Synthesis and X-ray Crystal Structure of the New Palladium(I) Dimer $[Pd_2(PMe_3)_6][hfac]_2$ and Its Conversion to $[PdMe(PMe_3)_3][hfac]$ via Activation of Phosphorus–Carbon Bonds

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Comproportionation of the palladium(0) compound $Pd(PMe_3)_4$ with the palladium(II) hexafluoroacetylacetonate compound $Pd(hfac)_2$ or $[Pd(hfac)(PMe_3)_2][hfac]$ gives the novel palladium(I) dimer $[Pd_2(PMe_3)_6][hfac]_2$ (**1**). The analogous mixed-metal complex $[PdPt(PMe_3)_6][hfac]_2$ (**2**) can be prepared similarly. The ^1H and ^{31}P NMR spectra are consistent with structures in which the two metal centers are connected by a metal–metal bond and the six terminal PMe_3 ligands complete two mutually perpendicular square-planar coordination environments; the hfac groups are not attached to the metal centers and instead serve as counterions for the $[M_2(PMe_3)_6]^{2+}$ cations. This structure has been established by X-ray crystallography for the dipalladium(I) compound; the cation has 2-fold crystallographic symmetry, and the Pd–Pd distance is 2.598(1) Å. The average Pd–P distances to the equatorial PMe_3 groups cis to the Pd–Pd bond are 2.342(1) Å while the Pd–P distances to the axial PMe_3 groups trans to the Pd–Pd bond are slightly longer at 2.371(1) Å; the lengthening of the axial Pd–P bonds may be ascribable to the larger trans influence of the metal–metal bond. The axial phosphine ligands in **1** can be replaced by treatment with LiCl or NaI in tetrahydrofuran to afford the nonionic dinuclear complexes $Pd_2(PMe_3)_4Cl_2$ and $Pd_2(PMe_3)_4I_2$. Surprisingly, thermolysis of **1** at 100 °C and 10^{-3} Torr yields the palladium(II) methyl complex $[PdMe(PMe_3)_3][hfac]$; the methyl group attached to palladium in this product evidently arises via P–C bond cleavage of a PMe_3 ligand. This result constitutes the first example of the isolation of a metal alkyl complex via P–C bond cleavage of a unidentate alkylphosphine. Analogously, thermolysis of **2** at 140 °C and 10^{-3} Torr yields a mixture of $[PdMe(PMe_3)_3][hfac]$ and the platinum(II) methyl complex $[PtMe(PMe_3)_3][hfac]$. These results are relevant to the incorporation of phosphorus and carbon impurities into metal films grown by metal–organic chemical vapor deposition from PMe_3-containing precursors. Crystal data for **1** at −75 °C: monoclinic, space group $C2/c$, $a = 25.499(6)$ Å, $b = 9.791(2)$ Å, $c = 18.424(5)$ Å, $\beta = 106.85(2)°$, $V = 4402(26)$ Å^3, $Z = 4$, $R_F = 0.032$, $R_{wF} = 0.033$ for 241 variables and 3054 reflections with $I > 2.58\sigma(I)$.

Introduction

In the last few years there has been great interest in the use of metal–organic precursors for the chemical vapor deposition of thin films.[1-3] One of the most attractive features of metal–organic precursors is that they are often considerably more volatile than corresponding inorganic precursors: for example, whereas palladium halides are nonvolatile ($PdCl_2$ decomposes without volatilizing at ca. 500 °C), there are several metal–organic derivatives of palladium that sublime readily in vacuum below 50 °C.[4-7] Of these metal–organic derivatives, several such as diallylpalladium(II)[4] and bis(hexafluoroacetylacetonato)palladium(II)[5] have been shown to be effective precursors for the low-temperature deposition of palladium films.

From a chemical perspective, some of the most interesting CVD processes are those in which film growth occurs via a disproportionation reaction;[8-12] such processes often result in very clean films because deposition occurs without fragmentation of the organic ligands.[13] We became interested in investigating whether this disproportionation method could be extended to the deposition of palladium thin films; such a process would involve, for example, the reaction of a palladium(I) complex to form palladium metal and a palladium(II) byproduct:

$$2Pd^{I} \rightarrow Pd^{0} + Pd^{II}$$

In related chemistry, the deposition of palladium thin films by photoreduction of palladium(I) compounds in the presence of electron acceptors was recently demonstrated.[14]

We now describe the synthesis and characterization of a new palladium(I) compound of stoichiometry "$Pd(hfac)(PMe_3)_3$". Not entirely unexpectedly, this compound actually adopts a dinuclear ionic structure, $[Pd_2(PMe_3)_6][hfac]_2$, in which there is a metal–metal bond. The analogous mixed metal complex $[PdPt(PMe_3)_6][hfac]_2$ can also be made. Thermolysis of the dipalladium(I) complex results in activation of one of the phosphorus–carbon bonds of the PMe_3 ligands to give the mononuclear palladium(II) alkyl complex $[PdMe(PMe_3)_3][hfac]$. The implications of this result relative to the utility of trialkylphosphine compounds as MOCVD precursors are also discussed.

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Results and Discussion

Synthesis and Characterization of $[Pd_2(PMe_3)_6][hfac]_2$. The new palladium(I) compound has been synthesized via a comproportionation reaction involving palladium(0) and palladium(II) starting materials. Interaction of equimolar quantities of $Pd(PMe_3)_4$[15] and $Pd(hfac)_2$[16,17] in diethyl ether gives an olive green precipitate which affords yellow crystals after recrystallization from diethyl ether/dichloromethane. The empirical formula of the product is "$Pd(hfac)(PMe_3)_3$", but in fact we will show below that this compound is dinuclear and ionic: $[Pd_2(PMe_3)_6][hfac]_2$ (**1**).

$$Pd(PMe_3)_4 + Pd(hfac)_2 + 2PMe_3 \rightarrow \underset{\mathbf{1}}{[Pd_2(PMe_3)_6][hfac]_2}$$

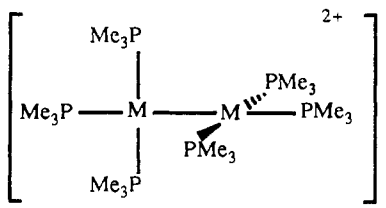
We have also been able to synthesize **1** in high yield by treatment of $Pd(PMe_3)_4$ with the palladium(II) trimethylphosphine complex $[Pd(hfac)(PMe_3)_2][hfac]$ (this new complex can be made by addition of PMe_3 to $Pd(hfac)_2$; see Experimental Section for details):

$$Pd(PMe_3)_4 + [Pd(hfac)(PMe_3)_2][hfac] \rightarrow \underset{\mathbf{1}}{[Pd_2(PMe_3)_6][hfac]_2}$$

The IR spectrum of **1** contains a strong band at 1672 cm^{-1} which can be assigned to the C=O stretches of the ionic hfac counterions; for comparison, the C=O stretch in $Pd(hfac)_2$ appears at 1603 cm^{-1} while the C=O stretches for other molecules containing free hfac anions have been reported to lie near 1670 cm^{-1}.[16,18,19] The molar conductivity of **1** in methanol of 174 Ω^{-1} cm^2 mol^{-1} (reckoned as the dimer) is within the 160–220 Ω^{-1} cm^2 mol^{-1} range found for other 2:1 electrolytes in this solvent.[20] The mass spectrum of **1** does not give peaks for the molecular ion; instead, the highest *m/e* peak corresponds to the species $Pd_2(hfac)_2(PMe_3)_2$ while the most intense peak is due to the species $Pd(hfac)(PMe_3)_2$.[21] These results suggest that some of the PMe_3 ligands are lost and the hfac groups become coordinated to the palladium centers when **1** is heated; alternatively, these palladium–hfac species may be the result of gas-phase reactions after ionization.

Since mononuclear Pd^I compounds should be paramagnetic, the observation that **1** is diamagnetic provides strong supporting evidence of its dinuclear nature. The NMR spectra of **1** clearly show that there are two PMe_3 environments: the ^1H NMR spectrum contains a triplet and a pseudotriplet for the PMe_3 protons with relative intensities of 36:18 (Figure 1a), and the $^{31}P\{^1H\}$ NMR spectrum corresponds to an A_2B spin system with $J_{AB} = 13$ Hz. The methine CH protons of the two hfac counterions appear in the ^1H NMR spectrum as a singlet at δ 5.45 of relative intensity 2.

The spectroscopic data are consistent with a structure for the dinuclear $[Pd_2(PMe_3)_6]^{2+}$ cation consisting of two square-planar palladium(I) centers that are joined by a metal–metal bond; the square planar coordination geometry about each Pd center is completed by an axial PMe_3 group (which is trans to the Pd–Pd bond) and two equatorial PMe_3 groups:



It should be pointed out that the virtually-coupled triplet ^1H NMR line shape for the axial PMe_3 groups in **1** (Figure 1a)

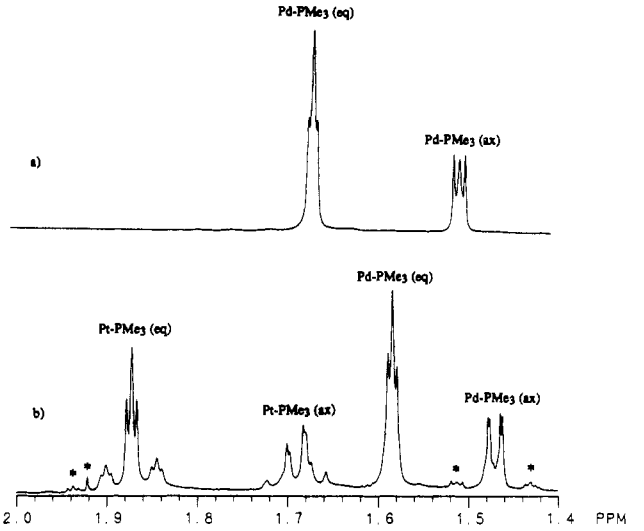


Figure 1. 500-MHz ^1H NMR spectra of the new dinuclear compounds in CD_2Cl_2 at 25 °C: (a) $[Pd_2(PMe_3)_6][hfac]_2$; (b) $[PdPt(PMe_3)_6][hfac]_2$. In each case, the resonance near δ 5.5 for the hfac methine proton is not shown. The asterisks indicate peaks due to traces of $[Pd_2(PMe_3)_6][hfac]_2$ and other impurities.

necessarily means that there must be a significant $^3J_{PP}$ coupling between the two ^{31}P nuclei *through* the Pd–Pd bond. A value for this $^3J_{PP}$ coupling constant of ca. 80 Hz can be estimated from the line shape; computer simulations of the $X_9AA'X'_9$ spin system[22] show that $^3J_{PP}$ coupling constants significantly different from this give virtually-coupled triplets in which the central component has the wrong shape or intensity.

Synthesis and Characterization of $[PdPt(PMe_3)_6][hfac]_2$. The analogous palladium–platinum complex $[PdPt(PMe_3)_6][hfac]_2$ (**2**) can be made via an essentially identical route by mixing equimolar quantities of appropriate palladium(0) and platinum(II) starting materials:

$$Pd(PMe_3)_4 + [Pt(hfac)(PMe_3)_2][hfac] \rightarrow \underset{\mathbf{2}}{[PdPt(PMe_3)_6][hfac]_2}$$

Interestingly, if one uses the platinum(0) and palladium(II) starting materials $Pt(PMe_3)_4$ and $[Pd(hfac)(PMe_3)_2][hfac]$, the product is contaminated with significant amounts of the dipalladium complex **1**. The ^1H NMR spectrum of the mixed-metal complex **2** shows that there are four PMe_3 environments: two triplets each of intensity 18 due to the equatorial phosphine ligands and two doublets of doublets each of intensity 9 due to the axial phosphines (Figure 1b). The line shapes of the axial phosphine resonances show that these protons are coupled to *both* of the axial phosphorus nuclei. Platinum satellites are evident for the phosphine ligands attached to Pt; the $^3J_{HPt}$ coupling constants are approximately 28 Hz. The $^{31}P\{^1H\}$ NMR spectrum of **2** corresponds to an A_2BC_2D spin system, where A and C are the equatorial ^{31}P nuclei and B and D are the axial ^{31}P nuclei; satellite peaks due to the mono-^{195}Pt isotopomer are also present that correspond to an A_2BC_2DM spin system.[23] The observed spectrum

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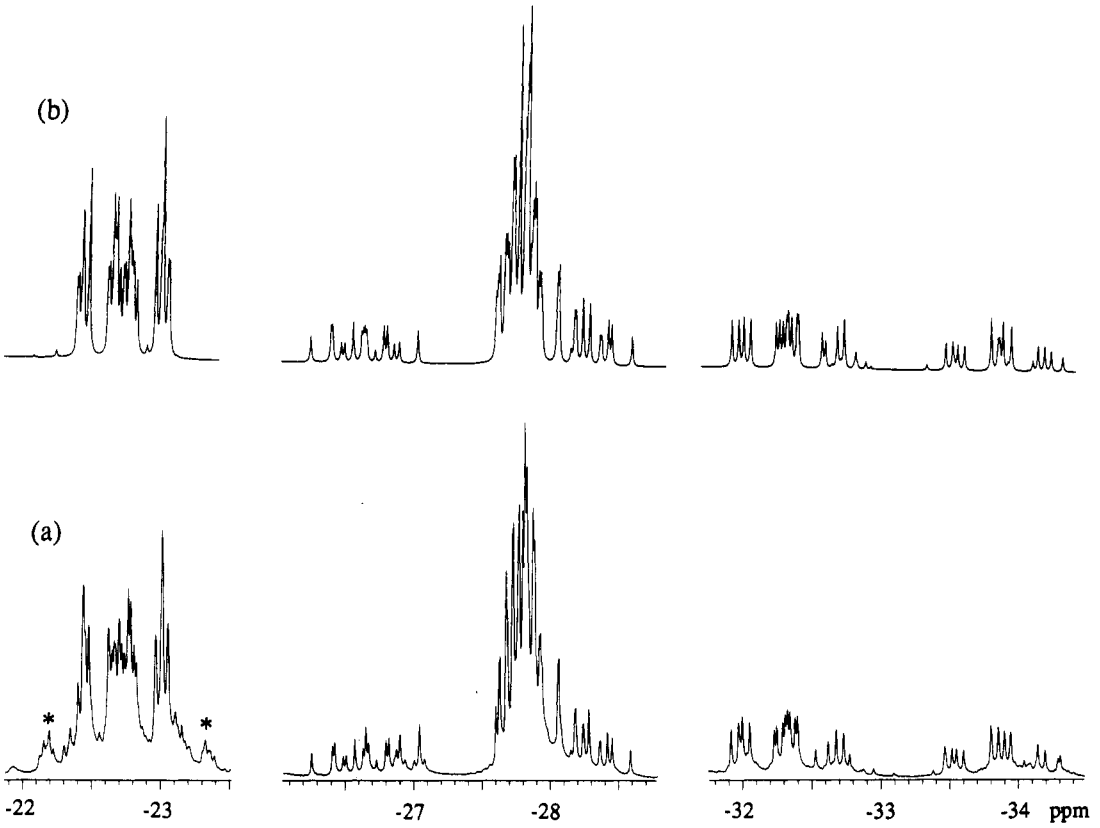

Figure 2. 121.64-MHz $^{31}P\{^1H\}$ NMR spectra of $[PdPt(PMe_3)_6][hfac]_2$ in CD_2Cl_2 at 25 °C: (a) observed; (b) computer simulated. The derived chemical shifts and coupling constants are given in the Experimental Section. The asterisks in the observed spectrum indicate ^{195}Pt satellite peaks of the equatorial phosphine ligands bound to the palladium center. The ^{195}Pt satellite peaks for the phosphines bound to the platinum center are not shown.

is compared with a computer-simulated spectrum in Figure 2; the derived J_{PP} and J_{PPt} coupling constants are given in the Experimental Section.

Perhaps the most interesting aspect of the $^{31}P\{^1H\}$ NMR spectrum of **2** is that the two axial phosphines, which lie on different metal centers, are in fact strongly coupled to each other. The $^3J_{PP}$ coupling in **2** is 185 Hz; for comparison, $^3J_{PP}$ couplings of 76 and 95 Hz have been noted in the unusual cyclopentadienyl- and allyl-bridged complexes $PdPt(\mu\text{-}C_5H_5)(\mu\text{-}C_3H_5)(PPr^i_3)_2$ and $PdPt(\mu\text{-}2\text{-}MeC_3H_4)_2(PPr^i_3)_2$.[24] The 185-Hz coupling in **2** is larger than the ca. 80 Hz coupling estimated for the dipalladium complex **1** (see above); in structurally related diplatinum(I) complexes with axial phosphine ligands, the $^3J_{PP}$ couplings through the Pt–Pt bond of ca. 220 Hz are larger still.[23,25] These observations suggest that platinum(I) is more effective than palladium(I) in communicating nuclear spin information.

The synthesis of the analogous diplatinum(I) complex from the reaction of $Pt(PMe_3)_4$ with $[Pt(hfac)(PMe_3)_2][hfac]$ is not straightforward; this comproportionation reaction is rather complicated, and the species isolated depends on the time, temperature, and solvent. Besides the expected diplatinum(I) complex $[Pt_2(PMe_3)_6][hfac]_2$, two other dinuclear species can also be obtained from this reaction: hfac salts of the octakis(trimethylphosphine)diplatinum dication, $[Pt_2(PMe_3)_8]^{2+}$, and the (μ-hexafluoroacetylacetonato)tetrakis(trimethylphosphine)diplatinum monocation, $[Pt_2(PMe_3)_4(\mu\text{-hfac})]^+$. This work will be reported separately.[26]

Table 1. Crystal Data for $[Pd_2(PMe_3)_6][hfac]_2$

$C_{28}H_{56}P_6F_6O_2Pd_2$	space gp: $C2/c$
a = 25.499(6) Å	T = −75 °C
b = 9.791(2) Å	λ = 0.710 73 Å
c = 18.424(5) Å	ρ_{calcd} = 1.634 g cm^{-3}
β = 106.85(2)°	μ_{calcd} = 11.01 cm^{-1}
V = 4402(26) Å^3	transm coeff = 0.834–0.919
Z = 4	R_F = 0.032[a]
mol wt = 1083.38	R_{wF} = 0.033[b]

[a] $R_F = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

X-ray Crystal Structure of $[Pd_2(PMe_3)_6][hfac]_2$. In order to determine the bond distances and angles characteristic of this dinuclear palladium(I) compound, a single-crystal X-ray diffraction study has been carried out. Single crystals of **1**, grown from diethyl ether/dichloromethane, crystallize in the monoclinic space group $C2/c$ with one half-molecule in the asymmetric unit. The cations in **1** lie on crystallographic 2-fold axes; the 2-fold axes bisect the Pd–Pd bond and thus render the two ends of the dimer crystallographically equivalent. There is also one hfac counterion per asymmetric unit that lies on a general position. Crystal data are collected in Table 1, atomic coordinates are listed in Table 2, and selected bond distances and angles are presented in Table 3.

As expected from the spectroscopic results, the dinuclear $[Pd_2(PMe_3)_6]^{2+}$ cation in **1** consists of two square-planar palladium(I) centers that are joined by a metal–metal bond; three PMe_3 groups attached to each palladium atom complete the square-planar coordination geometries (Figure 3). The two square planes are mutually orthogonal (dihedral angle of 89.0°). The structure resembles that of the related isonitrile complex of stoichiometry $[Pd_2(CNMe)_6^{2+}]$[27] but is unlike the structures of palladium(I) complexes with bridging bidentate phosphine ligands in which the the coordination spheres are twisted ca. 40° with respect to

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Table 2. Atomic Coordinates for $[Pd_2(PMe_3)_6][hfac]_2$[a]

	x/a	y/b	z/c
Pd	0.04544(1)	0.15849(3)	0.23153(2)
P1	0.00240(4)	0.3300(1)	0.14519(6)
P2	0.07122(5)	−0.0093(1)	0.32480(6)
P3	0.12830(4)	0.1555(1)	0.19759(6)
C11	−0.0696(2)	0.3703(5)	0.1308(3)
C12	0.0333(2)	0.4989(4)	0.1678(3)
C13	0.0020(2)	0.3096(5)	0.0464(2)
C21	0.0815(2)	−0.1756(4)	0.2858(3)
C22	0.1357(2)	0.0226(5)	0.3984(2)
C23	0.0301(2)	−0.0609(5)	0.3862(3)
C31	0.1819(2)	0.0308(5)	0.2353(3)
C32	0.1674(3)	0.3083(6)	0.2197(5)
C33	0.1201(3)	0.1328(10)	0.0980(3)
F1	0.3118(2)	0.0799(4)	0.1581(2)
F2	0.2398(1)	0.0579(4)	0.0672(2)
F3	0.2772(2)	0.2510(4)	0.0942(2)
F4	0.3216(2)	−0.1752(4)	−0.1729(2)
F5	0.2773(2)	−0.2404(5)	−0.1017(3)
F6	0.3589(2)	−0.2937(4)	−0.0764(2)
O1	0.3638(1)	0.1736(3)	0.0480(2)
O2	0.3877(1)	−0.0170(4)	−0.0593(2)
C1	0.2872(2)	0.1203(5)	0.0884(3)
C2	0.3247(2)	0.0954(5)	0.0374(2)
C3	0.3112(2)	−0.0171(5)	−0.0109(2)
C4	0.3438(2)	−0.0631(5)	−0.0546(2)
C5	0.3249(3)	−0.1917(6)	−0.1015(3)
H3	0.282(2)	−0.061(4)	−0.013(2)

[a] The atoms in the other half of the molecule are located at $(-x, y, {}^1/_2 - z)$.

Table 3. Selected Bond Distances and Angles for $[Pd_2(PMe_3)_6][hfac]_2$

	Bond Distances (Å)		
Pd–Pd′	2.598(1)	C1–C2	1.543(7)
Pd–P1	2.354(1)	C2–C3	1.395(6)
Pd–P2	2.330(1)	C3–C4	1.389(6)
Pd–P3	2.371(1)	C4–C5	1.524(7)
P1–C11	1.821(4)	C2–O1	1.226(5)
P1–C12	1.827(5)	C4–O2	1.233(6)
P1–C13	1.829(4)	C1–F1	1.316(6)
P2–C21	1.829(4)	C1–F2	1.309(6)
P2–C22	1.829(4)	C1–F3	1.316(6)
P2–C23	1.823(5)	C5–F4	1.304(7)
P3–C31	1.815(5)	C5–F5	1.304(9)
P3–C32	1.779(6)	C5–F6	1.315(8)
P3–C33	1.800(6)	C3–H3	0.86(4)
	Bond Angles (deg)		
Pd′–Pd–P1	84.29(3)	C1–C2–C3	115.6(4)
Pd′–Pd–P2	83.64(3)	C2–C3–C4	123.2(4)
Pd′–Pd–P3	179.29(4)	C3–C4–C5	116.9(5)
P1–Pd–P2	167.91(4)	C1–C2–O1	115.1(4)
P1–Pd–P3	96.15(4)	C3–C2–O1	129.2(4)
P2–Pd–P3	95.93(4)	C3–C4–O2	129.0(4)
Pd–P1–C11	120.4(1)	C5–C4–O2	114.1(4)
Pd–P1–C12	113.9(2)	C2–C1–F1	110.0(4)
Pd–P1–C13	117.5(2)	C2–C1–F2	115.3(4)
Pd–P2–C21	112.3(1)	C2–C1–F3	111.8(4)
Pd–P2–C22	115.3(2)	C4–C5–F4	112.7(5)
Pd–P2–C23	124.3(2)	C4–C5–F5	116.5(5)
Pd–P3–C31	122.5(2)	C4–C5–F6	111.1(5)
Pd–P3–C32	114.4(2)	C2–C3–H3	118(3)
Pd–P3–C33	114.9(2)	C4–C3–H3	118(3)

each other.[28-31] Undoubtedly, the two square-planar ligand sets in **1** adopt a mutually orthogonal arrangement so that steric repulsions between the PMe_3 groups attached to opposite palladium centers are minimized. The cation in **1** cannot be

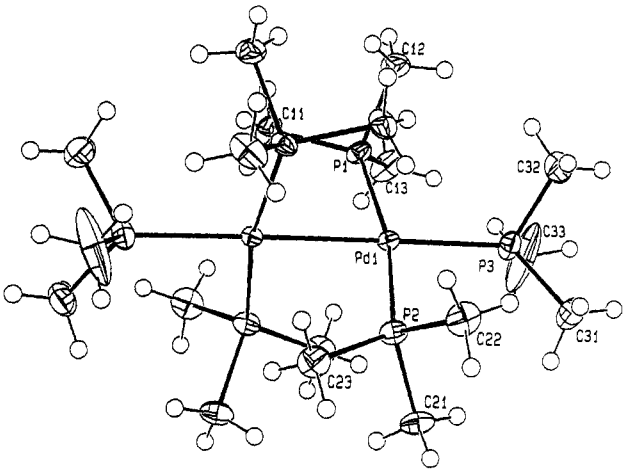

Figure 3. ORTEP diagram of the $[Pd_2(PMe_3)_6]^{2+}$ dication. The ellipsoids represent the 35% probability density surfaces.

overly crowded, however, since the Pd–Pd–P angles of 83.64(3) and 84.69(3)° for the phosphines cis to the Pd–Pd bond are all less than 90°. Evidently, the most important steric interactions are those between the PMe_3 ligands attached to the same palladium atom; similar Pd–Pd–C angles of 85.0(9)° were noted in the structure of $[Pd_2(CNMe)_6]^{2+}$.[27]

The Pd–Pd distance in **1** of 2.598(1) Å is slightly longer than the 2.531(1)-Å distance in $[Pd_2(CNMe)_6]^{2+}$; a listing of the Pd–Pd distances in other palladium(I) dimers is presented in Table 4.[27-61]

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Table 4. Compilation of Pd–Pd Bond Lengths <3 Å in Palladium(I) Complexes[a]

complex	d_{Pd-Pd}, Å	ref
$[Pd_2(o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3\text{-}2\text{-}C_5H_4N)_2]^{2+}$	2.500(1)	36
$[Pd_2(CNMe)_6]^{2+}$	2.531(1)	27
$Pd_2(CNBu^t)_4Cl_2$	2.532(2)	37
$Pd_2(CNMe)_4I_2$	2.533(1)	38
$[Pd_2(\mu\text{-}PhC_2Ph)(\eta^5\text{-}C_5Ph_5)(bipy)]^+$	2.541(3)	39
$Pd_2(\mu\text{-}C_6H_6)_2(AlCl_4)_2$	2.57(1)	40
$Pd_2(\mu\text{-}C_6H_6)_2(Al_2Cl_7)_2$	2.57(1)	40
$Pd_2(\mu\text{-}PBu^t_2)_2(PMe_3)_2$	2.571(2)	41
$[Pd_2(\mu\text{-}PhC_2Ph)(\eta^5\text{-}C_5Ph_5)(bipy)(NCMe)]^+$	2.571(3)	39
$[Pd_2(CNMe)_6(PPh_3)_2]^{2+}$	2.592(1)	42
$Pd_2(\mu\text{-}PBu^t_2)_2(PBu^t_2H)_2$	2.594(1)	43
$[Pd_2(PMe_3)_6]^{2+}$	2.598(1)	this work
$[Pd_2(Ph_2PC_2H_2PPh_2)_2(2,6\text{-}Me_2C_6H_3NC)_2]^{2+}$	2.602(1)	44
$Pd_2(\mu\text{-}Me_2PCH_2PMe_2)_2Br_2$	2.603(1)	28
$Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2$	2.604(1)	45
$Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}Br)(PPr^i_3)_2$	2.609(1)	46
$[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PHBu^t_2)(PHBu^t_2)_2]^+$	2.611(1)	47
$[Pd_2(Ph_2PC_3H_6PPh_2)_2(2,4,6\text{-}Me_3C_6H_2NC)_2]^{2+}$	2.617(2)	44
$[Pd_2(\mu\text{-}PhC_2Ph)(\eta^5\text{-}C_5Ph_5)(bipy)\{P(OPh)_3\}]^+$	2.622(3)	39
$Pd_2(\mu\text{-}C_2Ph_2)(\eta^5\text{-}C_5Ph_5)_2$	2.639(1)	48
$Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(SnCl_3)Cl$	2.644(2)	29
$Pd_2(\mu\text{-}\eta^3\text{-}C_9H_7)_2(CNBu^t)_2$	2.648(2)	49
$Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}\eta^2\text{-}O_3SCF_3)(PEtBu^t_2)_2$	2.648(2)	50
$Pd_2(\mu\text{-}\eta^3\text{-}C_9H_7)_2(2,5\text{-}Me_2C_6H_3NC)_2$	2.656(2)	49
$Pd_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2(py)_2Cl_2$	2.662(1)	51
$Pd_3(\mu\text{-}C_3Ph(p\text{-}MeOC_6H_4)_2]_2(acac)_2$	2.662(2)	52
$Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CMe)_4$	2.663(1)	53
$Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(C_6Cl_5)_2$	2.670(2)	30
$Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}2\text{-}MeC_3H_4)(PPh_3)_2$	2.679	54
$[Pd_2(\mu\text{-}PBu^t_2)(CO)_2(PHBu^t_2)_2]^+$	2.682(1)	47
$Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}I)(PPh_3)_2$	2.686(7)	55
$Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}2\text{-}MeC_3H_4)[P(O\text{-}o\text{-}tolyl)_3]_2$	2.689	54
$[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$	2.697(3)	56
$Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2Br_2$	2.699(5)	31
$[Pd_2\{Ph_2P(CH_2)_3PPh_2\}_2]^{2+}$	2.701(3)	57
$Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2(PPh_3)_2$	2.720(1)	58
$[Pd_2(\mu\text{-}\eta^3\text{-}Ph_2PCHCH_2)_2(Ph_2PCHCH_2)_2]^{2+}$	2.748(2)	59
$[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}\eta^4\text{-}CH_2CMeCHCH_2)\text{-}(PHBu^t_2)_2]^+$	2.751(2)	50
$[Pd_2(\mu\text{-}H)(\mu\text{-}CO)(Pr^i_2PC_3H_6PPr^i_2)_2]^+$	2.767(4)	60
$Pd_2(\mu\text{-}H)_2(\mu\text{-}LiBEt_4)(Pr^i_2PC_3H_6PPr^i_2)_2$	2.823(1)	61

[a] See also ref 32 and ref 95. bipy = 2,2′-bipyridyl, py = pyridine, acac = 2,4-pentanedionate.

The Pd–P distances in **1** fall into two classes: the Pd–P distances to the equatorial PMe_3 groups (which are cis to the Pd–Pd bond) range from 2.330(1) to 2.354(1) Å; in contrast, the Pd–P distances to the axial PMe_3 groups (which are trans to the Pd–Pd bond) are longer at 2.371(1) Å. The ca. 0.03 Å lengthening of the Pd–P bonds to the axial phosphines is small but may be ascribed to the trans influence of the metal–metal bond; a similar relative lengthening of 0.08 Å was observed for the Pd–C bonds to the axial isonitrile groups trans to the Pd–Pd bond in $[Pd_2(CNMe)_6]^{2+}$.[27]

The hfac anions adopt a U-shaped structure very similar to that found previously in several other hfac salts,[16,19] and the distances within the hfac anions are normal. The two C–O distances of 1.226(5) and 1.233(6) Å are essentially identical as are the two C–C distances to the methine carbon of 1.389(6) and 1.395(6) Å. The hfac groups are thus symmetrical and the π-system is delocalized. The C_5O_2 skeleton of the hfac anion is essentially planar: the C–C–C–C and C–C–C–O torsion angles are all very near 0 or 180°, and the largest deviation of the five carbon and two oxygen atoms from the mean plane is only 0.07 Å.

One other dinuclear palladium(I) complex is known with six phosphine ligands in the coordination sphere, the triphos complex $[Pd_2(triphos)_2]^{2+}$ where triphos = $PhP(CH_2CH_2PPh_2)_2$.[62] As judged from NMR data, this molecule adopts a bridged structure in which the triphos ligands are each bidentate toward one palladium center and unidentate toward the other; no crystallographic study of this complex has been carried out, however.

Fluxionality of $[Pd_2L_6]^{2+}$ Species. The only other dinuclear palladium(I) complexes with six identical unidentate ligands are the isonitrile complexes of stoichiometry $[Pd_2(CNR)_6]^{2+}$ prepared by Balch.[63] The axial and equatorial isonitrile ligands in these species undergo intramolecular exchange with activation barriers $\Delta G^{\ddagger}$ of about 13–14 kcal mol^{-1}. Studies of complexes in which the two ends of the dinuclear molecule are different, such as the mixed palladium/platinum complex $[PdPt(CNMe)_6]^{2+}$ [64] and the phosphine-substituted complex $[Pd_2(CNMe)_5(PPh_3)]^{2+}$,[63] have shown that axial–equatorial exchange occurs *without* scrambling of ligands between the two metal centers. Interestingly, whereas the isonitrile groups in the $[Pd_2(CNR)_6]^{2+}$ complexes exchange rapidly on the NMR time scale at temperatures above −30 °C, the present phosphine complexes **1** and **2** are nonfluxional even at 65 °C.

Two mechanisms have been proposed to be responsible for the axial/equatorial ligand exchange in the isonitrile complexes: an intramolecular process involving tetrahedral distortion of the square-planar coordination geometry combined with rotation about the metal–metal bond[62,63] and an intermolecular process in which solvent molecules promote the dissociation of isonitrile ligands.[65] If the intramolecular mechanism is responsible for the dynamic behavior of $[Pd_2(CNR)_6]^{2+}$, then the nonfluxionality of the PMe_3 analogue is probably ascribable to the weaker π-accepting nature of PMe_3 with respect to isonitrile ligands: the tetrahedral distortion responsible for the exchange process generates a transient polarization of the Pd–Pd bond in which the pseudotetrahedral center is formally Pd^0 while the undistorted center is formally Pd^{II}.[62,63] The pseudotetrahedral Pd^0 center will be stabilized if it is ligated by π-acceptor ligands such as isonitriles but will be destabilized if it is ligated by σ-donors such as PMe_3. Alternatively, if the solvent-assisted mechanism is responsible for the dynamic behavior of $[Pd_2(CNR)_6]^{2+}$, then the nonfluxionality of the PMe_3 analogue may be due to the larger size of the PMe_3 ligands, which should inhibit associative solvent-assisted ligand-exchange processes.

Synthesis and Characterization of $Pd_2(PMe_3)_4Cl_2$ and $Pd_2(PMe_3)_4I_2$. Since the title compound is a salt and is not sufficiently volatile to be an attractive CVD precursor, we have investigated the synthesis of related nonionic dipalladium(I) compounds that might exhibit higher vapor pressures. Treatment of **1** with exess LiCl in tetrahydrofuran affords a yellow product with the stoichiometry "$PdCl(PMe_3)_2$". The diamagnetic nature of this product suggests that it is, in fact, a neutral dipalladium(I) complex $Pd_2(PMe_3)_4Cl_2$ (**3**). The ^1H NMR spectrum of **3** shows only one pseudotriplet at δ 1.53, and the $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits a singlet at δ −20.2. These spectroscopic features indicate that there is only one PMe_3 environment in **3**, and we conclude that the axial PMe_3 ligands in **1** have been replaced by

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chloride. Similar complexes with isonitrile groups[37,38] and bridging bidentate phosphines[28,31] in place of the PMe_3 ligands are known.

$$[Pd_2(PMe_3)_6][hfac]_2 + 2LiCl \rightarrow Pd_2(PMe_3)_4Cl_2 + 2Li(hfac)$$
3

$$[Pd_2(PMe_3)_6][hfac]_2 + 2NaI \rightarrow Pd_2(PMe_3)_4I_2 + 2Na(hfac)$$
4

The analogous iodo complex $Pd_2(PMe_3)_4I_2$ (**4**) can be prepared similarly by treating **1** with NaI. Despite being nonionic, **3** and **4** do not sublime at 120 °C and 10^{-3} Torr, and so are not likely to serve as useful CVD precursors.

Attempts to prepare a nonionic hfac complex such as $Pd_2(PMe_3)_4(hfac)_2$ have been unsuccessful: **3** and **4** do not react with Na(hfac) or Ag(hfac) in solution. Treatment of **4** with Na(hfac) or Ag(hfac) in the solid state at 70–120 °C was also unavailing, since only the mononuclear palladium(II) complexes $PdI_2(PMe_3)_2$ and $Pd(hfac)_2$, respectively, were obtained.

Behavior of $[Pd_2(PMe_3)_6][hfac]_2$ upon Sublimation; Cleavage of Phosphorus–Carbon Bonds. Not surprisingly due to its ionic nature, $[Pd_2(PMe_3)_6][hfac]_2$ does not make an ideal CVD precursor because it is not appreciably volatile. Some sublimation does occur at 100 °C and 10^{-3} Torr, however, and NMR analysis shows that **1** is in fact present in the sublimate.

Interestingly, however, **1** is only a minor constituent of the sublimate; the major constituent (ca. 83 mol %) is a second species **5**. The low-temperature $^{31}P\{^1H\}$ NMR spectrum of **5** corresponds to an A_2B spin system like that for **1**, except that the J_{AB} coupling constant is much larger: 43 Hz in **5** vs 13 Hz in **1**. The low-temperature ^1H NMR spectrum of **5** contains, apart from resonances due to the PMe_3 ligands, a singlet of intensity 1 at δ 5.45 (ascribable to the methine proton of a hfac ligand) and a quartet of intensity 3 at δ 0.14. The latter resonance is most reasonably attributed to a palladium-bound methyl group coupled to three PMe_3 ligands (J_{HP} = 7 Hz), and we have identified **5** as the palladium(II) methyl compound $[PdMe(PMe_3)_3][hfac]$. The ^1H and ^{31}P NMR chemical shifts and coupling constants of the cation in **5** are essentially identical with those of the tetraphenylborate salt $[PdMe(PMe_3)_3][BPh_4]$ previously synthesized by Werner.[66]

This result shows that the solid-state thermolysis of **1** results in the unexpected cleavage of the phosphorus–methyl bonds of some of the PMe_3 ligands:

$$[Pd_2(PMe_3)_6][hfac]_2 \rightarrow [PdMe(PMe_3)_3][hfac] + ...$$
5

Presumably, some palladium dimethylphosphido complexes are also formed in this process; to date, however, we have not been able to isolate phosphido products from the thermolysis of **1**. The thermolysis of the mixed palladium/platinum complex **2** yields a mixture of $[PdMe(PMe_3)_3][hfac]$ and $[PtMe(PMe_3)_3][hfac]$ in a 1:6 molar ratio.

Although cleavage of phosphorus–aryl,[67-70] phosphorus–alkynyl,[71] and phosphorus–vinyl[72] bonds is well-known to be promoted by transition metal centers (including palladium), the isolation of organometallic complexes resulting from the metal-promoted cleavage of phosphorus–alkyl bonds is quite uncommon. Scattered examples have been reported for cobalt,[73-76] nickel,[76] tungsten,[77] platinum,[78-80] iridium,[81] tantalum,[82] iron,[83] and ruthenium[84] centers; most of these examples involve cleavage of the P–C bonds in bidentate phosphine ligands. Interestingly, while the phosphido fragment is without exception found in the resulting products, the alkyl ligand is almost invariably lost. In one case it has been proposed that the alkyl ligand is retained in the product;[82] however this claim must be viewed with caution since it has been shown subsequently that the starting material for this reaction, "$TaBr_3(PMe_2Ph)_2$", was incorrectly formulated.[85] Thus, the palladium(II) methyl compound **5** and the analogous platinum(II) methyl compound derived from the mixed-metal dimer are the only well-established examples of the isolation of a metal alkyl complex via P–C bond cleavage of a unidentate alkylphosphine.

Some insight into the mechanism of the conversion of **1** to **5** may be obtained from a previous example of P–C bond activation involving palladium: while investigating the reductive elimination of ethane from the palladium(II) methyl complex $Pd(CH_3)_2[P(CD_3)Ph_2]_2$, Stille observed that ethane-d_3 and ethane-d_6 are formed; this result suggested that the P–Me groups can oxidatively add to a palladium(0) species generated by reductive elimination of the two Pd–Me groups.[86] A theoretical study of the transfer of methyl groups of PMe_3 ligands to palladium centers has subsequently been carried out.[87] Although it is tempting to propose that the conversion of the dipalladium species **1** to the palladium(II) methyl complex **5** involves oxidative addition of a PMe_3 group across the Pd–Pd bond, we have no experimental evidence in support of this idea. It is more likely, given Stille's results, that thermolysis of **1** occurs via disproportionation back to Pd^0 and Pd^{II} products and that the former are responsible for the activation of the P–C bonds of PMe_3.

Possible Relevance of the P–C Bond Cleavage Reactions to MOCVD Processes. It is worth noting that these phosphorus–carbon bond cleavage reactions may have implications relative to the design and efficacy of MOCVD precursors. Trialkylphosphines have recently been used as ancillary ligands in several MOCVD precursors, and the films grown from them are typically of reasonable purity.[5,9,11,12,88,89] The present results suggest, however, that in some cases such precursors could generate films that contain impurities as a result of the activation of P–C bonds.

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Specifically, P–C bond activation under MOCVD conditions would generate surface-bound alkyl and dialkylphosphido intermediates; subsequent fragmentation of these intermediates would lead to the formation of carbon and phosphorus inclusions. The addition of hydrogen as a carrier gas may interrupt some of these subsequent fragmentation reactions; for example, hydrogenation of surface-bound alkyl intermediates to the corresponding alkane would prevent the incorporation of carbon impurities into the growing films. However, hydrogen may not be particularly effective in removing phosphorus impurities, since the conversion of surface-bound dialkylphosphido groups to dialkylphosphine molecules (HPR_2) is probably uphill thermodynamically.

We are continuing to explore the synthesis and chemistry of palladium(I) and platinum(I) species with an eye toward their potential use as MOCVD precursors.

Experimental Section

All operations were carried out under vacuum or under argon. Solvents were distilled under nitrogen from sodium benzophenone (diethyl ether and tetrahydrofuran), magnesium (methanol), or calcium hydride (dichloromethane). Trimethylphosphine,[90] diallyldichlorodipalladium(II),[91] and bis(hexafluoroacetylacetonato)palladium(II),[16] were prepared by following literature procedures. Bis(methallyl)dichlorodipalladium(II) was prepared by following the method described for the allyl analogue, except that 3-chloro-2-methyl-1-propene was used in place of 3-chloro-1-propene.[91] The platinum phosphine complexes $Pt(PMe_3)_4$ and $[Pt(hfac)(PMe_3)_2][hfac]$ were prepared as described elsewhere.[26]

Elemental analyses were performed by Mr. Thomas McCarthy of the University of Illinois Microanalytical Laboratory. The mass spectra were obtained on a Finnigan-MAT CH5 mass spectrometer with electron impact ionization potentials of 70 and 10 eV. The IR spectra were recorded on a Perkin-Elmer 599B instrument as Nujol mulls between KBr plates. The ^1H NMR data were recorded on a General Electric GN-500 spectrometer at 500 MHz, on a General Electric QE-300 spectrometer at 300 MHz, or on a Varian Unity 400 spectrometer at 400 MHz; the ^{31}P NMR data were recorded on a General Electric GN-300NB spectrometer at 121 MHz or on a Varian Unity 400 spectrometer at 160.9 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS (^1H) or 85% H_3PO_4 (^{31}P). The simulation of the ^1H NMR line shape of the dipalladium complex **1** was carried out with the QCPE Program No. 519 (DOKI77),[92] while the $^{31}P\{^1H\}$ NMR spectrum of complex **2** was simulated with the QCPE Program No. 459 (LAOCOON).[93] Melting points were determined on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon. Solution conductivities were measured at room temperature with a YSI Scientific Model 35 conductance meter and a glass dip cell with a cell constant of 1.0.

Hexakis(trimethylphosphine)dipalladium(I) 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate, $[Pd_2(PMe_3)_6][hfac]_2$ (1). Method A. To a cold (–78 °C) slurry of $Pd_2(C_3H_5)_2Cl_2$ (0.575 g, 1.57 mmol) in methanol (15 mL) was added trimethylphosphine (2.4 mL, 23.7 mmol). The mixture was warmed to room temperature and stirred for 12 h. The resulting white slurry was cooled to –78 °C, and the $Pd(PMe_3)_4$ precipitate was collected by filtration. To the cold solid was added a cold (–78 °C) solution of $Pd(hfac)_2$ (1.12 g, 2.15 mmol) in diethyl ether (30 mL). The dark solution was warmed to room temperature, and an olive green product began to precipitate. After the mixture had been stirred for 40 min, the precipitate was collected by filtration, washed with diethyl ether (10 mL), and dried under vacuum. Yield: 1.45 g (62% based on $Pd(hfac)_2$). The crude product can be further purified by recrystallization from a mixture of CH_2Cl_2 (ca. 15 mL) and Et_2O (ca. 10 mL) at –20 °C to give pale yellow crystals of the product. Mp: 145 °C dec. Anal. Calcd for $C_{28}H_{56}F_{12}O_4P_6Pd_2$: C, 31.0; H, 5.21; P, 19.3; Pd, 17.1. Found: C, 31.3; H, 5.29; P, 19.6; Pd, 16.5. ^1H NMR (CD_2Cl_2, 25 °C): δ 5.46 (s, $HC(COCF_3)_2$), 1.69 (t, $^2J_{HP} + {}^4J_{HP}$ = 5.3 Hz, equatorial PMe_3), 1.52 ("t", $^2J_{HP} + {}^5J_{HP}$ = 6.5 Hz, axial PMe_3). $^{31}P\{^1H\}$ NMR (thf-d_8, 25 °C): δ –25.4 (d, $^2J_{PP}$ = 13 Hz), –37.1 (t, $^2J_{PP}$ = 13 Hz). IR (cm^{-1}): 1672 (vs), 1553 (vs), 1530 (s), 1313 (w), 1299 (w), 1289 (w), 1246 (vs), 1183 (vs), 1172 (m), 1147 (s), 1120 (vs), 1067 (w), 948 (vs), 855 (m), 782 (w), 740 (m), 723 (m), 668 (m), 657 (m), 575 (m).

Method B. The palladium(0) compound $Pd(PMe_3)_4$ was prepared as described above from $Pd_2(C_4H_7)_2Cl_2$ (0.39 g, 0.99 mmol) and PMe_3 (1.6 mL, 15.8 mmol). To the cold solid was added a cold (–78 °C) solution of $[Pd(hfac)(PMe_3)_2][hfac]$ (1.03 g, 1.54 mmol) in diethyl ether (30 mL). The orange cloudy solution was warmed to room temperature, and the yellow product began to precipitate. After the mixture had been stirred for 2 h, the yellow precipitate was collected by filtration and washed with diethyl ether (5 mL). Yield: 1.40 g (84% based on $[Pd(hfac)(PMe_3)_2][hfac]$).

Hexakis(trimethylphosphine)palladium(I)platinum(I) 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate, $[PdPt(PMe_3)_6][hfac]_2$ (2). Method A. The palladium(0) compound $Pd(PMe_3)_4$ was prepared as described above from $Pd_2(C_4H_7)_2Cl_2$ (0.39 g, 0.99 mmol) and PMe_3 (1.6 mL, 15.8 mmol). To the cold (–78 °C) solid was added a slurry of $[Pt(hfac)(PMe_3)_2][hfac]$ (1.06 g, 1.39 mmol) in diethyl ether (50 mL). The red-orange cloudy solution was warmed to room temperature, and the pale yellow product began to precipitate. After the mixture had been stirred for 2 h, the yellow precipitate was collected by filtration, washed with diethyl ether (5 mL), and dried under vacuum. Yield: 1.25 g (63% based on $[Pt(hfac)(PMe_3)_2][hfac]$). The product can be further purified by recrystallization from a mixture of CH_2Cl_2 (15 mL) and Et_2O (8 mL) at –20 °C; the product prepared in this way contained a trace amount of the dipalladium complex **1**. Mp: 161 °C dec. Anal. Calcd for $C_{28}H_{56}F_{12}O_4P_6PdPt$: C, 28.7; H, 4.82; P, 15.9; Pd, 9.08, Pt, 16.6. Found: C, 28.6; H, 4.98; P, 14.4; Pd, 8.79; Pt, 15.5. ^1H NMR (CD_2Cl_2, 25 °C): δ 5.45 (s, $HC(COCF_3)_2$), 1.87 ("t", $^2J_{HP} + {}^4J_{HP}$ = 6.0 Hz, $^3J_{HPt}$ = 28 Hz, equatorial Pt–PMe_3), 1.68 (dd, $^2J_{HP}$ = 8.6 Hz, $^5J_{HP}$ = 1.5 Hz, $^3J_{HPt}$ = 24 Hz, axial Pt–PMe_3), 1.58 ("t", $^2J_{HP} + {}^4J_{HP}$ = 4.8 Hz, equatorial Pd–PMe_3), 1.47 (dd, $^2J_{HP}$ = 7.0 Hz, $^5J_{HP}$ = 1.1 Hz, axial Pd–PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): A_2BC_2D spin system (where sites A and B are bound to palladium), with δ_A = -22.8, δ_B = –33.0, δ_C = –27.8, δ_D = –27.6, J_{AB} = –43.0 Hz, J_{AC} = –5.4 Hz, J_{AD} = 30.3 Hz, J_{BC} = –7.0 Hz, J_{BD} = 185.6 Hz, J_{CD} = 19.6 Hz. The platinum satellites give the following J_{PPt} couplings: J_{APt} = 78 Hz, J_{BPt} = 517 Hz, J_{CPt} = 2605 Hz, J_{DPt} = 1910 Hz. There are some minor differences between the observed and calculated $^{31}P\{^1H\}$ NMR spectra; despite many attempts, a better agreement was not obtainable. IR (cm^{-1}): 1677 (s), 1560 (s), 1534 (m), 1319 (vw), 1304 (vw), 1292 (vw), 1252 (s), 1189 (s), 1177 (m), 1152 (m), 1127 (s), 1071 (vw), 952 (s), 861 (w), 786 (w), 745 (w), 729 (w), 672 (vw), 661 (m), 578 (w).

Method B. To a solution of $Pt(PMe_3)_4$ (0.20 g, 0.40 mmol) in diethyl ether (10 mL) was added a solution of $[Pd(hfac)(PMe_3)_2][hfac]$ (0.27 g, 0.40 mmol) in diethyl ether (15 mL). The initially orange cloudy solution turned yellow, and a yellow precipitate began to form after the mixture had been stirred for a few minutes. The mixture was stirred at room temperature for 2 h, and the yellow powder was collected by filtration, washed with diethyl ether (10 mL), and dried under vacuum. Yield: 0.30 g (64%). The product prepared in this way was contaminated with significant amounts of the dipalladium complex $[Pd_2(PMe_3)_6][hfac]_2$; the molar ratio of the PdPt compound to the Pd_2 compound was approximately 5:4 as judged from the ^1H NMR spectrum.

Dichlorotetrakis(trimethylphosphine)dipalladium(I), $Pd_2(PMe_3)_4Cl_2$ (3). To a mixture of **1** (0.64 g, 0.59 mmol) and LiCl (0.18 g, 4.2 mmol) at 25 °C was added tetrahydrofuran (40 mL). The resulting mixture was stirred at room temperature for 12 h to afford a yellow cloudy suspension. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (80 mL). The dichloromethane extract was filtered, and the filtrate was concentrated to ca. 20 mL and cooled to –20 °C to afford yellow microcrystals. Yield: 0.31 g (89%). Mp: 190 °C dec. Anal. Calcd for $C_{12}H_{36}Cl_2P_4Pd_2$: C, 24.5; H, 6.17; Cl, 12.1; Pd, 36.2, P, 21.0. Found: C, 24.4; H, 6.25; Cl, 12.7; Pd, 33.2; P, 18.3. ^1H NMR (CD_2Cl_2, 25 °C): δ 1.53 ("t", $^2J_{HP} + {}^4J_{HP}$ = 5.4 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ –20.2 (s). IR (cm^{-1}): 1425 (m), 1301 (w), 1283 (s), 1143 (vw), 951 (vs), 863 (vw), 850 (m), 733 (s), 675 (m).

Diiodotetrakis(trimethylphosphine)dipalladium(I), $Pd_2(PMe_3)_4I_2$ (4). To a mixture of **1** (0.71 g, 0.66 mmol) and NaI (0.35 g, 2.3 mmol) at 25 °C was added tetrahydrofuran (50 mL). The resulting mixture was stirred at room temperature for 18 h to afford an orange, cloudy suspension. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (70 mL). The dichloromethane extract was filtered, and the filtrate was concentrated to 30 mL and cooled to –20 °C to afford orange microcrystals. Yield: 0.46 g (91%). Mp: 200 °C dec. Anal. Calcd for $C_{12}H_{36}I_2P_4Pd_2$: C, 18.7; H, 4.71; I, 32.9; Pd, 27.6, P, 16.1.

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Found: C, 18.8; H, 4.82; I, 33.0; Pd, 24.5; P, 13.8. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.66 ("t", $^2J_{HP} + {}^4J_{HP}$ = 5.0 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ −27.4 (s). IR (cm^{-1}): 1420 (m), 1298 (m), 1281 (s), 945 (vs), 847 (s), 722 (s), 666 (s).

Sublimation of $[Pd_2(PMe_3)_6][hfac]_2$ and Identification of Methyltris(trimethylphosphine)palladium(II) 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate, $[PdMe(PMe_3)_3][hfac]$ (5). A sample of $[Pd_2(PMe_3)_6][hfac]_2$ (0.24 g, 0.22 mmol) was placed in a sublimator equipped with a cold finger cooled to −78 °C. The sublimator was evacuated and heated to 100 °C for ca. 3 h; a dark involatile residue (0.1 g) remained after the sublimation was complete. (At 120 °C, decomposition occurs within a few minutes and relatively little sublimate appears.) The yellow sublimate (0.12 g) was collected and examined by NMR spectroscopy. Apart from small peaks due to the dinuclear palladium(I) complex **1**, the spectra contained the following resonances due to the palladium(II) methyl compound **5**. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 5.42 (s, $HC(COCF_3)_2$), 1.39 (d, $^2J_{HP}$ = 7 Hz, PMe_3), 0.32 (s, Pd–Me). ^{1}H NMR (CD_2Cl_2, −80 °C): δ 5.45 (s, $HC(COCF_3)_2$), 1.39 (br s, PMe_3), 0.14 (q, $^2J_{HP}$ = 7 Hz, Pd-Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ −13.5 (d, $^2J_{PP}$ = 43 Hz), −25.9 (t, $^2J_{PP}$ = 43 Hz). Integration of the NMR spectra showed that **1** and **5** were present in about a 1:5 molar ratio, respectively. The room-temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectra of **5** are affected by intermolecular exchange with free PMe_3. The quartet line shape seen for the PdMe group at −80 °C does not mean that **5** is fluxional; the $^{31}P\{^1H\}$ NMR spectrum at this temperature shows clearly that it is not. Instead, the cis and trans $^3J_{PH}$ coupling constants must be accidentally identical. A similar situation pertains for the platinum analogue (see below).

Thermolysis of $[PdPt(PMe_3)_6][hfac]_2$ and Identification of Methyltris(trimethylphosphine)platinum(II) 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate, $[PtMe(PMe_3)_3][hfac]$ (6). A sample of $[PdPt(PMe_3)_6][hfac]_2$ (0.23 g, 0.20 mmol) was placed in a sublimator equipped with a cold finger cooled to −78 °C. The sublimator was evacuated and heated to 140 °C for ca. 3 h; a dark involatile residue (0.1 g) remained after the sublimation was complete. The yellow oily sublimate was collected and examined by NMR spectroscopy; the spectra contained the following resonances due to the platinum(II) complex $[PtMe(PMe_3)_3][hfac]$. ^{1}H NMR (CD_2Cl_2, −80 °C): δ 5.60 (s, $HC(COCF_3)_2$), 1.50 (br s, PMe_3), 0.23 (q, $^3J_{HP}$ = 8 Hz, $^2J_{HPt}$ = 57 Hz, Pt–Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ −17.1 (d, $^2J_{PP}$ = 23.6 Hz, $^1J_{PPt}$ = 2542 Hz), −24.1 (t, $^2J_{PP}$ = 23.6 Hz, $^1J_{PPt}$ = 1809 Hz). Also present in the sublimate in small amounts (<5 mol %) were the palladium(II) methyl complex $[PdMe(PMe_3)_3][hfac]$, the palladium(II) complex $[Pd(hfac)(PMe_3)_2][hfac]$, and the platinum(II) complex $[Pt(PMe_3)_4][hfac]_2$.[26]

(1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato)bis(trimethylphosphine)palladium(II) 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate, $[Pd(hfac)(PMe_3)_2][hfac]$. To a solution of $Pd(hfac)_2$ (0.62 g, 1.12 mmol) in diethyl ether (30 mL) was added PMe_3 (0.25 mL, 2.41 mmol). The solution turned yellow instantly. After the solution had been stirred at room temperature for 1 h, the yellow solution was filtered, and the filtrate was concentrated to ca. 15 mL and cooled to −20 °C. The pale yellow crystals of the product were collected and dried under vacuum. Yield: 0.72 g (90%). The product isolated from diethyl ether contained variable amounts of solvent; analytically pure material may be obtained by sublimation at 120 °C and 10^{-3} Torr. Mp: 101–102 °C. Anal. Calcd for $C_{16}H_{20}F_{12}O_4P_2Pd$: C, 28.6; H, 3.00; P, 9.21; Pd, 15.8. Found: C, 28.6; H, 3.05; P, 9.16; Pd, 15.7. ^{1}H NMR (C_6D_6, 25 °C): δ 6.17 (s, $HC(CO_2CF_3)_2$), 1.22 (d, $^2J_{HP}$ = 10.0 Hz, PMe_3). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 5.89 (s, $HC(CO_2CF_3)_2$), 1.81 (d, $^2J_{HP}$ = 11.4 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 11.0 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 11.4 (s). The appreciable solvent dependence of the ^{1}H NMR chemical shifts suggests that in nonpolar solvents (such as benzene) the cations and anions form close-contact ion pairs. IR (cm^{-1}): 1670 (s), 1643 (s), 1597 (vw), 1557 (s), 1527 (s), 1418 (w), 1348 (w), 1296 (w), 1267 (s), 1239 (w), 1207 (s), 1178 (s), 1150 (s), 1120 (s), 1100 (w), 977 (m), 948 (s), 930 (w), 860 (w), 850 (w), 810 (w), 795 (m), 778 (m), 740 (m), 680 (m), 670 (w), 655 (m), 594 (w), 570 (w).

This complex is similar to other 2:1 Lewis base adducts of $Pd(hfac)_2$ that have been described.[16,17] The ionic nature of $[Pd(hfac)(PMe_3)_2][hfac]$ is shown by the presence of *two* C=O stretches in its infrared spectrum: 1670 cm^{-1} (for the ionic hfac group) and 1643 cm^{-1} (for the coordinated hfac group). An alternative structural possibility with two unidentate hfac groups, $Pd(\eta^1\text{-hfac})_2(PMe_3)_2$, is ruled out by a conductivity of 24.2 Ω^{-1} cm^2 mol^{-1} measured in nitrobenzene, which is in the 20–30 Ω^{-1} cm^2 mol^{-1} range for 1:1 electrolytes in this solvent. The presence of only a single methine resonance in the ^{1}H NMR spectrum demonstrates that the ionic and coordinated hfac groups rapidly exchange in solution at 25 °C.[16,17]

Crystallographic Studies.[94] Single crystals of $[Pd_2(PMe_3)_6][hfac]_2$, grown from diethyl ether/dichloromethane, were mounted on glass fibers using Paratone-N oil (Exxon) and were immediately cooled to −75 °C in a nitrogen stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and the diffraction symmetry was supported by examinations of the axial photographs. Least-squares refinement using 25 reflections yielded the cell dimensions given in Table 1.

Data were collected in one quadrant of reciprocal space ($-h,+k,\pm l$). Systematic absences for hkl ($h + k \neq 2n$) and $h0l$ ($l \neq 2n$) were consistent with space groups $C2/c$ and Cc. The centrosymmetric choice $C2/c$ was subsequently confirmed by successful solution and refinement of the proposed model; attempted least-squares refinement of the structure in the acentric space group Cc led to non-positive definite thermal coefficients for several of the carbon and oxygen atoms. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by direct methods (SHELXS-86) and unweighted difference Fourier syntheses. The positions of the palladium atoms were deduced from an E map, and subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms and hydrogen atom H3. The remaining hydrogen atoms were included in the refinement as fixed contributors in "idealized" positions with C–H = 0.96 Å. The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1.41/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least squares, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients, an isotropic thermal parameter was refined for atom H3, and a common group isotropic thermal parameter was varied for the other hydrogen atoms. An empirical isotropic extinction parameter was also refined, which converged to 1.0×10^{-8}. Successful convergence was indicated by the maximum shift/error of 0.003 in the last cycle. Final refinement parameters are given in Table 1. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed no systematic errors.

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Supplementary Material Available: Tables of full crystal data, calculated hydrogen atom positions, anisotropic thermal parameters, and complete bond angles for $[Pd_2(PMe_3)_6][hfac]_2$ and an ORTEP diagram for the hfac anion (5 pages). Ordering information is given on any current masthead page.

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