved by substitution processes from dinuclear phosphido derivatives of Pd(I). The analogous complexes of Pt(I) have not been described.

The stoichiometry of **3**, which contains three PPh_3 ligands, suggests that other compounds are formed in the reaction. The ^{19}F and ^{31}P NMR spectra of the solid obtained from mother liquors show that it contains a mixture of products in which the starting material *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$, $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ (**3**), $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]$ (**4**), and $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)_2Pt(H)(PPh_3)]$ (**5**) (see below) can be identified.

The IR spectrum of **3** shows one absorption in the X-sensitive region of the C_6F_5 group. The absorption of the pentafluorophenyl group, which is usually located at ca. 950 cm^{-1}, is shifted toward lower wavenumber, 945 cm^{-1}, relative to its position in the platinum(II) starting material, 951 cm^{-1}, as expected, due to the decrease of the formal oxidation state of the metal center.[9] The ^{19}F NMR spectrum shows three signals in a 2:2:1 intensity ratio due to *o*-F, *m*-F, and *p*-F atoms, respectively. The ^{31}P NMR spectrum of **3** shows four signals due to the four inequivalent P atoms and is the result of the superposition of four subspectra, arising from the four different isotopomeric combinations of platinum nuclei having different nuclear spins (Pt/Pt 43.9%, $^{195}Pt/Pt$ 22.3%, $Pt/^{195}Pt$ 22.3%, and $^{195}Pt/^{195}Pt$ 11.4%). The signal due to the PPh_2 ligand, P(1), appears at low field, 150.8 ppm, as can be expected[13] for a PPh_2 ligand bridging two platinum atoms joined by a metal−metal bond. The signal appears as a broad doublet due to the coupling with the P(4) atom of the PPh_3 ligand in a trans position ($^2J_{P(1),P(4)} = 232$ Hz) and to poorly resolved coupling with P(2) or P(3). The signal due to P(4) appears at 31.8 ppm as a doublet (232 Hz). The resonances due to the PPh_3 ligands cis to the PPh_2 group, P(2) and P(3), show similar chemical shift signals and can be analyzed as an AB spin system from which values of $\delta(P_A)$ (17.3 ppm), $\delta(P_B)$ (23.1 ppm), and J_{AB} (199 Hz) can be calculated. The $^3J_{P(2),P(3)}$ value, 199 Hz, is in the range found for $^3J_{P,P}$ in dinuclear palladium(I)[15b−d] or platinum(I)[16] complexes which have a linear P−M−M−P arrangement. Moreover, signals due to P_A appear as doublets (25 Hz) due to coupling with P(1). The assignment of P_A to P(2) or P(3) cannot be made unambiguously. All signals show platinum satellites, from which the values of $J_{Pt,P}$ can be extracted (see the Experimental Section). It is noteworthy that in complex **3** the Pt(1)−P(4) distance (2.311(2) Å) is the longest while the value of the coupling constant between Pt(1) and P(4) is the highest (3443 Hz). Moreover, the signal of P(1) shows that $^1J_{Pt(1),P(1)}$ is nearly equal to $^1J_{Pt(2),P(1)}$ while the trans groups $P(4)Ph_3$ and C_6F_5, respectively, are different, as are the two Pt−P(1) distances, 2.262(2) and 2.223(2) Å. As we have shown previously,[13] it is necessary to be cautious about the structural information which can be deduced from $^1J_{Pt,P}$ values.

Reaction of *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ with $[Pt(C_7H_{10})_3]$ and PPh_3 in a 1:1:3 Molar Ratio. To try a more rational synthesis of **3**, we carried out the reaction in the presence of 3 equiv of PPh_3. In this process a very small amount of an insoluble red solid, not containing C_6F_5, was crystallized and identified by its ^{31}P NMR spectrum as the dinuclear platinum(I) complex $[Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$.[17] Complex **3** was isolated from the solution, although the yield was not much better (22%). From the mother liquors a complex mixture of products was obtained. The ^{19}F and ^{31}P NMR spectra indicate that *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$, **3**, and **5** are present in the mixture.

Syntheses of $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ (3), $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]$ (4), and $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)_2Pt(H)(PPh_3)]$ (5). Complex **3** contains only one PPh_2 bridging group, and it does not contain any PPh_2H ligand; therefore, in order to improve the yield of **3**, we carried out the reaction of a

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[15] (a) Leoni, P.; Pasquali, M.; Sommovigo, M.; Laschi, F.; Zanello, P.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1993**, *12*, 1702. (b) Leoni. P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1996**, *15*, 2047. (c) Leoni, P.; Pieri, G.; Pasquali, M. *J. Chem. Soc., Dalton Trans.* **1998**, 657. (d) Leoni, P.; Papucci, S.; Pasquali, M. *Inorg. Chim. Acta* **1999**, *284*, 246. (e) Leoni, P.; Pasquali, M.; Sommovigo, M.; Laschi, F.; Zanello, P.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1994**, *13*, 4017.

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toluene solution of *cis*-[$Pt(C_6F_5)_2(thf)_2$] and PPh_2H (molar ratio 1:1) with a toluene solution of [$Pt(C_7H_{10})_3$] and PPh_3 (1:3 molar ratio). Complex **3** was obtained in slightly better yield (37%).

As we have noted before, in the reactions that afford **3** a mixture of products is also obtained in which complexes **4** and **5** can be identified. Both complexes can be obtained by reasonable synthetic routes from complexes **1** and **3**, respectively. When PPh_3 is added to a solution of **1** in toluene, substitution of the PPh_2H ligand takes place and the dinuclear complex [$(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2$] (**4**) is obtained. As expected, the IR spectrum of **4** shows two absorptions of equal intensity in the 800 cm^{-1} region (due to the X-sensitive mode[9] of the C_6F_5 groups). The ^1H NMR spectrum shows a signal at −6.5 ppm, due to the hydride ligand, as a broad doublet, with splitting (80 Hz) due to the phosphorus atom of the PPh_3 group trans to the hydride ligand (P(3)). The signal shows platinum satellites from which two values of $^1J_{Pt,H}$ can be extracted, 520 and 412 Hz, in the range found for bridging hydrides. The ^{19}F and ^{31}P NMR spectra of **4** are analogous to those for complex **1**, and all data are given in the Experimental Section. Aiming to try a more direct synthesis of **4**, we prepared the mononuclear platinum(II) derivative *cis*-[$Pt(C_6F_5)_2(PPh_2H)(PPh_3)$] in order to study its reaction with [$Pt(C_7H_{10})_3$] and PPh_3. However, when *cis*-[$Pt(C_6F_5)_2(PPh_2H)(PPh_3)$] is added to toluene solutions of [$Pt(C_7H_{10})_3$] and PPh_3 in 1:1:1 molar ratio under the same reaction conditions (20 h at room temperature), complex **4** is not obtained and the starting material *cis*-[$Pt(C_6F_5)_2(PPh_2H)(PPh_3)$] is recovered from solution.

With the aim of establishing whether the dinuclear platinum(I) complex **3** is obtained from the dinuclear platinum(II) complex **4**, which contains both phosphido and hydride ligands, we carried out the reaction of complex **1** with 3 equiv of PPh_3. The solid obtained from the solution does not contain the diplatinum(I) complex **3** (by NMR spectroscopy), thus indicating that complex **3** is not formed from **1** (or **4**) through a reductive elimination of C_6F_5H and addition of PPh_3.

When PPh_2H is added to a solution of the platinum(I) derivative **3**, the dinuclear Pt(II) complex [$(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)_2Pt(H)(PPh_3)$] (**5**), which contains one terminal hydride and two PPh_2 bridging ligands, can be isolated.

The structure of **5** was established by a X-ray diffraction study (see Figure 3). Selected bond distances and angles are listed in Table 3. Compound **5** is a dinuclear Pt(II) complex in which the platinum centers are bridged by phosphido ligands and the two terminal PPh_3 ligands are mutually transoid. The Pt···Pt distance is 3.498(1) Å, which precludes any intermetallic bond, as expected for a total valence electron count skeleton of 32. In this case, it has been possible to locate the hydride ligand by using the program HYDEX[18] and, subsequently, to refine its position against the X-ray data. The square-planar environments of Pt(1) and Pt(2) are slightly distorted, since, as observed in other polynuclear Pt(II) complexes with no metal−metal bonds and diphenylphosphido bridging ligands, the P(1)−Pt(1)−P(2) and P(1)−Pt(2)−P(2) angles are slightly more acute (75.50(8) and 75.62(8)°, respectively) than the ideal. In accordance with this, the Pt(1)−P(1)−Pt(2) and Pt(1)−P(2)−Pt(2) angles are larger (97.55(9) and 95.77(8)°, respectively) than for **2** and **3** (see Tables 1 and 2), in which Pt−Pt bonds are present. Another substantial difference between complexes **2** and **3** and complex **5** is that, whereas the former are basically planar, **5** has a folded core (Figure 3b), with the dihedral angle between the coordination planes of the Pt atoms being 136.2°.

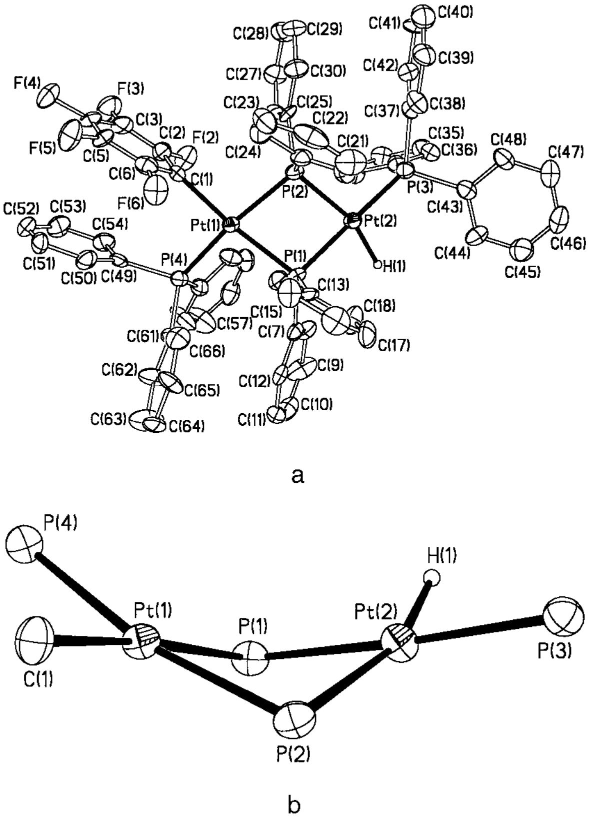

Figure 3. (a) Structure of the complex [$Pt_2H(C_6F_5)(\mu\text{-}PPh_2)_2(PPh_3)_2$] (**5**). Thermal ellipsoids are drawn at the 50% probability level. (b) Core of complex **5** showing its bent disposition.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [$Pt_2H(C_6F_5)(\mu\text{-}PPh_2)_2(PPh_3)_2$] (5)

Pt(1)−C(1)	2.073(9)	Pt(2)−P(3)	2.291(3)
Pt(1)−P(2)	2.352(2)	Pt(2)−H(1)	1.71(9)
Pt(2)−P(2)	2.364(2)	Pt(1)−P(1)	2.334(2)
Pt(1)−P(4)	2.326(2)	Pt(2)−P(1)	2.316(2)
C(1)−Pt(1)−P(4)	88.7(2)	C(1)−Pt(1)−P(1)	172.5(2)
P(4)−Pt(1)−P(1)	98.54(8)	C(1)−Pt(1)−P(2)	97.7(2)
P(4)−Pt(1)−P(2)	167.99(8)	P(1)−Pt(1)−P(2)	75.50(8)
P(3)−Pt(2)−P(1)	176.92(8)	P(3)−Pt(2)−P(2)	106.17(8)
P(1)−Pt(2)−P(2)	75.62(8)	P(1)−Pt(2)−H(1)	89(3)
P(2)−Pt(2)−H(1)	162(3)	P(3)−Pt(2)−H(1)	89(3)
Pt(2)−P(1)−Pt(1)	97.55(9)	Pt(1)−P(2)−Pt(2)	95.77(8)

The IR spectrum of **5** shows one absorption at 2038 cm^{-1}, in accord with the presence of a terminal Pt−H moiety.[8d,10a] Usually the ν(Pt−H) stretching mode for this type of hydride is in the range 1970−2250 cm^{-1}, whereas the ν(P−H) stretching mode in coordinated PPh_2H complexes appears at higher wavenumber (2329 cm^{-1} for *cis*-[$Pt(C_6F_5)_2(PPh_2H)_2$][5] and 2320 cm^{-1} for **1**). There is one absorption in the 800 cm^{-1} region due to the X-sensitive mode of the C_6F_5 group. The corresponding absorption at 945 cm^{-1} in the starting material **3** is shifted to higher wavenumber in **5**, 952 cm^{-1}, in

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(18) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

agreement with the increase of the formal oxidation state of the platinum centers.[9]

The ^{1}H NMR spectrum of **5** shows a signal centered at −5.6 ppm due to the hydride ligand. The signal is a doublet of broad multiplets due to the coupling with the P(2) of the PPh_2 group trans to the hydride ligand and to the two P atoms cis to the hydride. When the spectrum is measured with phosphorus decoupling in the PPh_3 region, the signal of the hydride ligand appears as a doublet of doublets, 148 and 16 Hz, with the large splitting due to P(2) and the smaller one due to the P atom of the cis μ-PPh_2 group, P(1). When the spectrum is measured with phosphorus decoupling in the diphenylphosphide region, the coupling with the PPh_3 ligand, P(3), is not well-resolved and the signal appears as a broad singlet. In all cases the signal shows platinum satellites from which the $^1J_{\mathrm{Pt,H}}$ value can be calculated, 1038 Hz. The value of coupling constant between hydride ligand and the trans P atom, $^2J_{\mathrm{P(2),H}} = 148$ Hz, as well as the $^1J_{\mathrm{Pt,H}}$ value are larger than those found for $^2J_{\mathrm{P(trans\ to\ H),H}}$ and $^1J_{\mathrm{Pt,H}}$ in complexes **1**, **2**, and **4**, in agreement with the presence of a terminal hydride ligand in **5**.[3c,8d,12] The ^{19}F NMR spectrum is similar to that for **3**, as expected.

The ^{31}P NMR spectrum of **5** shows signals in two very different regions. The signals due to the two inequivalent PPh_3 groups appear centered at 21.3 and 31.1 ppm. Both are doublets (297 and 292 Hz, respectively) by coupling with the *trans*-PPh_2 group and show platinum satellites from which the $^1J_{\mathrm{Pt,P}}$ values can be extracted, 2175 and 2394 Hz, respectively. The signals due to the two inequivalent diphenylphosphido ligands are both in the −105 ppm region and show a very complex pattern. Each of these two P atoms is coupled with one *trans*-PPh_3 ligand. For a structure, such as **5**, in which the two PPh_2 groups in a dinuclear complex are inequivalent, the coupling between the two cis P atoms is large.[19] Moreover, the two platinum atoms in **5** are inequivalent, so that each signal shows platinum satellites with different splittings. All these couplings make a very complex pattern of signals and prevent a reliable assignment. The chemical shift is in the region expected for two PPh_2 groups that are acting as bridging ligands between two platinum centers not joined by a metal−metal bond.[5,20]

The formation of **5** from complex **3** (a Pt(I)−Pt(I) derivative) is formally the result of the oxidative addition of PPh_2H to the dinuclear compound **3**, with concomitant elimination of PPh_3. Some dinuclear cationic phosphido complexes of Pd(I) with coordinated secondary phosphine are known, $[Pd_2(\mu\text{-}PBu^t_2)L_2(PR_2H)_2]^+$ (L = CO, R = Bu^t;[15a] L = PR_2H, R = Cy[15e]). Usually these complexes do not undergo oxidative addition of a P−H bond to a palladium center to afford palladium(II) complexes. In our case the P−H addition may be favored by both the neutrality of the intermediate and the higher stability of the Pt−H bond versus Pd−H.

Complex **5** contains both a C_6F_5 and a hydride ligand. To study the stability of this complex, a solution of complex **5** in toluene was heated to 40 °C for 3 h. No changes were detected in the solution, and complex **5** was recovered. Under these conditions complex **5** does not eliminate C_6F_5H to afford the well-known dinuclear platinum(I) compound $[Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$. Similarly, $[Pt_2(\mu\text{-}PBu^t_2)_2(H)_2(PBu^t_2H)_2]$ does not eliminate hydrogen to yield $[Pt_2(\mu\text{-}PBu^t_2)_2(PBu^t_2H)_2]$.[8d,10b]

Reaction of 3 with CO. To establish that the PPh_3 ligand trans to PPh_2 in the neutral Pt(I) derivative **3** may be easily substituted, we studied the reaction of **3** with CO. When CO is bubbled through an orange solution of **3** in CH_2Cl_2, the solution fades to yellow. After addition of *n*-hexane with further bubbling of CO, the yellow monocarbonyl derivative $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)Pt(PPh_3)(CO)]$ (**6**) is obtained. Nevertheless, if the yellow CH_2Cl_2 solution is evaporated under vacuum, the solution turns orange again and only the starting material can be crystallized, thus indicating the reversibility of the substitution process. The IR spectrum of **6** shows a strong absorption at 2039 cm^{-1}, due to ν(CO). This value is similar to those observed for other platinum(I) carbonyl derivatives, and it denotes some degree of π-back-donation in the Pt^I−CO bond. The absorptions due to the C_6F_5 group are analogous to those found for this group in complex **3**. The ^{19}F NMR spectrum of **6** shows three signals in a 2:2:1 intensity ratio, as expected, and the ^{31}P NMR spectrum displays three signals due to the three inequivalent P atoms. The signal due to the PPh_2 group (single bridging ligand between two platinum atoms joined by a metal−metal bond) appears at 136.5 ppm as a broad singlet. The signals due to the P atoms of the two inequivalent PPh_3 ligands appear at 27.2 and 18.9 ppm as two broad doublets, the splitting being due to the coupling of both P atoms ($^3J_{\mathrm{P,P}} = 119$ Hz). The three signals show platinum satellites, and two values of $^1J_{\mathrm{Pt,P}}$ for the PPh_2 signal and one value of $^1J_{\mathrm{Pt,P}}$ for each PPh_3 signal can be calculated. Moreover, in the signals due to the PPh_3 ligands, a pair of close platinum satellites are observed for each, so that the values of $^2J_{\mathrm{Pt,P}}$ can be extracted. The presence of a platinum−platinum bond in **6** (total valence electron count 30) is supported by the δ(P) value of the PPh_2 group (136.5 ppm), by the coupling observed between the two P atoms of the PPh_3 ligands ($^3J_{\mathrm{P,P}} =$ 119 Hz), and by the observed values of $^2J_{\mathrm{Pt,P}}$, 262 and 363 Hz.

Concluding Remarks

The reaction that affords **1** from *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ with $[Pt(C_7H_{10})_3]$ in the presence of 1 equiv of PPh_3 can be viewed as an oxidative addition of one P−H bond to a platinum(0) center, giving rise to a dinuclear derivative containing both a phosphido and a hydrido ligand, and a migration of the PPh_2H ligand from one platinum center to the other. The trinuclear complex **2** is formed as result of a double oxidative addition of *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ to 2 equiv of the zerovalent platinum derivative (Scheme 2). Nevertheless, the reaction with 2 or 3 equiv of PPh_3 seems to be more complex and it could be the result of several reaction paths. (a) The initial formation of complex **1** and its reaction with one PPh_3 ligand occurs, giving rise to complex **4**. (b) PPh_2H adds oxidatively to the dinuclear Pt(I) derivative **3**, leading to formation of

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[19] Falvello, L. R.; Forniés, J.; Fortuño, C.; Martínez, F. *Inorg. Chem.* **1994**, *33*, 6246.
[20] Alonso, E.; Forniés, J.; Fortuño, C.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3777.

complex **5**. (c) A reaction path of uncertain type leads to **3**. The oxidative addition of a P−H bond (of the mononuclear Pt(II) starting material) to the platinum(0) center, giving rise to the "$(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt$" fragment, as in the formation of **1**, can be ruled out, since complex **4** does not react with PPh_3 to give **3**. (d) The dinuclear platinum(I) complex $[Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$ forms at room temperature but does not result from C_6F_5H elimination from the dinuclear platinum(II) complex **5**. It is noteworthy that $[Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$ has been reported as a product of thermolysis of platinum(0) complexes, such as $[Pt(PPh_3)_4]$ in benzene and $[Pt(C_2H_4)(PPh_3)_2]$ in acetone, and that the conditions required to form it are critical.[17,21]

Experimental Section

General Data. All reactions were carried out under a nitrogen atmosphere. Literature methods were used to prepare the starting complexes *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$[5] and $[Pt(C_7H_{10})_3]$.[22] C and H 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 $SiMe_4$, $CFCl_3$, and 85% H_3PO_4 as external references for ^1H, ^{19}F, and ^{31}P, respectively.

Reaction of *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ with $[Pt(C_7H_{10})_3]$ and PPh_3. (a) 1:1:1 Molar Ratio. To a toluene solution (10 mL) of PPh_3 (0.117 g, 0.446 mmol) was added $[Pt(C_7H_{10})_3]$ (0.213 g, 0.446 mmol). After 10 min of stirring, *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ (0.402 g, 0.446 mmol) was added and the solution was stirred for 20 h at room temperature. The resulting solution was evaporated almost to dryness, and the residue was treated with a mixture of hexane (20 mL) and Et_2O (10 mL). The very pale yellow solid **1** crystallized, which was filtered off and washed with 2 × 0.5 mL of cold Et_2O (0.220 g, 36%). Anal. Found (calcd) for $C_{54}F_{10}H_{37}P_3Pt_2$: C, 47.45 (47.7); H, 2.4 (2.7). IR (Nujol): 790, 780 cm^{-1} (X-sensitive,[9] C_6F_5); 2320 cm^{-1} (ν(P−H)). ^1H NMR (298 K, $CDCl_3$, 300 MHz; δ): 6.8 (PPh_2H, $^1J_{P(3),H} = 360$ Hz, $^3J_{P(1),H} = 9$ Hz, $^2J_{Pt(2),H} = 41$ Hz), −6.0 (μ-H, $^2J_{P(3),H} = 81$ Hz, $^1J_{Pt(1),H} = 430$ Hz, $^1J_{Pt(2),H} = 537$ Hz) ppm. ^{19}F NMR (298 K, $CDCl_3$, 282.4 MHz; δ): −116.9 (2 *o*-F, $^3J_{Pt,F} = 281.5$ Hz), −117.9 (2 *o*-F, $^3J_{Pt,F} = 405.8$ Hz), −162.8 (1 *p*-F), −164.3 (1 *p*-F), −164.8 (2 *m*-F), −165.7 (2 *m*-F) ppm. ^{31}P NMR (298 K, $CDCl_3$, 121.4 MHz; δ): 111.5 (d, P(1), $^2J_{P(1),P(2)} = 305$ Hz, $^1J_{Pt(1,2),P(1)} = 1734$, 2068 Hz), 18.1 (d, P(2), $^2J_{P(1),P(2)} = 305$ Hz, $^1J_{Pt(2),P(2)} = 2636$ Hz), −8.0 (s, P(3), $^1J_{Pt(2),P(3)} = 3996$ Hz, $^2J_{Pt(1),P(3)} = 207$ Hz) ppm. The mother liquors of **1** were evaporated to dryness, and the residue was treated with a mixture of acetone (8 mL) and *i*-PrOH (2 mL) and left in the freezer for 3 days. The very pale yellow solid **2** crystallized, which was filtered off and washed with 4 × 0.5 mL of acetone (0.084 g, 21% based on $[Pt(C_7H_{10})_3]$). Anal. Found (calcd) for $C_{72}F_{10}H_{52}P_4Pt_3$: C, 47.9 (47.6); H, 2.8 (2.9). IR (Nujol): 793, 784 cm^{-1} (X-sensitive,[9] C_6F_5). ^1H NMR (298 K, $CDCl_3$, 300 MHz; δ): −5.6 (μ-H, $^2J_{P(trans),H} = 45$ Hz, $^1J_{Pt,H} = 442$ Hz, $^1J_{Pt,H} = 508$ Hz) ppm. ^{19}F NMR (298 K, $CDCl_3$, 282.4 MHz; δ): −117.6 (2 *o*-F, $^3J_{Pt,F} = 376.1$ Hz), −164.6 (1 *p*-F), −165.6 (2 *m*-F) ppm. ^{31}P NMR (298 K, $CDCl_3$, 121.4 MHz; δ): 106.8 (sharp d, PPh_2, $^2J_{P,P(trans)} = 308$ Hz, $^1J_{Pt,P} = 3195$ and 1918 Hz, $^2J_{Pt,P} = 132$ Hz), 19.9 (sharp d, PPh_3, $^2J_{P,P(trans)} = 308$ Hz, $^1J_{Pt,P} = 2708$ Hz, $^2J_{Pt,P} = 63$ Hz) ppm.

(b) 1:1:2 Molar Ratio. To a toluene solution (8 mL) of PPh_3 (0.087 g, 0.332 mmol) was added $[Pt(C_7H_{10})_3]$ (0.079 g, 0.165 mmol). After 10 min of stirring, *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ (0.149 g, 0.165 mmol) was added and the solution was stirred for 20 h at room temperature. The solution was evaporated to ca. 1 mL, and Et_2O (6 mL) was added. The resulting yellow solid **3** was filtered off and washed with 3 × 0.5 mL of Et_2O (0.050 g, 20%). Anal. Found (calcd) for $C_{72}F_5H_{55}P_4Pt_2$: C, 56.3 (56.55); H, 3.8 (3.6). IR (Nujol, C_6F_5): 945 cm^{-1}; 770 cm^{-1} (X-sensitive[9]). ^{19}F NMR (298 K, $CDCl_3$, 282.4 MHz; δ): −112.2 (2 *o*-F, $^3J_{Pt,F} = 367.1$ Hz), −165.8 (2 *m*-F), −168.7 (1 *p*-F) ppm. ^{31}P NMR (298 K, $CDCl_3$, 121.4 MHz; δ): 150.8 (broad d, P(1), $^2J_{P(1),P(4)} = 232$ Hz, $^1J_{Pt(1),P(1)} \approx {}^1J_{Pt(2),P(1)} = 2767$ Hz), 31.8 (d, P(4), $^2J_{P(1),P(4)} = 232$ Hz, $^1J_{Pt(1),P(4)} = 3443$ Hz), 17.3 (P_A, $^3J_{P(2),P(3)} = 199$ Hz, $^2J_{P(1),P(A)} = 25$ Hz, $^1J_{Pt,P(A)} = 3240$ Hz, $^2J_{Pt,P(A)} = 449$ Hz), 23.1 (P_B, $^3J_{P(2),P(3)} = 199$ Hz, $^1J_{Pt,P(B)} = 2997$ Hz, $^2J_{Pt,P(B)} = 605$ Hz) ppm. The filtrate of **3** was evaporated to dryness, and the residue was washed with hexane. This yellow solid is a mixture of complexes in which the starting material *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$, complex **3**, complex **4**, and complex **5** can be detected (NMR spectroscopy).

(c) 1:1:3 Molar Ratio. To a toluene solution (10 mL) of PPh_3 (0.130 g, 0.496 mmol) was added $[Pt(C_7H_{10})_3]$ (0.079 g, 0.165 mmol). After 10 min of stirring, *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ (0.149 g, 0.165 mmol) was added and the solution was stirred at room temperature for 22 h. A red solid was filtered off and washed with 3 × 0.5 mL of toluene (0.014 g). This compound was identified (^{31}P NMR, CD_2Cl_2) as $[Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$.[17] The toluene solution was evaporated to ca. 1 mL, and Et_2O (10 mL) was added. The yellow solid **3** thus obtained was filtered off and washed with 3 × 0.5 mL of Et_2O (0.056 g, 22%). The filtrate of **3** was evaporated to ca. 1 mL, hexane (10 mL) was added, and the yellow solid thus obtained (0.070 g) was filtered off and washed with hexane (3 mL). This yellow solid is (NMR spectroscopy) essentially the starting material *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2$, together with other complexes, among which complex **3** and complex **5** can be identified.

Preparation of $[\{(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)(\mu\text{-}H)\}_2Pt]$ (2). To a toluene solution (10 mL) of PPh_3 (0.058 g, 0.220 mmol) and $[Pt(C_7H_{10})_3]$ (0.105 g, 0.220 mmol) was added *cis*-$[Pt(C_6F_5)_2(PPh_2H)_2]$ (0.099 g, 0.110 mmol). After 20 h of stirring at room temperature the solution was evaporated to dryness, acetone (3 mL) was added, and a very pale yellow solid crystallized. **3** was filtered off and washed with 3 × 1 mL of acetone (0.097 g, 48%).

Preparation of $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ (3). To a toluene solution (5 mL) of PPh_3 (0.176 g, 0.671 mmol) and $[Pt(C_7H_{10})_3]$ (0.107 g, 0.224 mmol) was added a solution of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.150 g, 0.223 mmol) and PPh_2H (39 μL, 0.224 mmol) in toluene (10 mL). After 23 h of stirring at room temperature the solution was evaporated almost to dryness. Et_2O (5 mL) was added, and the yellow solid **3** was filtered off and washed with 3 × 1 mL of Et_2O (0.125 g, 37%).

Preparation of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]$ (4). To a toluene (5 mL) solution of **1** (0.060 g, 0.044 mmol) was added PPh_3 (0.012 g, 0.046 mmol). The solution was stirred for 1 h and evaporated to dryness. The oily residue was treated with hexane (10 mL), and by stirring a pale yellow solid was formed, which was filtered off and washed with 2 mL of hexane (0.039 g, 62%). The solid thus obtained is complex **4** together with a minor amount of starting material. Pure sample of **4** is obtained as pale yellow crystals by diffusion of hexane into CH_2Cl_2 solutions. Anal. Found (calcd) for $C_{60}F_{10}H_{41}P_3Pt_2$: C, 50.4 (50.2); H, 2.7 (2.9). IR (Nujol): 791, 782 cm^{-1} (X-sensitive, C_6F_5). ^1H NMR (298 K, $CDCl_3$, 300 MHz; δ): −6.5 ($^2J_{P(3),H} = 80$ Hz, $^1J_{Pt(1),H} = 412$ Hz, $^1J_{Pt(2),H} = 520$ Hz) ppm. ^{19}F NMR (298 K, $CDCl_3$, 282.4 MHz; δ): −117.1 (2 *o*-F, $^3J_{Pt,F} = 283.7$ Hz), −118.0 (2 *o*-F, $^3J_{Pt,F} = 398.2$ Hz), −163.7 (1 *p*-F), −164.4 (1 *p*-F), −164.8 (2 *m*-F), −165.6 (2 *m*-F) ppm. ^{31}P NMR (298 K, $CDCl_3$, 121.4 MHz; δ): 108.1 (d, P(1), $^2J_{P(1),P(2)} = 294$ Hz, $^1J_{Pt(1,2),P(1)} = 1863$, 2022 Hz), 20.2 (s, P(3), $^1J_{Pt(2),P(3)} = 4214$ Hz,

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(22) Crascall, L. E.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 126.

Table 4. Crystal Data and Structure Refinement Details for $[\{(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)(\mu\text{-}H)\}_2Pt]\cdot C_6H_{12}\cdot{}^3/_8C_6H_{14}$ ($2\cdot C_6H_{12}\cdot{}^3/_8C_6H_{14}$), $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)Pt(PPh_3)_2]\cdot{}^1/_2C_7H_8$ ($3\cdot{}^1/_2C_7H_8$), and $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)_2Pt(H)(PPh_3)]$ (5)

	$2\cdot C_6H_{12}\cdot{}^3/_8C_6H_{14}$	$3\cdot{}^1/_2C_7H_8$	5
empirical formula	$C_{72}H_{52}F_{10}P_4Pt_3\cdot C_6H_{12}\cdot{}^3/_8C_6H_{14}$	$C_{72}H_{55}F_5P_4Pt_2\cdot{}^1/_2C_7H_8$	$C_{66}H_{51}F_5P_4Pt_2$
unit cell dimens			
a (Å)	20.0988(8)	13.088(2)	21.606(2)
b (Å)	20.6592(8)	14.003(2)	13.364(3)
c (Å)	18.5612(7)	19.100(3)	21.930(4)
α (deg)	90	92.700(12)	90
β (deg)	99.7940(10)	104.261(11)	118.238(9)
γ (deg)	90	107.604(11)	90
V (Å^3); Z	7594.8(5); 4	3205.7(8); 2	5578(2); 4
wavelength (Å)	0.710 73	0.710 73	0.710 73
temp (K)	173(1)	293(1)	173(1)
radiation	graphite-monochromated Mo Kα		
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
crystal dimensions (mm)	0.16 × 0.13 × 0.10	0.50 × 0.40 × 0.10	0.50 × 0.40 × 0.30
abs coeff (mm^{-1})	5.663	4.517	5.183
transmission factors	1.956, 1.222	0.932, 0.435	0.791, 0.358
abs cor	30 086 equiv rflns	ψ scans	1940 equiv rflns
diffractometer	Bruker SMART	Siemens P3m	Siemens SMART
2θ range for data collecn (deg)	2.1−50.0 ($\pm h$, $\pm k$, $\pm l$)	3.0−50.0 ($\pm h$, $\pm k$, $+l$)	3.7−46.5 ($\pm h$, $\pm k$, $\pm l$)
no. of rflns collected	42 936	11 524	22 903
no. of indep rflns	13 398 (R(int) = 0.0372)	11 014 (R(int) = 0.0370)	7983 (R(int) = 0.0878)
refinement method	full-matrix least squares on F^2		
goodness of fit on F^2	1.016	1.007	1.320
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0293, wR2 = 0.0692	R1 = 0.0480, wR2 = 0.1270	R1 = 0.0514, wR2 = 0.0979
R indices (all data)	R1 = 0.0480, wR2 = 0.0752	R1 = 0.0787, wR2 = 0.0787	R1 = 0.0716, wR2 = 0.1094

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

${}^2J_{Pt(1),P(3)} = 225$ Hz), 18.6 (d, P(2), ${}^2J_{P(1),P(2)} = 294$ Hz, ${}^1J_{Pt(2),P(2)} = 2568$ Hz, ${}^2J_{Pt(1),P(2)} = 32$ Hz) ppm.

$[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)_2PtH(PPh_3)]$ (5). To a toluene (15 mL) solution of **3** (0.100 g, 0.065 mmol) was added PPh_2H (13.5 μL, 0.077 mmol). The solution was stirred at room temperature for 20 h and then evaporated almost to dryness. Et_2O (6 mL) was added, and the yellow solid **5** was filtered off and washed with 3 × 1 mL of Et_2O (0.030 g, 32%). Anal. Found (calcd) for $C_{66}F_5H_{51}P_4Pt_2$: C, 54.3 (54.55); H, 3.3 (3.5). IR (Nujol): 952 cm^{-1}; 781 cm^{-1} (X-sensitive, C_6F_5); 2038 cm^{-1} (ν(Pt−H)). ^{1}H NMR (298 K, $CDCl_3$, 300 MHz; δ): −5.6 (${}^2J_{P(2),H} = 148$ Hz, ${}^2J_{P(1),H} = 16$ Hz, ${}^1J_{Pt(2),H} = 1038$ Hz) ppm. ^{19}F NMR (298 K, $CDCl_3$, 282.4 MHz; δ): −115.8 (2 o-F, ${}^3J_{Pt,F} = 258.9$ Hz), −165.2 (2 m-F), −165.7 (1 p-F) ppm. ^{31}P NMR (298 K, $CDCl_3$, 121.4 MHz; δ): 31.1 (d, P(3) or P(4), ${}^2J_{P(1),P(3)}$ or ${}^2J_{P(2),P(4)} = 292$ Hz, ${}^1J_{Pt,P} = 2394$ Hz), 21.3 (d, P(4) or P(3), ${}^2J_{P(2),P(4)}$ or ${}^2J_{P(1),P(3)} = 297$ Hz, ${}^1J_{Pt,P} = 2175$ Hz), from −95 to −118 (complex signals due to P(1) and P(2) atoms) ppm.

$[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)Pt(PPh_3)(CO)]$ (6). CO was bubbled through a solution of **3** (0.123 g, 0.080 mmol) in CH_2Cl_2 (6 mL) for 10 min. Hexane (10 mL) was added, and the solution was evaporated to ca. 10 mL by bubbling CO. A yellow solid **6** crystallized, which was filtered off and washed with 2 × 1 mL of hexane. Anal. Found (calcd) for $C_{55}F_5H_{40}OP_3Pt_2$: C, 50.8 (51.0); H, 3.25 (3.1). IR (Nujol): 945 cm^{-1}; 776 cm^{-1} (X-sensitive, C_6F_5); 2039 cm^{-1} (ν(C≡O)). ^{19}F NMR (298 K, $CDCl_3$, 282.4 MHz; δ): −115.2 (2 o-F, ${}^3J_{Pt,F} = 362.7$ Hz), −165.7 (1 p-F + 2 m-F) ppm. ^{31}P NMR (298 K, $CDCl_3$, 121.4 MHz; δ): 136.5 (broad s, P(1), ${}^1J_{Pt,P(1)} = 2721$ and 2866 Hz), 27.2 (broad d, P(2) or P(3), ${}^3J_{P(2),P(3)} = 119$ Hz, ${}^1J_{Pt,P} = 3753$ Hz, ${}^2J_{Pt,P} = 262$ Hz), 18.9 (broad d, P(3) or P(2), ${}^3J_{P(2),P(3)} = 119$ Hz, ${}^1J_{Pt,P} = 3113$ Hz, ${}^2J_{Pt,P} = 363$ Hz) ppm.

Crystal Structure Analyses of $[\{(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)(\mu\text{-}H)\}_2Pt]\cdot C_6H_{12}\cdot{}^3/_8C_6H_{14}$ ($2\cdot C_6H_{12}\cdot{}^3/_8C_6H_{14}$), $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)Pt(PPh_3)_2]\cdot{}^1/_2C_7H_8$ ($3\cdot{}^1/_2C_7H_8$), and $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)_2Pt(H)(PPh_3)_2]$ (5). Crystal data and other details of the structure analysis are presented in Table 4. Suitable crystals of **2**, **3**, and **5** were obtained by slow diffusion of petroleum ether (**2**) or n-hexane (**3** and **5**) into a solution of ca. 0.025 g of the complex in toluene (**3**) or in CH_2Cl_2 (**2** and **5**). Crystals were mounted at the end of a glass fiber. For **2**, unit cell dimensions were initially determined from the positions of 267 reflections in 90 intensity frames measured at 0.3° intervals in ω and subsequently refined on the basis of positions of 4932 reflections from the main data set. An absorption correction was applied on the basis of 30 086 symmetry-equivalent reflection intensities. For **3**, unit cell dimensions were determined from 35 centered reflections in the range $15.1 < 2\theta < 28.9°$. An absorption correction was applied on the basis of 420 azimuthal scan data. For **5**, unit cell dimensions were initially determined from the positions of 259 reflections in 90 intensity frames measured at 0.3° intervals in ω and subsequently refined on the basis of positions of 5556 reflections from the main data set. An absorption correction was applied on the basis of 1940 symmetry-equivalent reflection intensities. Lorentz and polarization corrections were applied for all the structures.

The structures were solved by Patterson and Fourier methods. All refinements were carried out using the program SHELXL-93[23] or SHELXL-97.[24] 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 **2**, the asymmetric unit contains three half-molecules of cyclohexane (which were refined with occupancy 1, 0.75 and 0.25) and one half-molecule of n-hexane (refined with occupancy 0.75). The geometric parameters of these solvent molecules were restrained to idealized values. For **3**, in the final stages of the resolution the presence of toluene as crystallization solvent was observed. The toluene molecule lies astride an inversion center, so that only three of the ring carbon atoms are present in the asymmetric unit, the rest being generated by the symmetry operator. The structural parameters in the toluene molecule were restrained using DFIX and FLAT instructions. The attempts to locate the methyl group of the solvent in the Fourier density maps were

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[23] Sheldrick, G. M. SHELXL-93, a Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1993.

[24] Sheldrick, G. M. SHELXL-97, a Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997.

unsuccessful. The presence of toluene in the crystals was confirmed by spectroscopic analysis (^{1}H NMR). To complete the electron density in the structural model, three partial-occupancy methyl carbon atoms were geometrically placed, bonded to the ring carbon atoms present in the asymmetric unit with assigned $^1/_6$ occupancies and constrained bond distances. Finally, all the atoms of the toluene moiety were refined with a common isotropic thermal parameter. One molecule of acetone was refined with full occupancy. No attempts to include in the model the hydrogen atoms of the toluene were made. Full-matrix least-squares refinement of these models against F^2 converged to the final residual indices given in Table 4. Final difference electron density maps showed 11 features above 1 e/Å^3 (maximum/minimum 1.57/−1.05 e/Å^3) with the largest peaks lying closer than 1 Å to the platinum or solvent atoms for **2**, one feature above 1 e/Å^3 (maximum/minimum 1.07/−1.32 e/Å^3) being close to one of the platinum atoms for **3**, and 11 features above 1 e/Å^3 (maximum/minimum 1.57/−1.42 e/Å^3) with the largest peaks lying closer than 1 Å to the platinum atoms for **5**.

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Supporting Information Available: Tables of all atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, all bond distances and bond angles, hydrogen coordinates, and isotropic displacement parameters for the crystal structures and fully labeled figures of complexes **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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