the (C)H hydrogen atoms of 2 and 3 were included as fixed atoms with $U_{iso(fix)}$ = 0.05. The remaining hydrogen atoms were refined isotropically. No absorption corrections were carried out. One of the CCl_4 molecules in 1a was strongly disordered. Coordinates and equivalent isotropic thermal parameters are shown in Tables V–VII. Crystals of 1 obtained from ethyl acetate were found to crystallize in the triclinic space group $P\bar{1}$ with cell constants a = 12.411 (6), b = 14.863 (4), c = 33.298 (9) Å; α = 94.87 (2)°; β = 97.87 (3)°; γ = 103.99 (3)°, and probably six molecules in the cell. Programs used for calculations were SHELX 76, SHELXS 88, and PLATON-90.[21]

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Supplementary Material Available: Tables of atomic coordinates and anisotropic temperature factors for 1–3 (7 pages). Ordering information is given on any current masthead page.

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Preparation of Doubly Acetylide-Bridged Binuclear Platinum–Platinum and Platinum–Palladium Complexes. Structures of $[\{(dppe)Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ and $(PMePh_3)_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$

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The reaction between $[cis\text{-}Pt(C{\equiv}CR)_2L_2]$ (R = Ph, ^tBu; L_2 = 2 PPh_3, dppe, COD) and $[cis\text{-}M(C_6F_5)_2(THF)_2]$ (M = Pd, Pt; THF = tetrahydrofuran) in a 1:1 molar ratio affords neutral binuclear derivatives of the type $[\{L_2Pt(C{\equiv}CR)_2\}M(C_6F_5)_2]$ in which the RC≡C—Pt—C≡CR group is acting as a bidentate ligand to "$M(C_6F_5)_2$". In contrast, $[cis\text{-}M(C_6F_5)_2(THF)_2]$ reacts with $Q_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ and $Q_2[Pt(C_6F_5)(C{\equiv}CR)_3]$ (R = Ph, Q = $PMePh_3$; R = ^tBu, Q = NBu_4) to give anionic diplatinum and platinum–palladium complexes of types $Q_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2M(C_6F_5)_2]$ and $Q_2[(C_6F_5)(C{\equiv}CR)Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$, respectively. The crystal structures of the complexes $[\{(dppe)Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ (3) and $(PMePh_3)_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ (9) have been established by X-ray diffraction methods. 3 is a binuclear complex in which the unit "$(dppe)Pt(\sigma\text{-}C{\equiv}CPh)_2$" acts as a chelate metallo ligand to "$Pt(C_6F_5)_2$". In contrast, the crystal structure for 9 shows that two identical $[(C_6F_5)_2Pt{-}C{\equiv}CPh]$ units are joined together through η^2 bonding of C≡CPh groups. This indicates that the complex is formed from the bis(σ-alkynyl)bis(pentafluorophenyl)platinate and the synthon $Pt(C_6F_5)_2$ via migration of one σ-alkynyl group between the two platinum metal centers.

Introduction

Over the past decade there has been growing interest in homo- and heterobinuclear complexes stabilized through bridging acetylide ligands. Much of the interest in those organometallic systems stems from the special bonding situations of C≡CR groups.[1] In binuclear complexes the C≡CR ligand appears as a bridging group that exhibits a varying degree of bending (I–III; Chart I).

The bonding situations I and II are well represented in binuclear complexes containing main-groups and f orbital metals,[2] but only a few examples of the type III have been reported: $[Cp_2Ti(C{\equiv}CSiMe_3)]_2$,[3] $[(COD)Ir(C{\equiv}CSiMe_3)]_2$,[4] and $[(MeCp)_2Zr(C{\equiv}CPh)_2]$.[5] Interestingly, the titanium derivative having a stoichiometry similar to that of the Zr one seems to give initially the binuclear complex with two bridging acetylides but spontaneously undergoes an oxidative coupling at C_α of the acetylide ligands to form (μ-(1–3)η:(2–4)η-*trans*,*trans*-1,4-diphenylbutadiene)bis(bis(η^5-methylcyclopentadienyl)titanium).[6,7] A similar coupling of phenylethynyl ligands has recently been re-

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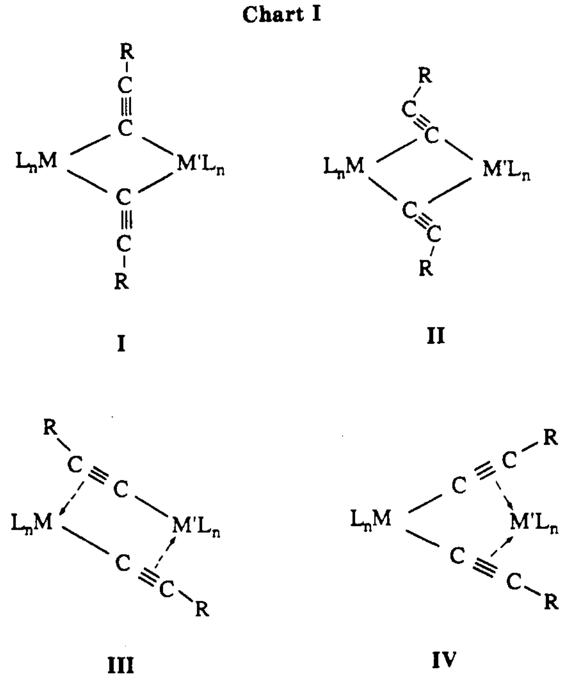
Table I. ^{19}F NMR Data for the Complexes in $CDCl_3$[a]

compd	temp, °C	F_{ortho}	F_{para}	F_{meta}	$^3J(Pt-F_{ortho})$[c]	$^3J(F_{para}-F_{meta})$[c]
1	20	−117.1 (d)	−164.4 (t)	−166.5 (br)	406	20
	−55	−116.5 (s, br), −118.3 (d)	−163.5 (t)	−165.3 (s, br), −166.4 (s, br)		
2	20	−114.5 (s, br), −115.7 (d)	−164.6 (t)	−165.8 (s, br), −166.8 (m)	405, 447	20
	50	−114.4 (s, br),[d] −115.6 (s, br)[d]	−164.8 (t)	−166.0 (br),[d] −166.5 (br)[d]		
3[b]	20	−115.14 (d)	−164.6 (t)	−166.2 (m)	405	19
	−80	−114.0 (s, br), −116.5 (s, br)	−163.1 (t)	−164.9, −165.2 (d, br)		
4	20	−114.5 (s, br), −116.5 (d)	−164.7 (t)	−165.9 (s, br),[d] −166.4 (m)[d]	402, 460	19
	50	−114.4 (s, br),[d] −116.4 (s, br)[d]	−164.9 (t)	−166.4 (s, br)		
5	20	−119.2 (s, br)	−163.1 (t)	−165.4 (m)	410	20
	−55	−117.2 (br),[d] −121.4 (br)[d]	−162.3 (t)	−164.7 (s, br)		
6	20	−114.7 (s), −121.0 (s)	−163.2 (t)	−164.9,[d] −165.5[d]	387, 466	20
	50	−114.5 (br), −121.0 (br)	−163.4 (t)	−165.4 (br)		
7	20	−115.1 (d)	−164.0 (t)	−166.2 (m)		20
	−55	−114.7 (d)	−162.5 (t)	−165.0 (br)		
8	20[e]	−111.9 (d), −113.0 (d)	−163.9 (t)	−165.9 (m), −166.7 (m)		20
9	20	−117.3 (d)	−166.2 (t)	−166.7 (m)	411	20
	−60	−117.3,[d] −117.85 (br)[d]	−165.3 (t)	−166.4 (br)		
10	20[f]	−116.1 (d)	−167.5 (t)	−168.3 (m)	442	20
11	20	−113.6 (d, −Pd), −115.1 (d, −Pt)	−165.1 (t, Pd)	−165.8 (m), −167.3 (m)[i]	390	
12[b,g]	20	−107.7 (d −Pd), −112.2 (d, −Pt)	−166.7 (t, −Pd)	−166.1 (m, −Pd), −168.6 (m, −Pt)	420	19 (−Pd), 20 (−Pt)
			−169.94 (t, −Pt)			
13	20	−116.9 (d), −117.3 (d), −118.0 (d)		−167.4 (m), −167.8 (m)		
14	20	−114.9,[h] −114.1,[h] −114.5 (d)		−168.5 (m), −169.4 (m)	412, 442, 431	

[a] Chemical shifts are given in δ, with reference to $CFCl_3$. [b] In CD_3COCD_3. [c] In Hz. [d] Overlapping of signals on base line. [e] The same sharp pattern is found at 50 °C. [f] The same pattern is found at −30 and −50 °C. [g] Identical spectra are found at 20 °C for **12a**. [h] Both signals partially overlap. [i] This multiplet also includes a signal due to F_{para} (Pt).

Chart I



ported for a samarium center.[8] Binuclear derivatives in which the $L_nM(C{\equiv}CR)_2$ unit acts as a chelate ligand toward a $M'L_n$ fragment are also rather scarce.[9,10] When the present work was already in progress, two molecular structures of binuclear complexes with bridging acetylides adopting the bonding situation IV were reported: $[\{L_2Ti(C{\equiv}CPh)_2\}Co(CO)]$ and $[\{L_2Ti(C{\equiv}CSiMe_3)_2\}FeCl_2]$ ($L = \eta^5-C_5H_4SiMe_3$).[10]

Although the chemistry of dinuclear platinum and palladium complexes stabilized through bridging ligands such as halide, SCN, pyrazole, SR, OOCR, PR_2, etc. is well established,[11] no similar complexes with two bridging acetylides have been described so far. The only few cases reported have been the titanium–platinum derivatives $[(\eta-C_5H_5)Ti(C{\equiv}CPh)_2\}Pt^0PR_3]$, which on the basis of spectroscopic data have been formulated as chelate complexes (type IV) with the Ph—C≡C—Ti—C≡CPh group acting as a bidentate ligand to platinum.[9b]

In this paper we wish to report on the synthesis and crystallographic characterization of two types of bis(μ-acetylide) complexes: some neutral diplatinum and platinum–palladium derivatives in which both acetylides are bound to one metal center in a η^1 fashion (σ-bonded) and to the other one in a η^2 fashion (π-bonded), i.e. adopting the bonding situation IV (Chart I), and several anionic diplatinum or heterometallic platinum–palladium complexes where the metal centers are doubly bridged by acetylide ligands adopting the bonding situation III (Chart I). Complexes of the first type have been obtained by reacting the neutral $[L_2Pt(C{\equiv}CR)_2]$ complexes with $[cis-M(C_6F_5)_2(THF)_2]$ (M = Pd, Pt), while the anionic symmetric complexes of the second type have been prepared through reactions between $Q_2[cis-Pt(C_6F_5)_2(C{\equiv}CR)_2]$ and $[cis-M(C_6F_5)_2(THF)_2]$.

Results and Discussion

Synthesis and Characterization of $[\{L_2Pt(C{\equiv}CR)_2\}M(C_6F_5)_2]$. $[cis-M(C_6F_5)_2(THF)_2]$ (M = Pd, Pt) reacts with the neutral acetylide complexes $[cis-Pt(C{\equiv}CR)_2L_2]$, yielding the binuclear derivatives $[\{L_2Pt(C{\equiv}CR)_2\}M(C_6F_5)_2]$, in which the bis(σ-alkynyl)platinum compound, after displacing the THF ligands of the $[M(C_6F_5)_2(THF)_2]$ substrate, is acting as a chelating metallo

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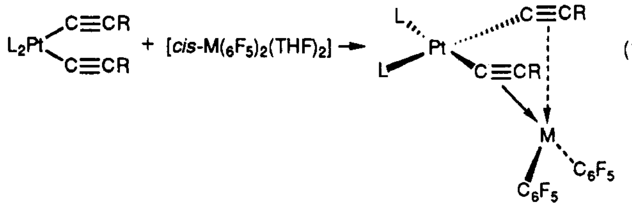
ligand toward the "$M(C_6F_5)_2$" fragment (eq 1).



(1)

M = Pt, L_2 = 2 PPh_3, R = Ph (**1**), R = ^tBu (**2**)
M = Pt, L_2 = dppe, R = Ph (**3**), R = ^tBu (**4**)
M = Pt, L_2 = COD, R = Ph (**5**), R = ^tBu (**6**)
M = Pt, L_2 = 2 PPh_3, R = Ph (**7**), R = ^tBu (**8**)

Elemental analyses, molecular weights, and other structural data for these complexes are given in the Experimental Section. ^{19}F NMR data are collected in Table I.

In order to ascertain the most relevant features of the acetylide bridges, an X-ray diffraction study of $[\{(dppe)Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ (**3**) was carried out. Single crystals were obtained by slow diffusion of *n*-hexane into an acetone solution of **3**. Figure 1 shows an ORTEP drawing of this molecule. Selected bond distances and angles are listed in Table II. The structure analysis reveals that the complex is nonplanar dimer with the acetylide bridging system displaying an structural situation of type IV (Chart I).

Pt(1) is in an approximately square-planar environment formed by two phosphorus atoms of the dppe ligand and one carbon atom of each C≡CPh ligand. The Pt(1)–C (Pt(1)–C(27) = 2.009 (12), Pt(1)–C(35) = 1.983 (12) Å) and Pt(1)–P distances (2.271 (6) and 2.282 (6) Å) are in the range found in the literature for σ-acetylide–[12] or phosphine–platinum(II)[12a–g,13] complexes. The angles P(2)–Pt(1)–P(1) and C(35)–Pt(1)–C(27) are 85.9 (2) and 79.3 (4)°, respectively. Pt(2) is located in a distorted-square-planar environment formed by the C(ipso) atoms of the C_6F_5 groups and the midpoints of the C–C triple bonds. The dihedral angle formed by the planes Pt(2)–C(43)–C(49) and Pt(2)–C(0)–C(0′) (C(0) and C(0′) are the midpoints of the C≡C triple bonds) is 13.14 (30°). The bonding mode between the C≡CPh groups and Pt(2) is schematized in Figure 2. As can be seen, the Pt(2)–C(acetylide) distances are equal (within experimental error) so that the interactions between the acetylide ligands and Pt(2) (η^2 linkages) are symmetric. The Pt(2)–C distances (see Figure 2) are similar to those reported for $[Pt(C_6F_5)_2(PhC{\equiv}CPh)_2]$,[14] and the C≡C bond distances (C(27)–C(28) = 1.234 (16), C(35)–C(36) = 1.229 (17) Å) are similar to distances reported for other σ–π-acetylide complexes.[4,10,12h,i,15] As a consequence of the η^2 coordination on the acetylide ligands to Pt(2), these groups are not linear; the angles Pt(1)–C(27)–C(28) = 167.2 (10), Pt(1)–C(35)–C(36) = 159.2 (10), C(27)–C(28)–C(29) = 164.6 (12), and C(35)–C(36)–C(37) = 156.2 (12)° are in the range

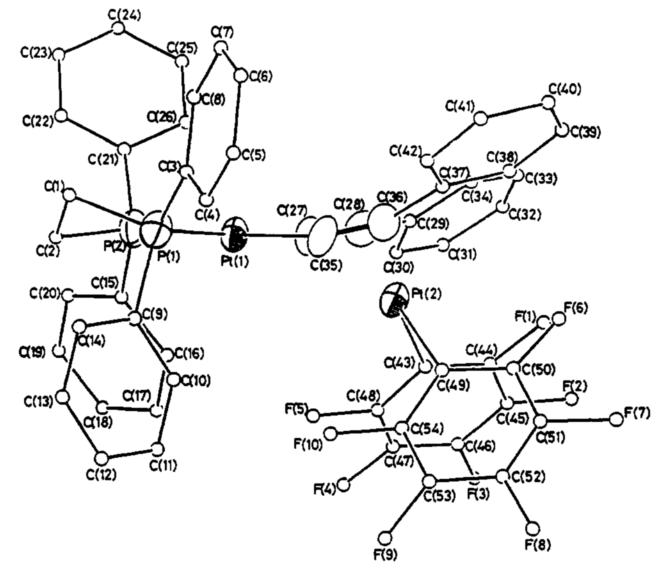


Figure 1. View of the structure of complex $[\{(dppe)Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ (**3**) with the atomic numbering scheme.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for Complex 3

Pt(1)–P(1)	2.271 (6)	Pt(1)–P(2)	2.282 (6)
Pt(1)–C(27)	2.009 (12)	Pt(1)–C(35)	1.983 (12)
Pt(2)–C(27)	2.345 (12)	Pt(2)–C(28)	2.336 (12)
Pt(2)–C(35)	2.279 (12)	Pt(2)–C(36)	2.269 (13)
Pt(2)–C(43)	2.033 (13)	Pt(2)–C(49)	2.033 (14)
P(1)–C(1)	1.842 (14)	P(1)–C(3)	1.809 (10)
P(1)–C(9)	1.816 (10)	P(2)–C(2)	1.848 (14)
P(2)–C(15)	1.809 (9)	P(2)–C(21)	1.818 (10)
C(1)–C(2)	1.573 (21)	C(27)–C(28)	1.234 (16)
C(28)–C(29)	1.427 (14)	C(35)–C(36)	1.229 (17)
C(36)–C(37)	1.462 (15)	C(43)–C(44)	1.358 (16)
C(43)–C(48)	1.375 (18)	C(44)–C(45)	1.415 (18)
C(44)–F(1)	1.352 (15)	C(45)–C(46)	1.357 (21)
C(45)–F(2)	1.353 (15)	C(46)–C(47)	1.336 (20)
C(46)–F(3)	1.342 (17)	C(47)–C(48)	1.382 (20)
C(47)–F(4)	1.358 (17)	C(48)–F(5)	1.337 (16)
C(49)–C(50)	1.346 (19)	C(49)–C(54)	1.383 (21)
C(50)–C(51)	1.375 (22)	C(50)–F(6)	1.364 (18)
C(51)–C(52)	1.304 (29)	C(51)–F(7)	1.403 (18)
C(52)–C(53)	1.350 (28)	C(52)–F(8)	1.337 (22)
C(53)–C(54)	1.341 (23)	C(53)–F(9)	1.354 (24)
C(54)–F(10)	1.385 (17)		
P(1)–Pt(1)–P(2)	85.9 (2)	P(1)–Pt(1)–C(27)	173.4 (3)
P(2)–Pt(1)–C(27)	100.1 (3)	P(1)–Pt(1)–C(35)	94.6 (3)
P(2)–Pt(1)–C(35)	177.8 (3)	C(27)–Pt(1)–C(35)	79.3 (4)
C(27)–Pt(2)–C(28)	30.6 (4)	C(35)–Pt(2)–C(36)	31.4 (4)
C(43)–Pt(2)–C(49)	88.1 (5)	Pt(1)–P(1)–C(1)	107.3 (5)
Pt(1)–P(1)–C(3)	114.5 (3)	C(1)–P(1)–C(3)	107.8 (6)
Pt(1)–P(1)–C(9)	114.5 (3)	C(1)–P(1)–C(9)	105.7 (6)
C(3)–P(1)–C(9)	106.6 (4)	Pt(1)–P(2)–C(2)	107.2 (4)
Pt(1)–P(2)–C(15)	117.4 (3)	C(2)–P(2)–C(15)	103.7 (5)
Pt(1)–P(2)–C(21)	115.1 (3)	C(2)–P(2)–C(21)	107.9 (5)
C(15)–P(2)–C(21)	104.7 (4)	P(1)–C(1)–C(2)	105.7 (9)
P(2)–C(2)–C(1)	108.4 (9)	Pt(1)–C(27)–C(28)	167.2 (10)
C(27)–C(28)–C(29)	164.6 (12)	Pt(1)–C(35)–C(36)	159.2 (10)
C(35)–C(36)–C(37)	156.2 (12)		

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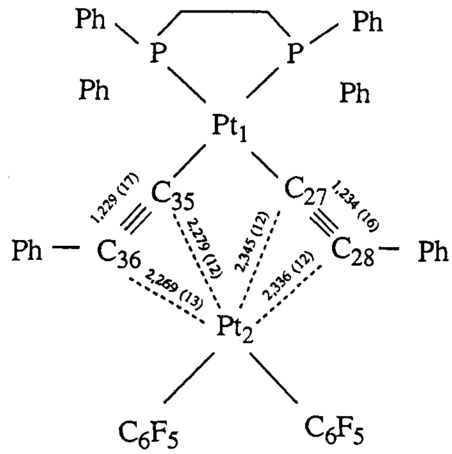

Figure 2. Schematic view of the μ-η^2-bonded acetylide groups for the complex $[\{(dppe)Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ (3) with bond lengths in Å.

found in other similar μ–η^2 bridging acetylide complexes.[3–5,10,12h,i,16,17] Both acetylide ligands have a trans-bent arrangement. Although usually cis-bent arrangements have been observed in metal–olefin or –acetylene complexes,[18] cis- and/or trans-bent arrangements have been found in acetylide complexes containing σ- and π-acetylide bonds.[12h,i,17]

On the other hand, the dihedral angle formed by the best least-squares planes around each platinum environment is 133.74°; the angles formed by C≡C triple bonds and the corresponding vectors defined by Pt(2) and the midpoints of the C≡C bonds are 91.59 and 90.48°, respectively, and C≡C triple bonds are inclined by 40.87 and 39.39° to the normal to the coordination plane of Pt(2) (best least-squares plane defined by C(ipso) atoms of the C_6F_5 groups, Pt(2), and the midpoints of the C≡C triple bonds). Finally, the distance between Pt(1) and Pt(2) is 3.27 Å, excluding any metal–metal bonding interaction.

IR and NMR Spectra. All complexes show two absorptions in the 805–775-cm^{-1} region due to the X-sensitive mode of the C_6F_5 groups, thus indicating that both C_6F_5 groups are in cis positions.[19] Complexes **4**, **5**, **6**, and **8** exhibit one weak absorption in the 2017–2053-cm^{-1} region assignable to ν(C≡C) of the acetylide groups, in the range expected for carbon–carbon triple bonds side-on coordinated to a transition-metal center.[9b,12h,i] Absorptions due to ν(C≡C) for complexes **1**, **2**, **3**, and **7** were not observed in their IR spectra.

The ^1H and ^{31}P NMR data for complexes **1**–**8** are in good agreement with the proposed structures. According to the proposed formulas the complexes must have a symmetry plane which makes the two phosphorus atoms (for complexes **1**–**4**, **7**, and**8**) and the two ^tBu groups (for **2**, **4**, **6**, and **8**) equivalent. In keeping with all this, ^1H NMR

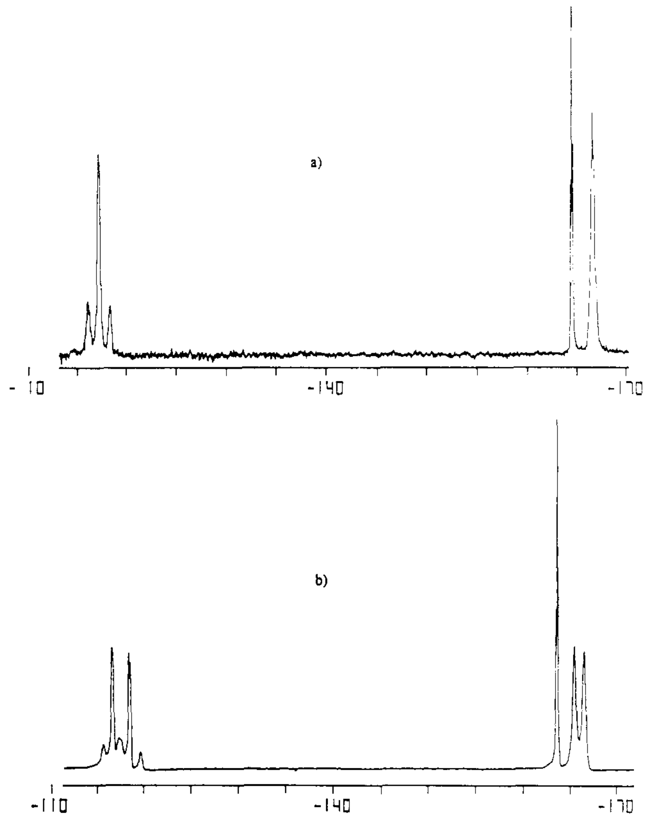

Figure 3. ^{19}F NMR spectra for the complex $[\{(PPh_3)_2Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ (1): (a) at 20 °C; (b) at −55 °C.

spectra of *tert*-butylacetylide complexes show only one resonance singlet due to ^tBu groups. The signals due to the phosphorus atoms of PPh_3 (complexes **1**, **2**, **7**, and **8**) and dppe (complexes **3** and **4**) appear as a pseudotriplet (1:4:1) because of coupling with ^{195}Pt (abundance 33.7%). For the heterometallic complexes **7** and **8**, these phosphorus signals with platinum satellites indicate that both phosphines are bonded to the platinum atom.

The ^{19}F NMR spectra are more interesting. The spectra of complexes with R = ^tBu (**2**, **4**, **6**, and **8**) are typical of static molecules on the NMR time scale. They consist of five signals of equal intensity, thus indicating that both C_6F_5 groups are equivalent but the five fluorine atoms on each C_6F_5 are inequivalent. This pattern is in keeping with the structure found for complex **3** (see Figure 1), for which the bent conformation of the diplatinacycle should give rise to the inequivalence of the two ortho fluorine and the two meta fluorine (endo and exo) atoms.

In contrast, at room temperature the ^{19}F NMR spectra of phenylacetylide complexes (**1**, **3**, **5**, and **7**) only exhibit three signals (2:1:2). This pattern is typical of an AA′MXX′ system in which the two ortho fluorines are (although magnetically inequivalent) isochronous, and the same applies to the two meta fluorine atoms (see Figure 3, for complex **1**). This spectral pattern can be explained in terms of the occurrence of a dynamic process involving a rapid intramolecular exchange of the $M(C_6F_5)_2$ unit which equilibrates the two ortho fluorines (and the two meta fluorines as well) on each C_6F_5.

A plausible mechanism via an intermediate or a transition state with one of the acetylide ligands symmetrically bridging the two metal atoms is presented in eq 2. It should be noted that this process can be more favorable for the phenyl derivatives, since the positive charge developed at the β-position of acetylide can be stabilized by conjugation with the π electrons of the phenyl group.

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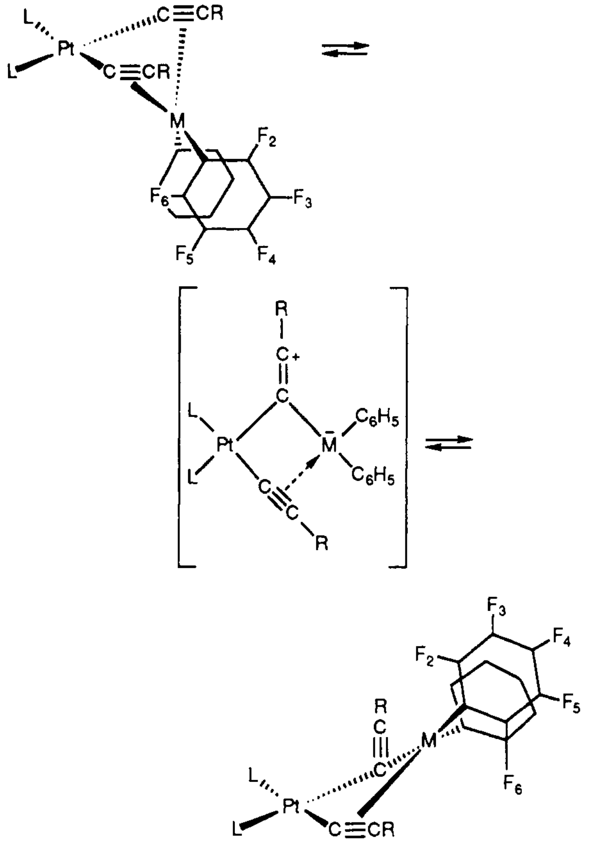


(2)

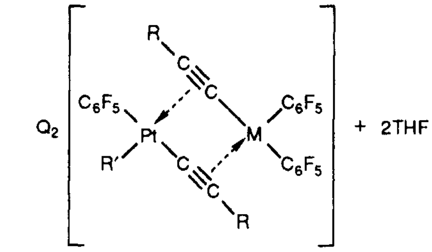
When complexes 1 and 3 were cooled, the F_{ortho} and F_{meta} signals split into two different absorptions (−55 °C for 1 (see Figure 3) and −80 °C for 3). The spectrum of complex 5 at 55 °C shows two signals corresponding to the F_{ortho} atoms, and F_{meta} appears as a broad signal (see Table I); however, when complex 7 is cooled to −55 °C, the F_{ortho} signals do not split but the F_{meta} signal is slightly broadened.

On the other hand, we sought to probe the dynamic behavior of *tert*-butylacetylide derivatives (2, 4, 6, and 8) at high temperature. When the temperature was increased to 50 °C, the resonance due to para fluorine atoms remained unchanged in all complexes but the resonances due to the ortho and meta fluorine atoms clearly broadened for complexes 2, 4, and 6 (for complex 6 the signal due to meta fluorine atoms even appears as a broad signal), suggesting the beginning of the occurrence of the dynamic behavior. However, complex 8 shows the same sharp pattern even when heated to 50 °C.

Synthesis and Characterization of $Q_2[(C_6F_5)R'Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ (R′ = C_6F_5, C≡CR). In contrast with the above-mentioned reactions (eq 1), the anionic platinum substrates $Q_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ (R = Ph, Q = $PMePh_3$; R = ${}^tBu$, Q = NBu_4)[12i] and $Q_2[Pt(C_6F_5)(C{\equiv}CR)_3]$ (R = Ph, Q = $PMePh_3$; R = ${}^tBu$, Q = NBu_4) (see the Experimental Section) react with $[cis\text{-}M(C_6F_5)_2(THF)_2]$ (M = Pt, Pd; THF = tetrahydrofuran), yielding anionic binuclear derivatives (see eq 3) with the double acetylide bridges adopting the bonding situation III depicted in Chart I.

The reactions yielding 9, 10, 13, and 14 were carried out at room temperature, while the low stability of the binuclear mixed-metal complexes (palladium–platinum) requires the use of lower temperature (−10 °C) and a N_2 atmosphere. Analytical results (C, H, and N), molar conductivities, and relevant IR and ^{1}H NMR data for these complexes are given in the Experimental Section. Their conductivities in acetone solutions are those expected for

$Q_2[cis\text{-}Pt(C_6F_5)R'(C{\equiv}CR)_2]$ + $[cis\text{-}M(C_6F_5)_2(THF)_2]$ ⟶



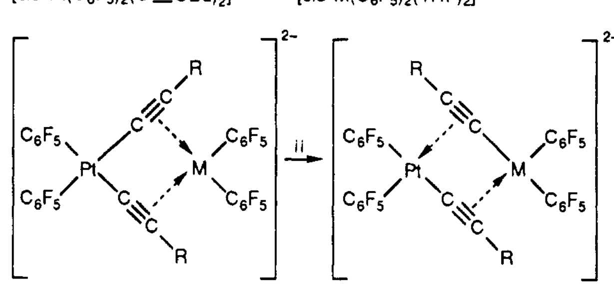
(3)

9: M = Pt, R′ = C_6F_5, R = Ph, Q = $PMePh_3$
10: M = Pt, R′ = C_6F_5, R = ${}^tBu$, Q = NBu_4
11: M = Pd, R′ = C_6F_5, R = Ph, Q = $PMePh_3$
12a,b: M = Pd, R′ = C_6F_5, R = ${}^tBu$, Q = NBu_4
13: M = Pt, R′ = C,≡CR, R = Ph, Q = $PhMePh_3$
14: M = Pt, R′ = C≡CR, R = ${}^tBu$, Q = NBu_4

2:1 electrolytes.[20] The structural characterization of these complexes has been carried out on the basis of their IR and NMR spectra. The structure of complex 9 has been established by a single-crystal X-ray diffraction study and is described below.

The reaction between $(NBu_4)_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]$ and $[cis\text{-}Pd(C_6F_5)_2(THF)_2]$ deserves some comment. If an equimolar mixture of $(NBu_4)_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]$ and $[cis\text{-}Pd(C_6F_5)_2(THF)_2]$ in diethyl ether is stirred at −10 °C for 15 min, the two products **12a** and **12b** can be obtained (see the Experimental Section). Complex **12a** (60% yield) precipitates as a white solid during the reaction time, and the evaporation of the filtrate affords the yellow solid **12b** (15% yield). However, if the mixture is stirred for 6 h, **12b** is the only resulting product (65% yield). Both complexes are analyzed as $(NBu_4)_2[PtPd(C_6F_5)_4(C{\equiv}C^tBu)_2]$, and **12a** isomerizes is solution to **12b** (see Experimental Section). Both facts suggest that **12a** is an intermediate in the formation of **12b**.

$[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CBu)_2]^{2-}$ + $[cis\text{-}M(C_6F_5)_2(THF)_2]$ $\xrightarrow{i}$



(4)

A B
M = Pd, R = ${}^tBu$ (anion of **12a**) M = Pd, R = ${}^tBu$ (anion of **12b**)

Bearing in mind the results described in the above section (eq 3), it seems sensible to assume that complexes 9–14 are formed in two steps: (i) the initial formation of the bis(alkyne)-type adducts A (**12a** is probably the only one of these intermediates stable enough to be isolated) and (ii) the rearrangement to give the binuclear doubly bridged acetylide complexes B (in the case of 12 the transformation of **12a** to **12b**). This rearrangement is in fact an alkynylating process of the fragment $M(C_6F_5)_2$. Such a process does not take place when the neutral derivatives $cis\text{-}L_2Pt(C{\equiv}CR)_2$ are reacted with $M(C_6F_5)_2(THF)_2$ (eq 1), in keeping with previous observations in anionic pentafluorophenyl or pentachlorophenyl palladate or platinate substrates which indicate that the metallic substrate with the higher negative charge has the higher

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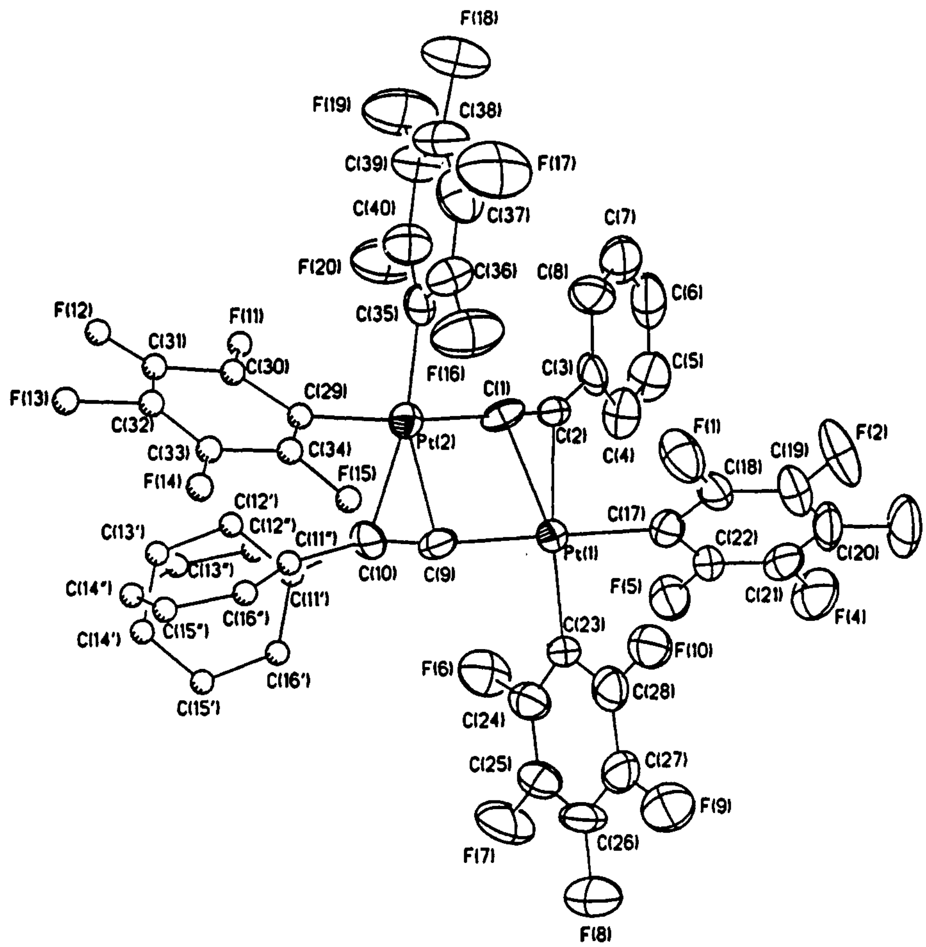

Figure 4. Structure of the anion $[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]^{2-}$ in complex **9** showing the two orientations of the phenyl groups.

arylating capability.[21] On the other hand, the transferral of one acteylide group from one metal center (eq 4) to the other yields a complex less polar (eq 4, B) than would have been expected otherwise (eq 4, A).

Structure of $(PMePh_3)_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ (9). The structure of one complex of this family **9** has been established by an X-ray diffraction study. Suitable crystals were obtained by slow diffusion of *n*-hexane through an acetone solution of **9** at room temperature.

An ORTEP drawing of the anion is presented in Figure 4. Selected bond distances and angles are listed in Table III. As can be seen, the anion is an alkynyl-bridged dimer formed by the mutual interaction of two nearly identical $(C_6F_5)_2Pt(C{\equiv}CPh)$ units so that in each unit the platinum atom is σ-bonded to two C_6F_5 groups (in cis positions) and to one C≡CPh group and π-bonded to the C≡C triple bond of the phenylacetylide ligand of the other unit. The acetylide ligands adopt the bonding situation III depicted in Chart I. The central C_4Pt_2 core is not planar, and the best least-squares planes defined by the atoms Pt(1), Pt(2), C(1), and C(2) and Pt(1), Pt(2), C(9), C(10) form a dihedral angle of 135.83°. A similar nonplanar structure has been found in $[(COD)Ir(C{\equiv}CPh)]_2$[4] (C) (dihedral angle 129°), but $[Cp_2Ti(C{\equiv}CSiMe_3)]_2$[3] (D) and $[(MeCp)_2Zr(C{\equiv}CPh)]_2$[5] (E) display planar C_4M_2 cores. The bond lengths Pt(1)–C(1), Pt(1)–C(2) (2.263 (12), 2.267 (12) Å) and Pt(2)–C(9), Pt(2)–C(10) (2.369 (15), 2.304 (15) Å) are similar to those found in **3** and show that the platinum π-linkages are nearly symmetric. The C≡C distances (C(1)–C(2) = 1.230 (19), C(9)–C(10) = 1.219 (17) Å) are identical (within experimental error) with the corresponding distances found in other similar complexes: C, 1.21 (3) and 1.23 (2) Å;[4] D, 1.253 (15) Å;[3] E, 1.261 Å.[5]

Despite the complexation of the acetylide π-system to the second platinum center, the C≡C distances found in **9** are similar to the average of C≡C distances found in acetylenes (1.20 Å)[22] and the Pt–C_α–C_β fragments remain almost linear (Pt(1)–C(9)–C(10) = 173.2 (1.1), Pt(2)–C(1)–C(2) = 170.4 (1.0)°). However, the deviations from linearity are more pronounced in the fragment containing the C atoms which bear the phenyl substituent (C(1)–C(2)–C(3) = 152.6 (1.2)°, C(9)–C(10)–C(11′) = 147.5 (2.0) or C(9)–C(10)–C(11″) = 160.5 (1.7)°). A similar situation has been found in the related acetylide dimers C–E, for which a considerable π-component in bonding has been proposed.

The distances between the Pt atoms is 3.43 Å, indicating that no metal–metal interaction is present.

Disorder was observed in the phenyl group of one of the alkynyl ligands. A model in which two orientations of the arylic group were given equal weight allowed proper refinement of the structure. Figure 4 shows these orientations, along with their numbering scheme (rings C(11′)–C(16′) and C(11″)–C(16″)).

The disorder of this group accommodates the packing of the molecules in the crystal in a fashion which can be seen clearly in a drawing of the extended structure. The

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Table III. Selected Bond Distances (Å) and Bond Angles (deg) for Complex 9

C(1)-Pt(1)	2.263 (12)	C(2)-Pt(1)	2.267 (12)
C(17)-Pt(1)	2.049 (12)	C(23)-Pt(1)	2.029 (13)
C(9)-Pt(1)	2.023 (13)	C(1)-Pt(2)	1.978 (14)
C(9)-Pt(2)	2.369 (15)	C(10)-Pt(2)	2.304 (15)
C(29)-Pt(2)	2.057 (14)	C(35)-Pt(2)	2.002 (16)
C(41)-P(1)	1.802 (19)	C(42)-P(1)	1.779 (11)
C(48)-P(1)	1.778 (10)	C(54)-P(1)	1.777 (10)
C(60)-P(2)	1.787 (13)	C(66)-P(2)	1.776 (12)
C(72)-P(2)	1.787 (9)	C(78)-P(2)	1.816 (14)
C(2)-C(1)	1.230 (19)	C(3)-C(2)	1.458 (14)
C(18)-C(17)	1.397 (21)	C(22)-C(17)	1.429 (22)
C(19)-C(18)	1.380 (18)	F(1)-C(18)	1.378 (20)
C(20)-C(19)	1.350 (27)	F(2)-C(19)	1.321 (21)
C(21)-C(20)	1.382 (25)	F(3)-C(20)	1.349 (16)
C(22)-C(21)	1.358 (18)	F(4)-C(21)	1.335 (20)
F(5)-C(22)	1.346 (19)	C(24)-C(23)	1.388 (25)
C(28)-C(23)	1.374 (18)	C(25)-C(24)	1.365 (23)
F(6)-C(24)	1.328 (16)	C(26)-C(25)	1.327 (24)
F(7)-C(25)	1.381 (25)	C(27)-C(26)	1.381 (30)
F(8)-C(26)	1.339 (19)	C(28)-C(27)	1.391 (21)
F(9)-C(27)	1.329 (18)	F(10)-C(28)	1.367 (19)
C(10)-C(9)	1.219 (17)	C(11′)-C(10)	1.517 (25)
C(11″)-C(10)	1.429 (18)	C(30)-C(29)	1.470 (20)
C(34)-C(29)	1.383 (21)	C(31)-C(30)	1.505 (29)
F(11)-C(30)	1.222 (20)	C(32)-C(31)	1.319 (31)
F(12)-C(31)	1.297 (22)	C(33)-C(32)	1.366 (32)
F(13)-C(32)	1.464 (32)	C(34)-C(33)	1.471 (34)
F(14)-C(33)	1.316 (31)	F(15)-C(34)	1.340 (20)
C(36)-C(35)	1.381 (22)	C(40)-C(35)	1.381 (18)
C(37)-C(36)	1.339 (26)	F(16)-C(36)	1.372 (15)
C(38)-C(37)	1.380 (21)	F(17)-C(37)	1.353 (19)
C(39)-C(38)	1.307 (27)	F(18)-C(38)	1.382 (22)
C(40)-C(39)	1.397 (25)	F(19)-C(39)	1.345 (17)
F(20)-C(40)	1.349 (19)		
C(2)-Pt(1)-C(1)	31.5 (5)	C(17)-Pt(1)-C(1)	109.5 (5)
C(17)-Pt(1)-C(2)	84.6 (5)	C(23)-Pt(1)-C(1)	160.1 (5)
C(23)-Pt(1)-C(2)	167.5 (6)	C(23)-Pt(1)-C(17)	88.0 (5)
C(9)-Pt(1)-C(1)	70.8 (5)	C(9)-Pt(1)-C(2)	96.7 (5)
C(9)-Pt(1)-C(17)	176.5 (5)	C(9)-Pt(1)-C(23)	91.1 (5)
C(9)-Pt(2)-C(1)	69.2 (5)	C(10)-Pt(2)-C(1)	96.1 (5)
C(10)-Pt(2)-C(9)	30.2 (4)	C(29)-Pt(2)-C(1)	175.2 (5)
C(29)-Pt(2)-C(9)	115.5 (5)	C(29)-Pt(2)-C(10)	88.2 (6)
C(35)-Pt(2)-C(1)	90.0 (5)	C(35)-Pt(2)-C(9)	158.6 (5)
C(35)-Pt(2)-C(10)	169.1 (4)	C(35)-Pt(2)-C(29)	85.4 (6)
C(42)-P(1)-C(41)	106.8 (7)	C(48)-P(1)-C(41)	110.9 (7)
C(48)-P(1)-C(42)	110.4 (6)	C(54)-P(1)-C(41)	109.3 (7)
C(54)-P(1)-C(42)	111.1 (5)	C(54)-P(1)-C(48)	108.3 (5)
C(66)-P(2)-C(60)	110.4 (5)	C(72)-P(2)-C(60)	106.6 (5)
C(72)-P(2)-C(66)	112.3 (5)	C(78)-P(2)-C(60)	108.7 (7)
C(78)-P(2)-C(66)	110.5 (7)	C(78)-P(2)-C(72)	108.1 (6)
Pt(2)-C(1)-Pt(1)	107.8 (6)	C(2)-C(1)-Pt(2)	170.4 (10)
C(3)-C(2)-Pt(1)	132.5 (9)	C(3)-C(2)-C(1)	152.6 (12)
C(43)-C(42)-P(1)	119.6 (9)	C(47)-C(42)-P(1)	120.4 (10)
C(49)-C(48)-P(1)	121.6 (9)	C(53)-C(48)-P(1)	118.4 (6)
C(55)-C(54)-P(1)	118.2 (6)	C(59)-C(54)-P(1)	121.8 (7)
Pt(2)-C(9)-Pt(1)	102.5 (6)	C(10)-C(9)-Pt(1)	173.2 (11)
C(11′)-C(10)-Pt(2)	133.7 (14)	C(11′)-C(10)-C(9)	147.5 (20)
C(11″)-C(10)-Pt(2)	121.4 (12)	C(11″)-C(10)-C(9)	160.5 (17)
C(12′)-C(11′)-C(10)	118.9 (22)	C(16′)-C(11′)-C(10)	119.5 (19)
C(30)-C(29)-Pt(2)	118.8 (10)	C(34)-C(29)-Pt(2)	121.0 (10)
C(34)-C(29)-C(30)	120.1 (14)	C(31)-C(30)-C(29)	116.1 (14)
F(11)-C(30)-C(29)	122.0 (16)	F(11)-C(30)-C(31)	121.9 (15)
C(32)-C(31)-C(30)	116.2 (18)	F(12)-C(31)-C(30)	113.6 (17)
F(12)-C(31)-C(32)	130.1 (21)	C(33)-C(32)-C(31)	132.6 (26)
F(13)-C(32)-C(31)	112.1 (19)	F(13)-C(32)-C(33)	115.0 (21)
C(34)-C(33)-C(32)	111.7 (21)	F(14)-C(33)-C(32)	127.1 (26)
F(14)-C(33)-C(34)	121.1 (20)	C(33)-C(34)-C(29)	123.2 (15)
F(15)-C(34)-C(29)	123.6 (17)	F(15)-C(34)-C(33)	112.8 (16)
C(61)-C(60)-P(2)	120.2 (10)	C(65)-C(60)-P(2)	119.8 (8)
C(67)-C(66)-P(2)	119.6 (8)	C(71)-C(66)-P(2)	120.4 (8)
C(73)-C(72)-P(2)	119.9 (7)	C(77)-C(72)-P(2)	120.1 (7)

disordered congeneric phenyl group C(11′)–C(16′), in the absence of disorder, would make an impossibly short contact with the same group of a neighboring molecule related by a crystallographic inversion center.[23] If the neighboring molecule presents the second congener of the disordered phenyl moiety C(11″)–C(16″), no short contacts exist between the two molecules. It is thus clear that the disorder is the result of packing effects and does not represent features primarily attributable to the conformational predispositions of the free molecule.

IR and NMR Spectra. The IR spectra of the anionic complexes **9–14** exhibit in all cases one strong absorption in the 1931–2041-cm^{-1} region which is assigned to the ν(C≡C) stretching vibration of the Pt(μ-C≡C)$_2$M moiety. The shift to lower wavenumber with respect to those of the starting complexes is consistent with the coordination of the acetylenic group to the adjacent metal atom.[9b,12h,i] On the other hand, the "asymmetric" diplatinum complexes $Q_2[(C_6F_5)(C{\equiv}CR)Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ (R = Ph, Q = $PMePh_3$ (**13**); R = ^{t}Bu, Q = NBu_4 (**14**), in addition to the absorptions attributable to the Pt(μ-C≡CR)$_2$Pt moiety (1956 cm^{-1}, **13**; 1934 cm^{-1}, **14**), exhibit another band at 2109 cm^{-1} assignable to the ν(C≡C) band of the terminal acetylide ligand. Furthermore, complexes **10**, **12b**, and **14** show two IR absorptions in the 800–780-cm^{-1} region due to the X-sensitive mode of the C_6F_5 group, indicating that the cis geometry is retained after the reaction.[19] Complex **12a** exhibits in this region three absorptions with different intensities. For **9**, **11**, and **13** the absorptions around 800 cm^{-1} cannot be unambiguously assigned since the cation $[PMePh_3]^+$ shows internal absorptions in this zone.

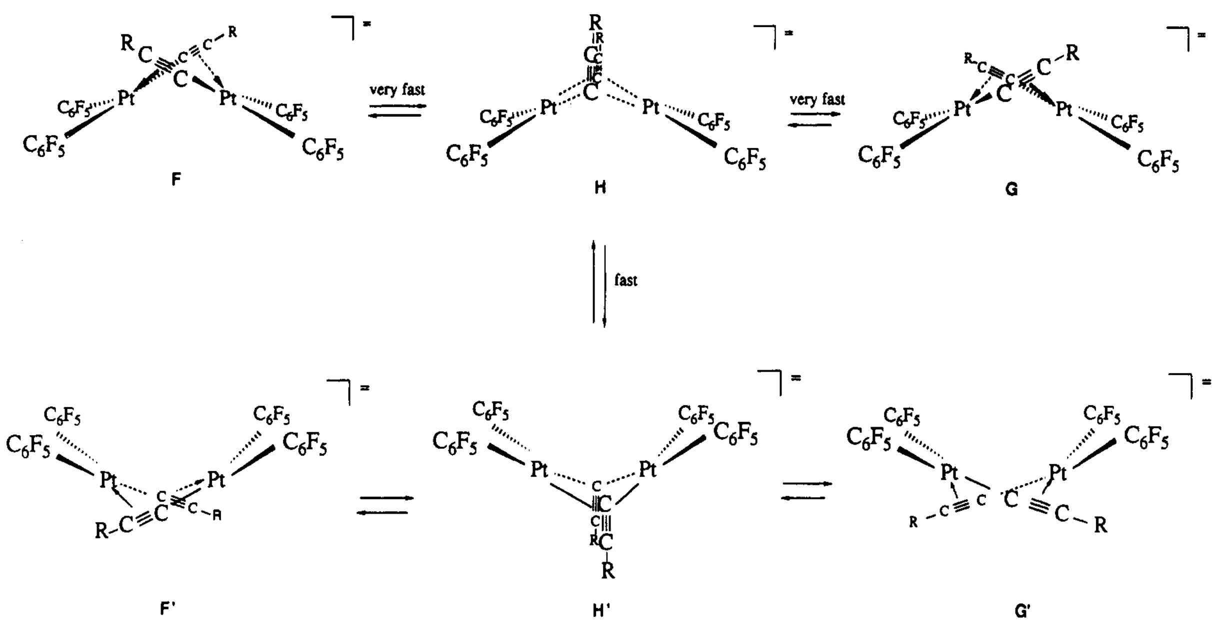
The ^{19}F NMR spectra of complexes **9–14** reveal that, as is usual for other σ–π-acetylide complexes,[5,16c,24] these derivatives display a dynamic behavior on the NMR time scale. For complexes **9** and **10** one should expect to observe signals due to the presence of two nonequivalent pentafluorophenyl groups; in addition, the bent disposition of the dimers (see X-ray structure of **9**) should give rise to inequivalence of the ortho fluorine atoms (and the meta fluorine atoms as well), on each C_6F_5 group. Thus, for a static behavior of **9** and **10** the ^{19}F NMR spectra should present a complex pattern with four ortho, two para, and four meta fluorine resonances. However, at room temperature the spectra show only three signals (2:1:2) (see Table I), indicating an apparent overall D_{2h} symmetry. When the temperature is lowered, (−60 °C), the spectrum of **9** shows inequivalence of the two ortho fluorines and a broad but unresolved signal can be assigned to the meta fluorines. However, the ^{19}F spectrum of **10** at −60 °C shows the same pattern that is observed at room temperature (see Table I). All these facts can be satisfactorily explained by assuming the following: (a) An intramolecular C≡CR migration occurs between the platinum atoms even at low temperature (very fast transformation of F into G or vice versa; Scheme I). Such migration could proceed via an intermediate such as H with symmetrical acetylide bridges. (b) On the other hand, since at room temperature the C_6F_5 ligands give an spectrum with equivalent F_{ortho} atoms and equivalent F_{meta} atoms as well, a second temperature-dependent process must be operating. Since the molecule has a bent arrangement, an inversion of the diplatinacycle is required to produce a time-averaged plane of symmetry. A plausible mechanism for the inversion process is depicted in Scheme I.

Finally, the ^{19}F NMR spectrum of **9** seems to indicate that in this case the energy barrier between F and G or

(23) A drawing showing the interactions between two neighboring molecules is available as supplementary material.

(24) (a) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, *9*, 816. (b) Hwang, D.-K.; Chi, Y.; Peng, S.-H.; Lee, G.-H. *Organometallics* 1990, *9*, 2709. (c) Koridze, A. A.; Kizas, O. A.; Petrovskii, P. V.; Kolobova, N. E.; Struchkov, Yu. T.; Yanovsky, A. I. *J. Organomet. Chem.* **1988**, *338*, 81.

Scheme I



F′ and G′ is smaller than that of the inversion process involving H and H′.

If it is assumed that the mixed-metal complexes **11** and **12b** display a structure similar to that of **9**, one should expect a ^{19}F NMR spectrum corresponding to four inequivalent C_6F_5 ligands and five signals for each C_6F_5 group. However, the spectra of **11** and **12b** (since **12a** isomerizes to **12b** in solution, both complexes have identical spectra) display only two sets of three signals corresponding to two inequivalent C_6F_5 rings, the one bonded to palladium and the other one bonded to platinum. Table I collects the ^{19}F NMR data. The assignment has been carried out tentatively on the following bases: (a) signals due to ortho fluorine atoms of the C_6F_5 groups bonded to platinum display satellites and (b) the signals due to F atoms of C_6F_5 groups bonded to platinum generally appear at higher field than the similar signals corresponding to C_6F_5 groups bonded to palladium, in accordance with previous results on related pentafluorophenyl mixed-Pd–Pt complexes.[21a] This pattern can easily be understood by assuming the **11** and **12b** exhibit in solution a dynamic process similar to those described for **9** and **10**. Further indication of the dynamic behavior of the acetylide is observed in the ^{1}H NMR spectrum of **12b**, in which only one singlet corresponding to the *tert*-butyl groups is observed at room temperature, while a static structure would have two signals for the CH_3 groups of the Bu^t.

In the static structures of the "asymmetric" diplatinum complexes **13** and **14** there are three chemically distinct C_6F_5 groups and three different C≡CR ligands as well. However, it should be noted that, even with rapid interchange of acetylide ligands between the two metals, the C_6F_5 rings and likewise C≡CR groups will not be equivalent. At low field the ^{19}F NMR spectra of complexes **13** and **14** display three ortho fluorine resonances, each probably corresponding to one nonequivalent C_6F_5 ring, but overlapping of the signals due to para and meta fluorine atoms of all C_6F_5 groups is observed in both complexes (see Table I). The ^{1}H NMR spectrum of complex **14** also exhibits three different *tert*-butyl single resonances corresponding to three nonequivalent C≡C^{t}Bu ligands, in addition to signals due to NBu_4^+.

Experimental Section

C, N, and H analyses were determined with a Perkin-Elmer 240-B microanalyzer. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 spectrometer using Nujol mulls between polyethylene sheets. Internal absorptions of the C_6F_5 groups are observed at ca. 1630, 1500, 1060, and 950 cm^{-1} in all complexes. In addition, complexes with C≡C^{t}Bu groups show bands at ca. 1240 and 1200 cm^{-1} and complexes with C≡CPh groups at ca. 755 and 690 cm^{-1}. For complexes **9**, **11**, and **13** the absorptions due to $\nu(C_6F_5)_{X\text{-sens}}$ cannot be unambiguously assigned since the cation $(PMePh_3)^+$ (used for solubility reasons) shows internal absorptions in this zone. Proton, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057, 188.220, and 80.984 MHz, respectively; chemical shifts (ppm) are reported relative to $SiMe_4$, $CFCl_3$, and 85% H_3PO_4 (as external references). Molecular weights were determined with a Knauer osmometer using chloroform solutions. Conductivities were measured in ca. 5 × 10^{-4} mol dm^{-3} acetone or nitromethane solutions using a Phillips 9501/01 conductimeter.

The starting materials $(PMePh_3)_2[Pt(C_6F_5)_2(C{\equiv}CPh)_2$,[12i] $(NBu_4)_2[Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]$,[12i] $[Pt(C{\equiv}CPh)_2(COD)]$[25] [*cis*-$Pt(C{\equiv}CPh)_2(PPh_3)_2$],[25] [*cis*-$M(C_6F_5)_2(THF)_2$] (M = Pt, Pd),[26] and $[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$[27] were prepared by following literature methods. [*cis*-$Pt(C{\equiv}CPh)_2$(dppe)][28] was prepared by reacting $[Pt(C{\equiv}CPh)_2(COD)]$ with dppe. Other starting materials were prepared as described below.

Preparation of $[Pt(C{\equiv}C^tBu)_2(COD)]$. To a suspension of $[PtCl_2(COD)]$ (0.6 g, 1.6035 mmol) in ethanol (10 mL) at 0 °C and under nitrogen was added a freshly prepared mixture of ^{t}BuC≡CH (0.2769 g, 3.36735 mmol) and sodium ethoxide (prepared from 0.15 g of sodium and 10 mL of ethanol) dropwise with constant stirring. After 2 h of stirring the resulting suspension was evaporated to dryness and the residue was extracted with dichloromethane. The solution was evaporated to dryness, and *n*-hexane was added to the residue to give $[Pt(C{\equiv}C^tBu)_2(COD)]$ as a white solid. A second amount was collected when the hexane filtrate was stored overnight in the freezer (78% yield). Anal. Found (calcd): C, 51.46 (51.59); H, 6.60 (6.49). ^{1}H NMR ($CDCl_3$): δ 1.2 (s, ^{t}Bu), 2.48 (s, CH_2, COD), 5.43 (t, =CH, COD). Molecular weight found (calcd): 460.3 (465.55).

Preparation of *cis*-$[Pt(C{\equiv}C^tBu)_2L_2]$ (L_2 = 2 PPh_3, dppe). Both complexes were prepared from $[Pt(C{\equiv}C^tBu)_2(COD)]$. Solid triphenylphosphine (0.1127 g, 0.4296 mmol) or 1,2-bis(diphenylphosphino)ethane (0.0856 g, 0.2148 mmol) was added to

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(27) Usón, R.; Forniés, J.; Espinet, P.; Alfranca, G. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 579.
(28) Nast, R.; Voss, J.; Kramolowsky, R. *Chem. Ber.* **1975**, *108*, 1511.

a solution of [Pt(C≡C^{t}Bu)$_2$(COD)] (0,1 g, 0.2148 mmol) in diethyl ether (30 mL) for L$_2$ = 2 PPh$_3$ or acetone (20 mL) for L$_2$ = dppe, and the mixture was stirred for 2 h at room temperature. [*cis*-Pt(C≡C^{t}Bu)$_2$(PPh$_3$)$_2$] precipitated as a white solid, which was filtered, washed with diethyl ether, and air-dried. The pale yellow solution obtained for L$_2$ = dppe was evaporated to dryness, and addition of diethyl ether to the residue rendered [Pt(C≡C^{t}Bu)$_2$(dppe)] as a white solid, which was isolated by filtration, washed with diethyl ether, and air-dried.

[*cis*-Pt(C≡C^{t}Bu)$_2$(PPh$_3$)$_2$]: yield 96%. Anal. Found (calcd): C, 65.35 (65.37); H, 5.78 (5.48). IR (cm^{-1}): ν(C≡C) 2123 (w). ^{1}H NMR (CDCl$_3$): δ 0.796 (s, ^{t}Bu), 7.42, 7.21, 7.12 (m, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 17.141 (J(^{195}Pt–^{31}P) = 2302 Hz).

[Pt(C≡C^{t}Bu)$_2$(dppe)]: yield 96%. Anal. Found (calcd): C, 60.22 (60.39); H, 5.74 (5.60). IR (cm^{-1}): ν(C≡C) 2116 w. ^{1}H NMR (CDCl$_3$): δ 1.03 (s, ^{t}Bu), 7.95, 7.38 (m, Ph), 2.36 (m, CH$_2$CH$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 40.69 (J(^{195}Pt–^{31}P) = 2267 Hz).

Preparation of Q$_2$[Pt(C$_6$F$_5$)(C≡CR)$_3$] (R = Ph, Q = PMePh$_3$; R = ^{t}Bu, Q = NBu$_4$). A solution of LiBu^n in hexane (2.72 mol dm^{-3}, 1.6 cm^3, 4.3218 mmol for R = Ph and 1.36 cm^3, 3.7044 mmol for R = ^{t}Bu) was added dropwise under N$_2$ over 5 min to a diethyl ether (20 cm^3) solution of RC≡CH (0.44 g, 4.3218 mmol for R = Ph and 0.31 g, 3.7044 mmol for R = ^{t}Bu) at 0 °C. After 20 min of stirring, [Pt$_2$(μ-Cl)$_2$(C$_6$F$_5$)$_2$(tht)$_2$] (0.3 g, 0.3087 mmol) was added and the mixture was stirred for 0.5 h (R = Ph) or 1.5 h (R = ^{t}Bu) at room temperature. The resulting white suspension (R = Ph) or colorless solution (R = ^{t}Bu) was evaporated to dryness, and deoxygenated water (50 mL) was added. The resulting aqueous solution was filtered and added dropwise to a solution of PMePh$_3$Br (0.496 g, 1.389 mmol) for R = Ph or NBu$_4$Br (0.445 g, 1.389 mmol) for R = ^{t}Bu in water (10 mL) to give the complexes (PMePh$_3$)$_2$[Pt(C$_6$F$_5$)(C≡CPh)$_3$] and (NBu$_4$)$_2$[Pt(C$_6$F$_5$)(C≡C^{t}Bu)$_3$] as white solids, which were filtered off, washed with water, and air-dried.

(PMePh$_3$)$_2$[Pt(C$_6$F$_5$)(C≡CPh)$_3$]: yield 63%. Anal. Found (calcd): C, 66.94 (66.94); H, 4.40 (4.21). Λ$_M$ (in nitromethane solution): 157 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C≡C) 2100 (s), 2076 (vs). ^{19}F NMR: δ -118.0 (F$_o$), -166.7 (F$_p$, F$_m$).

(NBu$_4$)$_2$[Pt(C$_6$F$_5$)(C≡C^{t}Bu)$_3$]: yield 88%. Anal. Found (calcd): N, 2.49 (2.52); C, 60.28 (60.67); H, 9.05 (9.18). Λ$_M$ (in nitromethane solution): 154 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C≡C) 2083 (s), ν(C$_6$F$_5$)$_{X\text{-sens}}$ 773 (s). ^{1}H NMR: δ 1.0 (s, 2 ^{t}Bu), 1.21 (s, ^{t}Bu of C≡C^{t}Bu group trans to C$_6$F$_5$), 0.94 [t, –CH$_3$(^{n}Bu)], 1.48 [m, –CH$_2$(^{n}Bu)], 1.67 [m, –CH$_2$(^{n}Bu)], 3.18 [m, NCH$_2$(^{n}Bu)]. ^{19}F NMR: δ -114.4 (d, F$_o$, ^3J(Pt–F) = 361.7 Hz, ^3J(F$_o$–F$_m$) = 27 Hz), -171.5 (t, F$_p$, ^3J(F$_p$–F$_m$) = 19.7 Hz), -170.8 (m, F$_m$).

[{L$_2$Pt(C≡CR)$_2$}Pt(C$_6$F$_5$)$_2$] (L$_2$ = 2 PPh$_3$, R = Ph (1), ^{t}Bu (2); L$_2$ = dppe, R = Ph (3), ^{t}Bu (4); L$_2$ = COD, R = Ph (5), ^{t}Bu (6)). A typical preparation (complex 1) was as follows: to a suspension of [*cis*-Pt(C≡CPh)$_2$(PPh$_3$)$_2$] (0.1 g, 0.1085 mmol) in acetone (10 mL) was added [*cis*-Pt(C$_6$F$_5$)$_2$(THF)$_2$] (0.073 g, 0.1085 mmol), and the mixture was stirred for 1 h at room temperature. Evaporation to ~1 mL and slow addition of EtOH gave white crystals of 1. Complexes 2–6 were obtained similarly. For 2 THF was used as solvent and the reaction was carried out at reflux temperature (3 h). For 5 CH$_2$Cl$_2$ was used as solvent and the mixture was stirred for 15 min. For 6 the reaction time was 5 min.

[{(PPh$_3$)$_2$Pt(C≡CPh)$_2$}Pt(C$_6$F$_5$)$_2$] (1): yield 90%. Anal. Found (calcd): C, 52.74 (52.97); H, 2.61 (2.78). Molecular weight found (calcd): 1361 (1451). IR (cm^{-1}): ν(C≡C) not observed, ν(C$_6$F$_5$)$_{X\text{-sens}}$ 803 (s), 791 (s). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 12.6 (^1J(^{195}Pt–^{31}P) = 2645 Hz).

[{(PPh$_3$)$_2$Pt(C≡C^{t}Bu)$_2$}Pt(C$_6$F$_5$)$_2$] (2): yield 48%. Anal. Found (calcd): C, 51.10 (51.07); H, 3.58 (3.43). Color: white. Molecular weight found (calcd): 1287 (1412). IR (cm^{-1}): ν(C≡C) not observed, ν(C$_6$F$_5$)$_{X\text{-sens}}$ 800 (s), 788 (s). ^{1}H NMR (CDCl$_3$): δ 0.70 (s, ^{t}Bu), 7.44, 7.29, 7.16, (m, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 11.9 (^1J(^{195}Pt–^{31}P) = 2640 Hz).

[{(dppe)Pt(C≡CPh)$_2$}Pt(C$_6$F$_5$)$_2$] (3): yield 70%. Anal. Found (calcd): C, 49.64 (48.95); H, 3.13 (2.59). Color: white. Molecular weight: not soluble enough in CHCl$_3$. IR (cm^{-1}): ν(C≡C) not observed, ν(C$_6$F$_5$)$_{X\text{-sens}}$ 804 (s), 792 (m). ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$): δ 44.6 (^1J(^{195}Pt–^{31}P) = 2591 Hz).

[{(dppe)Pt(C≡C^{t}Bu)$_2$}Pt(C$_6$F$_5$)$_2$] (4): yield 75%. Anal. Found (calcd): C, 46.75 (46.74); H, 3.55 (3.45). Color: white. Molecular weight found (calcd): 1153 (1285). IR (cm^{-1}): ν(C≡C) 2019 (w), ν(C$_6$F$_5$)$_{X\text{-sens}}$ 801 (s), 787 (s). ^{1}H NMR (CDCl$_3$): δ 1.02 (s, ^{t}Bu), 2.5 [m, –CH$_2$CH$_2$], 7.7, 7.3, (m, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 40.7 (^1J(^{195}Pt–^{31}P) = 2597 Hz).

[{(COD)Pt(C≡CPh)$_2$}Pt(C$_6$F$_5$)$_2$] (5): yield 50%. Anal. Found (calcd): C, 41.88 (41.79); H, 2.07 (2.34). Color: yellow. Molecular weight found (calcd): 978 (934). IR (cm^{-1}): ν(C≡C) 2027 (w), ν(C$_6$F$_5$)$_{X\text{-sens}}$ 804 (vs) 795 (vs).

[{(COD)Pt(C≡C^{t}Bu)$_2$}Pt(C$_6$F$_5$)$_2$] (6): yield 75%. Anal. Found (calcd): C, 38.19 (38.64); H, 3.21 (3.04). Color: white. Molecular weight found (calcd): 936 (994). IR (cm^{-1}): ν(C≡C) 2017 (m), ν(C$_6$F$_5$)$_{X\text{-sens}}$ 802 (s), 792 (s). ^{1}H NMR (CDCl$_3$): δ 1.11 (s, ^{t}Bu), 2.65 (s, br, –CH$_2$, COD), 5.78 (t, =CH, COD).

[{(PPh$_3$)$_2$Pt(C≡CR)$_2$}Pd(C$_6$F$_5$)$_2$] (R = Ph (7), ^{t}Bu (8)). [*cis*-Pd(C$_6$F$_5$)$_2$(THF)$_2$] (0.0634 g, 0.1085 mmol) was added to a suspension of the corresponding [*cis*-Pt(C≡CR)$_2$(PPh$_3$)$_2$] (0.1 g, 0.1085 mmol for R = Ph; 0.0964 g, 0.1085 mmol for R = ^{t}Bu) in acetone (20 mL). The mixture was stirred (30 min for R = Ph, 6 h for R = ^{t}Bu) and then filtered through Kieselguhr. Evaporation of the yellow filtrate to ca. 1 mL and addition of EtOH (10 mL) gave 7 as yellow crystals or 8 as a white solid. The complexes were isolated by filtration, washed with cold EtOH, and air-dried.

[{(PPh$_3$)$_2$Pt(C≡CPh)$_2$}Pd(C$_6$F$_5$)$_2$] (7): yield 75%. Anal. Found (calcd): C, 57.08 (56.42); H, 3.05 (2.96). Molecular weight found (calcd): 1491 (1362). IR (cm^{-1}): ν(C≡C) not observed, ν(C$_6$F$_5$)$_{X\text{-sens}}$ 788 (s), 776 (s). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 14.1 (^1J(^{195}Pt–^{31}P) = 2606 Hz.

[{(PPh$_3$)$_2$Pt(C≡C^{t}Bu)$_2$}Pd(C$_6$F$_5$)$_2$] (8): yield 76%. Anal. Found (calcd): C, 54.26 (54.49); H, 4.03 (3.66). Molecular weight found (calcd): 1276 (1322). IR (cm^{-1}): ν(C≡C) 2053 (m), ν(C$_6$F$_5$)$_{X\text{-sens}}$ 788 (s), 775 (m). ^{1}H NMR (CDCl$_3$): δ 0.69 (s, ^{t}Bu), 7.45, 7.36, 7.17 (m, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 13.8 (^1J(^{195}Pt–^{31}P) = 2627 Hz).

(PMePh$_3$)$_2$[(C$_6$F$_5$)$_2$Pt(μ-C≡CPh)$_2$Pt(C$_6$F$_5$)$_2$] (9). [*cis*-Pt(C$_6$F$_5$)$_2$(THF)$_2$] (0.0715 g, 0.1062 mmol) was added to an acetone solution (10 mL) of (PMePh$_3$)$_2$[*cis*-Pt(C$_6$F$_5$)$_2$(C≡CPh)$_2$] (0.13657 g, 0.1062 mmol), and the mixture was stirred at room temperature for 30 min. The solution was evaporated to ca. 2 mL, and then diethyl ether was added to give a white solid, which was collected by filtration and air-dried: yield 87%. Anal. Found (calcd): C, 51.14 (51.61); H, 2.45 (2.55). Λ$_M$ (in acetone solution): 197 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C≡C) 1956 (s).

(NBu$_4$)$_2$[(C$_6$F$_5$)$_2$Pt(μ-C≡C^{t}Bu)$_2$Pt(C$_6$F$_5$)$_2$] (10). [*cis*–Pt(C$_6$F$_5$)$_2$(THF)$_2$] (0.0858 g, 0.1275 mmol) was added to a solution of (NBu$_4$)$_2$[*cis*-Pt(C$_6$F$_5$)$_2$(C≡C^{t}Bu)$_2$] (0.15 g, 0.1275 mmol) in diethyl ether (30 mL) to immediately give a white suspension, which was stirred at room temperaure for 1 h. The solid was separated by filtration, washed with diethyl ether, and air-dried: yield 80%. Anal. Found (calcd): N, 1.77 (1.64); C, 48.07 (47.88); H, 5.79 (5.32). Λ$_M$ (in acetone solution): 235 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C≡C) 1931 (m), ν(C$_6$F$_5$)$_{X\text{-sens}}$ 793 (s), 778 (m). ^{1}H NMR (CDCl$_3$): δ 0.75 (s, ^{t}Bu), 0.97 [t, –CH$_3$(^{n}Bu)], 1.48 [m, –CH$_2$(^{n}Bu)], 1.68 [m, –CH$_2$(^{n}Bu)], 3.34 (m, NCH$_2$(^{n}Bu)].

(PMePh$_3$)$_2$[(C$_6$F$_5$)$_2$Pt(μ-C≡CPh)$_2$Pd(C$_6$F$_5$)$_2$] (11). [*cis*-Pd(C$_6$F$_5$)$_2$(THF)$_2$] (0.0703 g, 0.1202 mmol) was added, under N$_2$, to a suspension of (PMePh$_3$)$_2$[*cis*-Pt(C$_6$F$_5$)$_2$(C≡CPh)$_2$] (0.1546 g, 0.1202 mmol) in diethyl ether (30 mL) at -10 °C. The mixture was stirred, at room temperature, for 1 h and filtered through Kieselguhr under N$_2$. The resulting yellow solution was evaporated to dryness, and the slow addition of 2-propanol rendered a yellow solid, which was filtered off, washed with *n*-hexane, and air-dried: yield 75%. Anal. Found (calcd): C, 54.15 (54.26); H, 2.88 (2.68). Λ$_M$ (in acetone solution): 179 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C≡C) 2037 (m).

(NBu$_4$)$_2$[(C$_6$F$_5$)$_2$Pt(μ-C≡C^{t}Bu)$_2$Pd(C$_6$F$_5$)$_2$] (12a,b). [*cis*-Pd(C$_6$F$_5$)$_2$(THF)$_2$] (0.1243 g, 0.2127 mmol) was added, under N$_2$, to a solution of (NBu$_4$)$_2$[*cis*-Pt(C$_6$F$_5$)$_2$(C≡C^{t}Bu)$_2$] (0.25 g, 0.2127 mmol) in diethyl ether (15 mL) at -10 °C. Immediately the solution turned yellow and began to precipitate a white solid. After 15 min of stirring at -10 °C a white solid (**12a**, 60% yield) and a yellow filtrate were obtained. Evaporation of the filtrate to small volume (~2 cm^3) rendered a yellow solid, **12b** (15% yield). However, if the initial mixture was stirred for 6 h at -10 °C, the suspension turned from white to yellow. The yellow solid (**12b**) was separated by filtration, washed with diethyl ether, and air-

Table IV. Crystallographic Data for the Structural Analyses of Complexes 3 and 9

complex	3	9
formula	$Pt_2P_2C_{54}F_{10}H_{34}$	$Pt_2P_2C_{78}F_{20}H_{46}$
M_r	1324.97	1815.19
color	yellow	colorless
cryst size, mm	0.27 × 0.32 × 0.51	0.3 × 0.3 × 0.76
space group	$P2_1/n$	$P2_1/c$
a, Å	10.741 (3)	13.176 (2)
b, Å	25.233 (5)	41.656 (7)
c, Å	20.032 (6)	13.447 (2)
β, deg	90.882 (3)	111.27 (1)
V, Å^3	5428.69	6877.55
T, °C	room temp	room temp
Z	4	4
D_{calc}, g/cm^3	1.62	1.75
$F(000)$	2570.00	3519.64
μ, cm^{-1}	53.5	43.76
2θ range, deg	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 47$
no. of unique data	8609	9111
no. of data with $I > 2.5\sigma(I)$	6180	6493
$R(F)$	0.0502	0.0513
$R_w(F)$	0.0557	0.0516
P ($w = [\sigma^2(F) + PF^2]^{-1}$)	0.011 523	0.001 064
max D/s	0.014	0.026
scan type	learnt profile method[31] using $\omega-\theta$	ω
scan range, deg		1.224 + 0.34 tan ω
bkgd intens measuring		first and last 11.4%
max resid electron intens, e/Å^3	1.05	1.6
transmissn factors		
max	0.2511	0.2231
min	0.1184	0.1618
no. of params refined	541	430

dried. Concentration of the filtrate afforded a second fraction of **12b**: total yield 65%.

When **12a** (0.05 g, 0.0309 mmol) was dissolved in $CHCl_3$ (15 mL), the solution turned yellow instantaneously. Evaporation of the solvent and addition of diethyl ether (~2 mL) to the residue rendered **12b** (85% yield). Analogous results were obtained using acetone or CH_2Cl_2 as solvents.

$(NBu_4)_2[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}C^tBu)_2Pd(C_6F_5)_2]$ (12a): Anal. Found (calcd): N, 1.73 (1.73); C, 50.08 (50.51); H, 5.56 (5.61). Λ_M (in acetone solution): 218 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{\equiv}C)$ not observed, $\nu(C_6F_5)_{X\text{-sens}}$ 793 (m), 777 (s).

$(NBu_4)_2[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}C^tBu)_2Pd(C_6F_5)_2]$ (12b): Anal. Found (calcd): N, 1.72 (1.73); C, 50.29 (50.51); H, 5.65 (5.61). Λ_M (in acetone solution): 216 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2041 (m), $\nu(C_6F_5)_{X\text{-sens}}$ 785 (s), 776 (s). ^1H NMR (CD_3COCD_3): δ 0.99 (s, ^tBu) overlap*, 0.97 [t, $-CH_3(^nBu)$] overlap*, 1.43 [m, $-CH_2(^nBu)$], 1.83 [m, $-CH_2(^nBu)$], 3.46 (m, $NCH_2(^nBu)$].

$Q_2[(C_6F_5)(C{\equiv}CR)Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ (R = Ph, Q = $PMePh_3$ (13); R = ^tBu, Q = NBu_4 (14)). [*cis*-$Pt(C_6F_5)_2(THF)_2$] (0.0828 g, 0.1229 mmol) was added to a suspension of $(PMePh_3)_2[Pt(C_6F_5)(C{\equiv}CPh)_3]$ (0.1 g, 0.1229 mmol) in acetone (20 mL) or a solution of $(NBu_4)_2[Pt(C_6F_5)(C{\equiv}C^tBu)_3]$ (0.1363 g, 0.1229 mmol) in diethyl ether (20 mL), and the mixture was stirred for 30 min (R = Ph) or 1 h (R = ^tBu) at room temperature. The resulting orange (R = Ph) or yellow (R = ^tBu) solution was evaporated to dryness for R = Ph or ~1 mL for R = ^tBu. Addition of 2-propanol (5 mL) gave **13** as a beige solid. Complex **14** was obtained as a white solid by addition of 2-propanol (3 mL) and cooling to −25 °C for 24 h.

$(PMePh_3)_2[Pt(C_6F_5)(C{\equiv}CPh)(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ (13): yield 61%. Anal. Found (calcd): C, 53.91 (53.55); H, 3.07 (2.94). Λ_M (in acetone solution): 169 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2109 (m), 1956 (br).

$(NBu_4)_2[Pt(C_6F_5)(C{\equiv}C^tBu)_2Pt(C_6F_5)_2]$ (14): yield 44%. Anal. Found (calcd): N, 1.62 (1.73); C, 49.89 (50.43); H, 6.15 (6.16). Λ_M (in acetone solution): 199 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2109 (s), 1934 (m), $\nu(C_6F_5)_{X\text{-sens}}$ 790 (s); 777 (s). ^1H NMR ($CDCl_3$): δ 1.30 (s, ^tBu), 0.99 (s, ^tBu), 0.79 (s, ^tBu), 0.94 [t, $-CH_3(^nBu)$], 1.40 [m, $-CH_2(^nBu)$], 1.65 [m, $-CH_2(^nBu)$], 3.30 [m, $NCH_2(^nBu)$].

X-ray Crystallography. Accurate cell dimensions and intensity data were obtained with a STOE AED2-Siemens diffractometer using graphite-monochromated Mo Kα X-radiation (0.710 69 Å). Crystallographic details are summarized in Table IV. For complex 3 an empirical absorption correction was applied.[29] For complex 9 absorption corrections were based on ϕ-scan solutions (heavy metal atom) and refinements (full-matrix least squares based on F) used SHELX76[30] and SHELXTL PLUS. For

Table V. Positional Parameters (×10^4) for Complex 3

	x/a	y/b	z/c
Pt(1)	−894 (1)	5147 (1)	2035 (1)
Pt(2)	−1563 (1)	3897 (1)	2269 (1)
P(1)	973 (3)	5558 (1)	1925 (2)
P(2)	−1612 (3)	5949 (1)	2389 (2)
C(1)	671 (14)	6277 (5)	1902 (8)
C(2)	−247 (12)	6289 (5)	2490 (7)
C(3)	1797 (8)	5385 (4)	1175 (4)
C(4)	2911	5101	1207
C(5)	3496	4949	620
C(6)	2968	5082	2
C(7)	1854	5366	−30
C(8)	1269	5517	557
C(9)	2052 (8)	5455 (3)	2619 (4)
C(10)	1735	5091	3112
C(11)	2534	5007	3657
C(12)	3650	5287	3710
C(13)	3968	5652	3217
C(14)	3169	5736	2672
C(15)	−2341 (9)	5973 (3)	3196 (3)
C(16)	−2282	5520	3595
C(17)	−2773	5529	4236
C(18)	−3322	5990	4477
C(19)	−3381	6442	4078
C(20)	−2891	6434	3438
C(21)	−2716 (8)	6272 (3)	1824 (4)
C(22)	−2715	6816	1705
C(23)	−3614	7039	1280
C(24)	−4513	6718	975
C(25)	−4514	6173	1095
C(26)	−3615	5950	1519
C(27)	−2478 (11)	4724 (4)	2052 (6)
C(28)	−3322 (11)	4397 (5)	1981 (6)
C(29)	−4503 (7)	4141 (4)	1921 (5)
C(30)	−5401	4236	2403
C(31)	−6550	3979	2362
C(32)	−6801	3628	1839
C(33)	−5903	3533	1358
C(34)	−4754	3789	1399
C(35)	−301 (10)	4455 (4)	1694 (6)
C(36)	−307 (11)	4035 (5)	1385 (6)
C(37)	−17 (8)	3675 (3)	837 (4)
C(38)	−855	3285	627
C(39)	−598	2978	66
C(40)	497	3062	−285
C(41)	1335	3452	−74
C(42)	1078	3759	486
C(43)	−2730 (11)	3624 (5)	2981 (6)
C(44)	−3488 (11)	3199 (5)	2892 (6)
C(45)	−4404 (11)	3055 (5)	3359 (8)
C(46)	−4510 (13)	3339 (5)	3930 (7)
C(47)	−3789 (14)	3765 (6)	4022 (7)
C(48)	−2880 (12)	3895 (5)	3570 (7)
F(1)	−3457 (7)	2897 (3)	2334 (4)
F(2)	−5152 (7)	2633 (3)	3235 (5)
F(3)	−5395 (8)	3203 (3)	4364 (5)
F(4)	−3916 (10)	4067 (4)	4578 (4)
F(5)	−2157 (9)	4314 (3)	3704 (4)
C(49)	−311 (12)	3340 (5)	2573 (7)
C(50)	−226 (14)	2837 (5)	2352 (8)
C(51)	638 (16)	2488 (6)	2611 (11)
C(52)	1412 (14)	2612 (8)	3094 (12)
C(53)	1359 (14)	3107 (7)	3346 (12)
C(54)	523 (13)	3448 (5)	3088 (9)
F(6)	−1023 (9)	2653 (3)	1868 (5)
F(7)	623 (11)	1970 (4)	2356 (7)
F(8)	2217 (9)	2253 (5)	3335 (9)
F(9)	2130 (11)	3255 (5)	3854 (8)
F(10)	509 (9)	3956 (4)	3349 (5)

(29) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A.* **1983**, *39*, 158.

Table VI. Positional Parameters (×10⁴) for Complex 9

	x/a	y/b	z/c		x/a	y/b	z/c
Pt(1)	295 (1)	1501 (1)	1659 (1)	C(10)	−1093 (11)	848 (3)	864 (11)
Pt(2)	−2101 (1)	1159 (1)	1582 (1)	C(11′)	−1326 (22)	542 (5)	204 (21)
P(1)	7152 (3)	3504 (1)	2504 (3)	C(12′)	−2406	460	−376
P(2)	1115 (3)	977 (1)	5469 (3)	C(13′)	−2660	150	−789
C(1)	−1492 (9)	1575 (3)	1367 (9)	C(14′)	−1835	−76	−621
C(2)	−1188 (9)	1825 (3)	1072 (10)	C(15′)	−755	7	−41
C(3)	−1389 (8)	2133 (2)	520 (7)	C(16′)	−501	316	371
C(4)	−737	2248	−20	C(11″)	−1451 (14)	536 (3)	440 (15)
C(5)	−1027	2528	−627	C(12″)	−1986	516	−663
C(6)	−1970	2693	−693	C(13″)	−2420	224	−1136
C(7)	−2622	2579	−153	C(14″)	−2319	−48	−505
C(8)	−2332	2299	454	C(15″)	−1785	−29	−599
C(17)	1132 (10)	1917 (3)	2238 (10)	C(16″)	−1351	263	1071
C(18)	1105 (11)	2067 (3)	3157 (12)	C(29)	−2853 (11)	745 (3)	1795 (11)
C(19)	1729 (14)	2326 (3)	3667 (13)	C(30)	−3908 (15)	656 (4)	983 (14)
C(20)	2393 (13)	2460 (3)	3218 (13)	C(31)	−4437 (17)	359 (5)	1211 (17)
C(21)	2466 (11)	2335 (3)	2295 (12)	C(32)	−3899 (21)	210 (6)	2114 (21)
C(22)	1866 (11)	2073 (3)	1831 (12)	C(33)	−2910 (22)	265 (6)	2900 (22)
F(1)	481 (8)	1930 (2)	3675 (7)	C(34)	−2405 (15)	561 (4)	2707 (14)
F(2)	1661 (10)	2452 (2)	4543 (8)	F(11)	−4318 (9)	809 (3)	159 (9)
F(3)	3009 (8)	2717 (2)	3671 (8)	F(12)	−5329 (13)	280 (3)	442 (12)
F(4)	3127 (7)	2467 (2)	1857 (8)	F(13)	−4435 (15)	−89 (4)	2227 (14)
F(5)	1956 (7)	1950 (2)	942 (7)	F(14)	−2451 (14)	96 (4)	3776 (14)
C(23)	1752 (11)	1278 (3)	2006 (12)	F(15)	−1414 (11)	614 (3)	3443 (10)
C(24)	2051 (12)	1121 (3)	1245 (13)	C(35)	−3222 (11)	1389 (3)	1997 (11)
C(25)	3046 (14)	978 (4)	1496 (15)	C(36)	−3163 (11)	1440 (3)	3031 (12)
C(26)	3803 (13)	977 (4)	2470 (18)	C(37)	−3907 (14)	1593 (4)	3319 (12)
C(27)	3558 (12)	1131 (3)	3264 (14)	C(38)	−4808 (13)	1722 (4)	2532 (15)
C(28)	2548 (12)	1278 (3)	3007 (12)	C(39)	−4896 (12)	−1703 (4)	1534 (13)
F(6)	1337 (8)	1095 (2)	254 (7)	C(40)	−4109 (12)	1540 (4)	1259 (12)
F(7)	3279 (9)	828 (2)	688 (9)	F(16)	−2314 (8)	1306 (3)	3851 (7)
F(8)	4780 (8)	838 (3)	2711 (10)	F(17)	−3770 (9)	1638 (3)	4357 (7)
F(9)	4283 (8)	1137 (2)	4256 (9)	F(18)	−5535 (8)	1891 (2)	2857 (8)
F(10)	2378 (6)	1419 (2)	3853 (6)	F(19)	−5765 (9)	1828 (3)	754 (8)
C(41)	7092 (14)	3575 (4)	3803 (13)	F(20)	−4271 (8)	1533 (3)	209 (7)
C(42)	6805 (9)	3872 (2)	1788 (9)	C(60)	468 (9)	739 (2)	6173 (9)
C(43)	7194	3935	972	C(61)	199	420	5882
C(44)	6902	4219	387	C(62)	−295	233	6442
C(45)	6223	4440	619	C(63)	−520	366	7291
C(46)	5834	4376	1436	C(64)	−251	685	7582
C(47)	6125	4092	2020	C(65)	243	872	7023
C(48)	8478 (7)	3379 (2)	2612 (8)	C(66)	1669 (8)	728 (8)	4721
C(49)	9399	3463	3488	C(67)	1137	703	3618 (8)
C(50)	10426	3359	3549	C(68)	1582	515	3020
C(51)	10533	3171	2733	C(69)	2558	351	3524
C(52)	9612	3088	1856	C(70)	3089	376	4627
C(53)	8585	3191	1796	C(71)	2645	564	5225
C(54)	6215 (8)	3195 (2)	1852 (8)	C(72)	2136 (8)	1209 (2)	6449 (8)
C(55)	6409	2887	2280	C(73)	2738	1073	7436
C(56)	5687	2638	1800	C(74)	3542	1252	8199
C(57)	4771	2699	890	C(75)	3744	1568	7975
C(58)	4577	3008	461	C(76)	3142	1704	6988
C(59)	5299	3256	942	C(77)	2337	1524	6226
C(9)	−509 (10)	1082 (3)	1181 (11)	C(78)	118 (12)	1251 (3)	4594 (13)

3 all atoms were anisotropically refined, and for 9 all atoms were anisotropically refined except the C atoms of the disordered phenyl ring and the atoms of the C_6F_5 group containing C(29). Positional parameters for 3 and 9 are given in Tables V and VI, respectively. For complex 3 at the end of the refinement, we observed in a difference Fourier map a large number (ca. 11) of weak peaks lying in an interstitial region. Two of these peaks were larger than 1 e/Å^3; however, it was not possible to refine any reasonable combination of these sites (modeled as disordered acetone), either with or without distance restraints or thermal parameter constraints. A packing diagram (available as supplementary material) shows an interstitial cavity capable of accommodating a molecule of acetone. We conclude from our observations that there is a small partial occupation of this cavity by a moiety sufficiently disordered so as to be rendered indeterminate in attempts to refine it. Quantities related to the stoichiometry of the crystal (Table IV) have been calculated on the basis of $[Pt_2(C_6F_5)_2\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2\}\{\mu\text{-}C_2(C_6H_5)\}_2]$ alone.

(30) Sheldrick G. M. SHELX 76, Program for Crystal Structure Determination; University of Cambridge: Cambridge, U.K., 1976.
(31) Clegg, W. *Acta Crystallogr., Sect. A* 1981, *37*, 22.

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Supplementary Material Available: Tables of bond distances, bond angles, and anisotropic thermal parameters for 3 and 9 and figures giving additional views of 3 and 9 (17 pages). Ordering information is given on any current masthead page.

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