

Synthesis and Structure of Two Dinuclear Anionic Complexes, with Pt(III)–Pt(III) Bonds and Unprecedented (C₆F₄O)²⁻ or {C₆F₄(OR)₂}²⁻ (R = Me, Et) Quinone-like Bridging Ligands

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Abstract: A previously reported compound [NBu₄][Pt₂(μ-C₆F₅Cl)(μ-C₆F₅)(C₆F₅)₄] (A) reacts with OH⁻ or OR⁻ (R = Me, Et) to give the dinuclear Pt(III) complexes [NBu₄]₂[Pt₂(μ-C₆F₄O)₂(C₆F₅)₄] (1) or [NBu₄]₂[Pt₂{μ-C₆F₄(OR)₂}₂(C₆F₅)₄] with R = Me (2) or Et (3). These three products contain pairs of quinone (C₆F₄O) or quinon-like (C₆F₄(OR)₂) bridges and 1 and 2 have Pt–Pt single bonds with lengths of 2.570(1) and 2.584(1) Å, respectively. The anions are strictly centrosymmetric and the central C₂Pt(μ-C)₂PtC₂ cores have effective *mmm* symmetry. The μ-C₆F₄(OR)₂ ligands are readily hydrolyzed to give μ-C₆F₄O ligands. The crystallographic data are as follows. For 1, P1̄, *a* = 12.055(2) Å, *b* = 12.915(2) Å, *c* = 13.055(2) Å, α = 98.12(1)°, β = 114.30(1)°, γ = 86.02(1)°, *V* = 1833.7(5) Å³, *Z* = 1. For 2, P2₁/c, *a* = 12.220(1) Å, *b* = 21.552(2) Å, *c* = 16.272(2) Å, β = 96.66(1)°, *V* = 4256(1) Å³, *Z* = 2.

Introduction

The C–F bonds in fluoroarenes and fluoroaryls show generally a low reactivity, as is to be expected from the high C–F dissociation energy. However, the activation of such bonds has been proved or postulated in some cases of different nature:^{1,2} (a) intramolecular activation of an *ortho* C–F bond, in a coordinated fluoroaryl leading to the formation of a cycle, which maintains its aromaticity;^{2a–h} (b) intermolecular C–F activation by organometallic complexes, which causes oxidative addition to the metal center of the fluoroaryl and fluoride fragment;^{2i–k} and (c) hypothetical, postulated but not detected intermediates with perturbation of the ring to adopt a non-aromatic structure.^{2a,k}

We have recently described³ the synthesis of the dark garnet Pt(III)–Pt(III) complex [NBu₄][Pt₂(μ-C₆F₅Cl)(μ-C₆F₅)(C₆F₅)₄] (A) achieved by the reaction between [NBu₄][(C₆F₅)₄(μ-C₆F₅)₂Pt₂Ag(OEt₂)] and Cl₂. The formation of A takes place through an electrophilic intermolecular attack at the *para* carbon atom of one of the C₆F₅ bridging groups giving rise to a μ-C₆F₅Cl ligand (2,3,4,5,6-pentafluoro-4-chlorocyclohexadiene dianion) which is not aromatic and which is bonded to the metal centers through a non-electronically deficient bonding system, while the other bridging C₆F₅ group remains unaltered.

Here, we report the results of a study on the reactivity of A with OH⁻ or OR⁻ which affords the synthesis of dinuclear Pt(III)

complexes [NBu₄]₂[Pt₂(μ-C₆F₄O)₂(C₆F₅)₄] (1) or [NBu₄]₂[Pt₂{μ-C₆F₄(OR)₂}₂(C₆F₅)₄] [R = Me (2), Et (3)] containing quinone-like bridging ligands (μ-C₆F₄O)²⁻ (2,3,5,6-tetrafluorocyclohexadiene-4-one dianion) or {μ-C₆F₄(OR)₂}²⁻ (4,4-dialkoxy-2,3,5,6-tetrafluorocyclohexadiene dianion, R = Me, Et) (Chart I) which are unprecedented in organometallic chemistry. These Pt(III)–Pt(III) complexes display an unusual planar skeleton with the Pt–Pt bond coplanar with the coordination planes of both platinum atoms. For the formation of 1, 2, and 3 two different processes should take place: (a) a nucleophilic attack at the bridging C₆F₅ group and (b) substitution processes involving the C–F and C–Cl bonds.

Results and Discussion

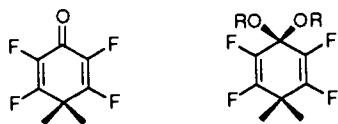
(a) **Synthesis of [NBu₄]₂[Pt₂(μ-C₆F₄O)₂(C₆F₅)₄] (1).** Acetone (or THF) solutions of [NBu₄][Pt₂(μ-C₆F₅Cl)(μ-C₆F₅)(C₆F₅)₄] undergo facile hydrolysis at room temperature as illustrated in Scheme 1 to give complex 1. If only water is added, the isolation of the anion of 1 in the form of the tetrabutylammonium salt [NBu₄]₂[Pt₂(μ-C₆F₄O)₂(C₆F₅)₄] affords a yield of ≈40% and there remains an uncrystallizable oil. Since the ¹⁹F NMR spectrum of a wet (CD₃)₂CO solution of [NBu₄][Pt₂(μ-C₆F₅Cl)(μ-C₆F₅)(C₆F₅)₄] after 2 h at room temperature shows the signals due to 1 but not those corresponding to the starting material, the oil should contain the anion of 1 which needs a bulky cation to produce crystals. For that reason, the addition of NBu₄OH or NBu₄ClO₄ increases the yield of 1 (see Experimental Section). However, 1 can be obtained more easily and in better yield when NBu₄OH is added, probably because the increase of the concentration of OH⁻ favors the total reaction of the starting material.^{2b} The formation of 1 can presumably take place via the tetrahydroxy intermediate B for the formation of which a substitution reaction on the (μ-C₆F₅Cl) ring and a nucleophilic attack (by the OH⁻ groups) plus a substitution process on the bridging pentafluorophenyl ring would be required. It is noteworthy that as a result of the reaction the pentafluorophenyl bridging ligand which is acting in the starting material as an electronically deficient group loses its aromaticity and the *ipso*-C

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Chart 1



atom is transformed into a sp^3 hybridized atom forming two covalent bonds with the platinum centers.

Analytical and conductance data for **1** are in agreement with the proposed stoichiometry. The IR spectrum shows two very strong bands at 1738 and 1721 cm^{-1} which are characteristic of a quinonic system,⁴ along with the typical absorptions which are to be expected for the C_6F_5 ligands (see Experimental Section).

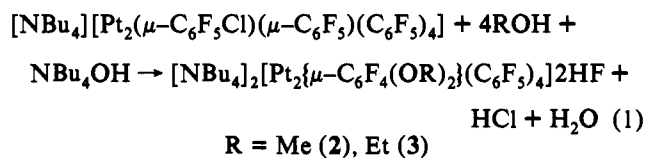
(i) ^{19}F NMR Spectrum of Complex **1**. The ^{19}F NMR spectrum of **1** which provides valuable structural information is presented in Figure 1 and shows five multiplet signals. The two signals that appear at higher frequencies (displaying platinum satellites) are to be assigned to the *ortho* fluorine atoms (1:2 ratio) of the bridging and terminal fluorinated groups.³ The relative intensity of the platinum satellites of signal A (approximately 1:1) requires it to be assigned to the *o*-F atoms of the bridging rings, while signal B can be assigned to the *o*-F atoms of the terminal C_6F_5 groups. Presumably, the small coupling constant of signal A (207 Hz) is a consequence of the absence of aromaticity in the bridging ligands. At lower frequencies, in the usual range for terminal *meta* and *para* fluorine atoms of pentafluorophenyl groups^{5,6} three multiplets appear, two of which are partially overlapped (C, D) and are to be assigned to the *meta* fluorine atoms of terminal (8F) and bridging (4F) rings; the remaining multiplet (signal E) is due to the *para* fluorine atoms (4F) of the pentafluorophenyl rings. In contrast to the precursor, the comparative simplicity of the ^{19}F spectrum of **1** is a consequence of its higher symmetry.

(ii) Crystal Structure of Complex **1**. The structure of **1** has been determined by single-crystal X-ray diffraction. General crystallographic information is collected in Table 1. Selected bond distances and angles are given in Table 2. The structure of the anion of **1** is shown in Figure 2. The entire anion is centrosymmetric, and thus the two platinum atoms have identical slightly distorted square-planar environments. The Pt–C(7) and Pt–C(13) terminal distances, 2.069(11) and 2.057(12) Å, are in the usual range for other pentafluorophenyl complexes of platinum.^{3,5,7} However, the Pt– $\text{C}_6\text{F}_4\text{O}$ bridging distances are equal, within the experimental error, to the terminal ones, 2.086(11) and 2.093(10) Å. This contrasts with the situation in previously reported compounds with Pt– C_6F_5 bridging systems, in which these distances are longer than the terminal ones.^{3,5} The reason for these short Pt– $\text{C}_6\text{F}_4\text{O}$ bridging distances is that in compound **1** the Pt–C–Pt bridging system is not electronically deficient owing to the loss of aromaticity of the $\text{C}_6\text{F}_4\text{O}$ ring. The “ $\text{Pt}_2(\mu\text{-C})_2$ ” fragment is rigorously planar (as required by the inversion center) and the $\text{C}_6\text{F}_4\text{O}$ groups lie almost perpendicular to the central plane; the dihedral angle is 89.7(3)°, while the angles formed by the “ $\text{Pt}_2(\mu\text{-C})_2$ ” plane with the terminal C_6F_5 groups are 80.3(4)° and 76.2(3)°. The short distance between the two platinum atoms, 2.570(1) Å, indicates the existence of a Pt–Pt bond. This distance is similar to those previously found in $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5\text{Cl})(\mu\text{-C}_6\text{F}_5)(\text{C}_6\text{F}_5)_4]$ (Pt–Pt distance 2.573(2) Å)³ or in the mixed-valence Pt(II)–Pt(III) complex $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_4]$ (Pt–Pt distance 2.611(2) Å)³ and is shorter than those in other dinuclear Pt(III)–Pt(III) or Pt(II)–Pt(III)

face-to-face complexes with different bridging systems.⁸ For all these complexes Pt–Pt bonds have been postulated. As in **1** it is noteworthy that all bonds in which the platinum centers are involved are coplanar, in contrast with the more common structure presented by the polynuclear complexes, where the Pt–Pt bonds are perpendicular to the coordination plane of the metal center.⁹

The most striking feature of compound **1** is the presence of an oxygen atom in the *para* position of each bridging ring. This leads to the loss of aromaticity of these rings, the $C_{ortho}\text{--}C_{meta}$ distances (C(2)–C(3) 1.327(14) Å and C(5)–C(6) 1.335(15) Å) being shorter than the other C–C distances in the ring (C(1)–C(2) 1.438(15) Å, C(1)–C(6) 1.442(11) Å, C(3)–C(4) 1.440(14) Å, and C(4)–C(5) 1.435(18) Å). The $\text{C}_6\text{F}_4\text{O}$ rings remain planar. The C(4)–O distance, 1.246(15) Å, is consistent with a C=O double bond.⁹ All these data are in agreement with a quinone-like structure for the $\text{C}_6\text{F}_4\text{O}$ bridging rings.

(b) Synthesis of $[\text{NBu}_4]_2[\text{Pt}_2\{\mu\text{-C}_6\text{F}_4(\text{OR})_2\}_2(\text{C}_6\text{F}_5)_4]$ [R = Me (2), Et (3)]. It is to be expected that the hypothetical tetrahydroxy intermediate **B** postulated in Scheme 1 will undergo a facile and rapid dehydration to give the final complex **1** and thereafter no efforts have been made to demonstrate its previsible ephemeral formation. Instead, we thought that substitution of the OH-group by alkoxy groups might lead to stabilization and thus to isolation of a tetraalkoxy derivative similar to the postulated intermediate **B**. To achieve this result the initial reaction in Scheme 1 was run with alcohols. When $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5\text{Cl})(\mu\text{-C}_6\text{F}_5)(\text{C}_6\text{F}_5)_4]$ was added to a methanolic or ethanolic solution of NBu_4OH the expected tetramethoxy (2) or tetraethoxy (3) derivative was isolated (eq 1).



Analytical and conductance data are in agreement with the proposed stoichiometry. The ^{19}F NMR spectra of **2** and **3** display a pattern similar to that of complex **1**, the only difference being the chemical shifts at which the different signals appear. The ^1H NMR spectra shows the signals due to the methoxy or ethoxy groups (see Experimental Section).

(i) Crystal Structure of $[\text{NBu}_4]_2[\text{Pt}_2\{\mu\text{-C}_6\text{F}_4(\text{OMe})_2\}_2(\text{C}_6\text{F}_5)_4]\cdot\text{C}_2\text{H}_6$ (2). The structure of **2** has been determined by single-crystal X-ray diffraction. General crystallographic information is collected in Table 1. Selected bond distances and angles are given in Table 3. The structure of the anion of **2** is shown in Figure 3 and is similar to that of the anion of **1**. The entire anion is centrosymmetric, and thus the two platinum atoms have identical slightly distorted square-planar environments. The Pt–C(1) and Pt–C(7) terminal distances, 2.073(11) and 2.074(12) Å, are in the usual range for other platinum pentafluorophenyl complexes^{3,5,7} and the Pt– $\text{C}_6\text{F}_4(\text{OMe})_2$ bridging distances are equal, within the experimental error, to the terminal ones, 2.070(10) and 2.060(10) Å as in complex **1** because the Pt–C–Pt bridging system is no longer an electronically deficient one. The “ $\text{Pt}_2(\mu\text{-C})_2$ ” fragment is rigorously planar (as required by the inversion center) and the $\text{C}_6\text{F}_4(\text{OMe})_2$ groups lie almost per-

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Scheme 1

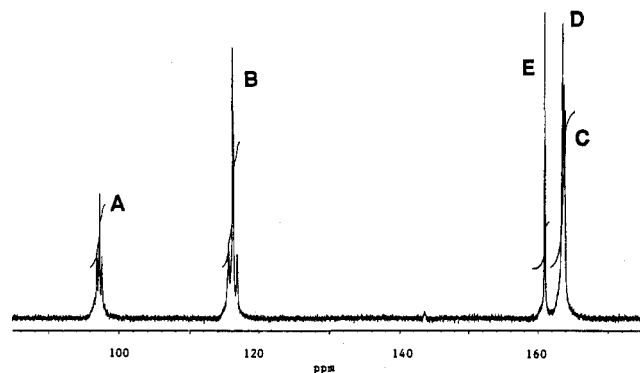
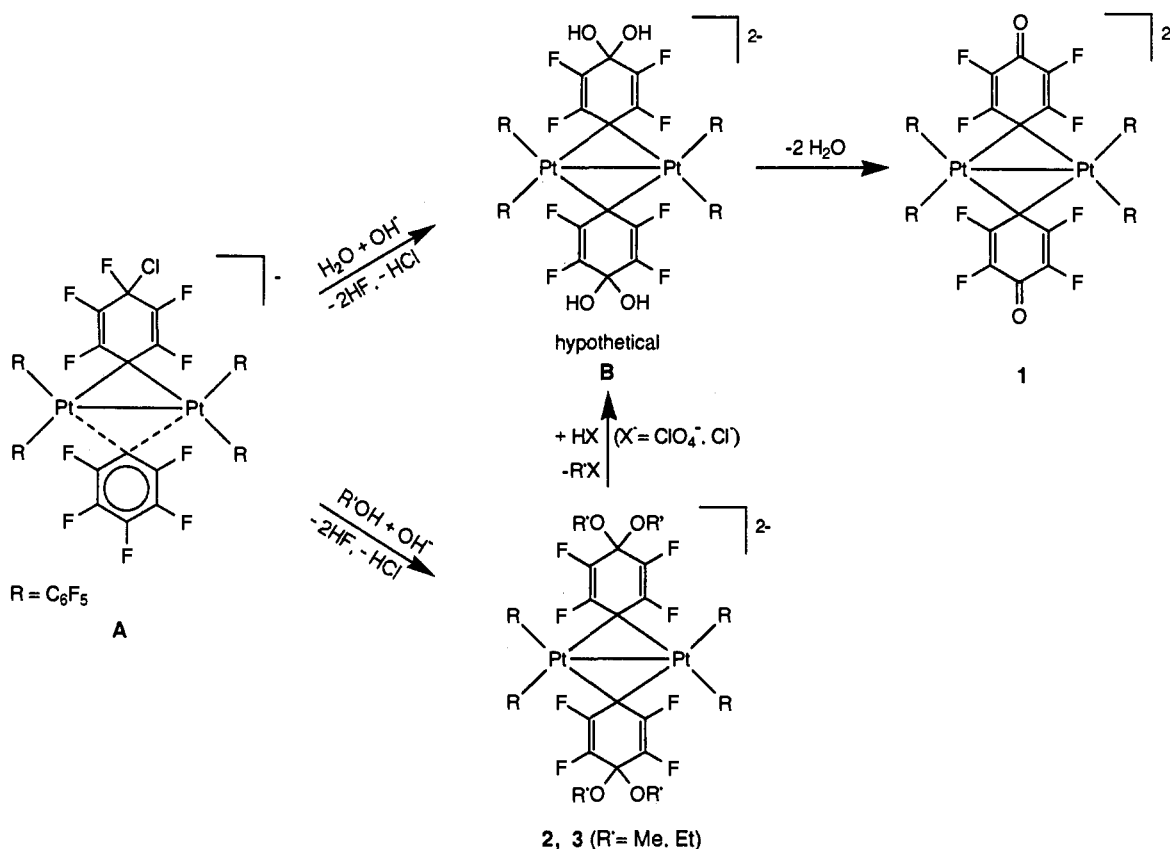


Figure 1. The ^{19}F NMR spectrum of $[\text{NBu}_4]_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_4\text{O})_2(\text{C}_6\text{F}_5)_4]$ (1) in HDA. The horizontal axis is labeled in ppm. The spectrum was recorded on a Varian Unity 300 spectrometer.

pendicular to the central plane; the dihedral angle is $88.1(4)^\circ$, while the angles formed by the “ $\text{Pt}_2(\mu\text{-C})_2$ ” plane with the terminal C_6F_5 groups are $86.7(4)^\circ$ and $88.3(4)^\circ$. The short distance between the two platinum atoms, $2.584(1)$ Å, indicates the existence of a Pt–Pt bond and is similar to that found in complex 1 and in other polynuclear Pt(III) compounds (see above).

The bridging rings in complex 2 are also quinone-like. They are planar and the $C_{\text{ortho}}\text{-}C_{\text{meta}}$ distances ($\text{C}(14)\text{-}\text{C}(15)$ $1.296(19)$ Å and $\text{C}(17)\text{-}\text{C}(18)$ $1.299(19)$ Å) are again noticeably shorter than the other C–C distances which range from 1.43 to 1.53 Å ($\text{C}(13)\text{-}\text{C}(14)$ $1.434(15)$ Å, $\text{C}(13)\text{-}\text{C}(18)$ $1.467(16)$ Å, $\text{C}(15)\text{-}\text{C}(16)$ $1.521(19)$ Å, and $\text{C}(16)\text{-}\text{C}(17)$ $1.527(18)$ Å).

(c) **Reactivity of Complexes 1, 2, and 3.** Addition of HCl (1:2), PPh_3 (1:2) or $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$ (1:5) to CH_2Cl_2 solutions of 1 and subsequent stirring over several hours at room temperature (see Experimental Section) caused no change. The bridge system resists cleavage by these three ligands. It is also notable that HCl does not cleave any of the terminal Pt– C_6F_5 bond as happened in other pentafluorophenyl platinate complexes.¹⁰

Table 1. Crystallographic Data for Complexes 1 and 2

	complex 1	complex 2
formula	$\text{C}_{68}\text{H}_{72}\text{F}_{28}\text{N}_2\text{O}_2\text{Pt}_2$	$\text{C}_{79}\text{H}_{92}\text{F}_{28}\text{N}_2\text{O}_4\text{Pt}_2$
fw	1871.5	2055.8
space group	$P\bar{1}$	$P2_1/c$
crystal system	triclinic	monoclinic
<i>a</i> , Å	12.055(2)	12.200(1)
<i>b</i> , Å	12.915(2)	21.552(2)
<i>c</i> , Å	13.055(2)	16.272(2)
α , deg	98.12(1)	90
β , deg	114.30(1)	96.66(1)
γ , deg	86.02(1)	90
<i>V</i> , Å ³	1833.7(5)	4256.4(10)
d_{calc} , g/cm ³	1.70	1.59
μ (MoK α), cm ⁻¹	41.4	33.9
diffractometer	PF/3 modification of syntax $P\bar{1}$	Siemens/STOE AED-2
temp, °C	22 ± 1	20 ± 1
R^a	0.0417	0.0403
R_w^b	0.0510	0.0532
quality of fit indicator ^c	0.95	1.00

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$. ^d $W^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$.

Complex 2 also remains unchanged upon stirring with PPh_3 or H_2O ; again, the bridge system resists the action of neutral ligands. However, complexes 2 and 3 react with aqueous HCl (excess) or with HClO_4 (excess) to give complex 1. Presumably, acid hydrolysis of 2 or 3 leads to the postulated tetrahydroxy intermediate B which then spontaneously gives complex 1 and water, as previously discussed (Scheme 1).

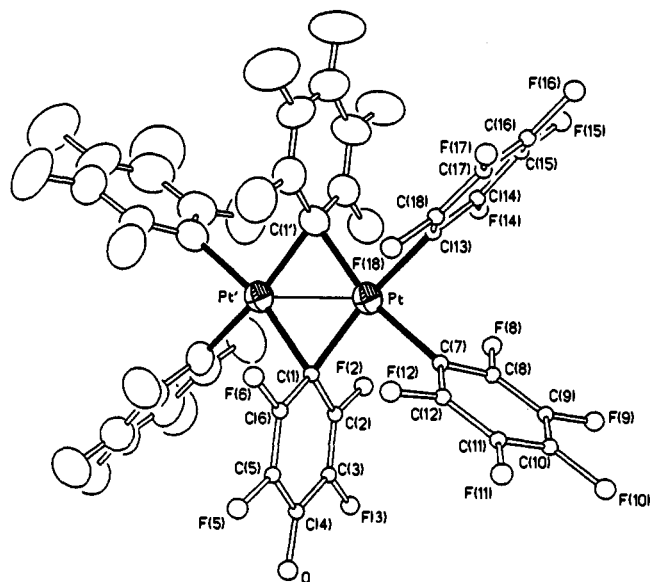
Experimental Section

General Methods. C, H, and N analyses were performed with a Perkin-Elmer 240B microanalyzer. The IR spectra were recorded over the range $4000\text{-}200$ cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol

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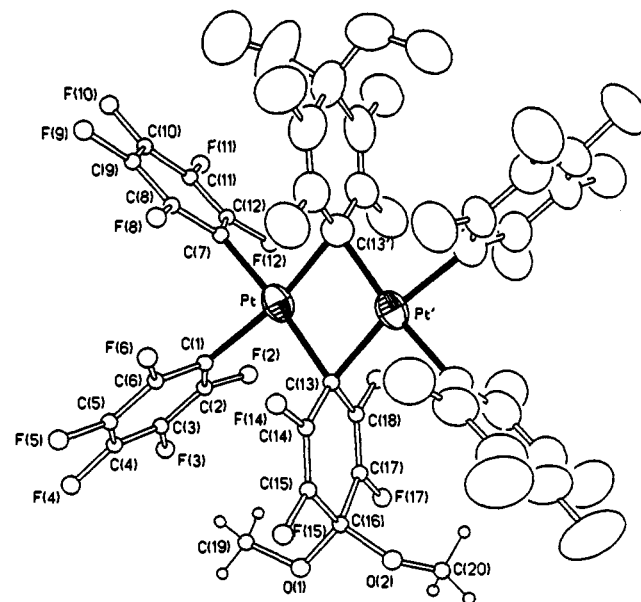
Table 2. Selected Bond Distances and Angles and Their Estimated Standard Deviations for $[\text{NBu}_4]_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_4\text{O})_2(\text{C}_6\text{F}_5)_4]^-$ (1)

Distances, Å			
Pt–Pt'	2.570(1)	Pt–C(1)	2.086(11)
Pt–C(7)	2.069(11)	Pt–C(13)	2.057(12)
Pt'–C(1)	2.093(10)	C(1)–C(2)	1.438(15)
C(2)–C(3)	1.327(14)	C(3)–C(4)	1.440(14)
C(4)–C(5)	1.435(18)	C(5)–C(6)	1.335(12)
C(1)–C(6)	1.442(11)	C(4)–O	1.246(15)
Angles, deg			
C(1)–Pt–C(7)	87.9(4)	C(1)–Pt–C(13)	168.6(4)
C(1)–Pt–C(1')	104.1(4)	C(7)–Pt–C(13)	82.5(4)
C(7)–Pt–C(1')	167.0(4)	C(13)–Pt–C(1')	86.0(4)
Pt–C(1)–Pt'	75.9(3)	C(2)–C(1)–C(6)	113.2(8)
C(1)–C(2)–C(3)	124.9(9)	C(2)–C(3)–C(4)	121.7(10)
C(3)–C(4)–C(5)	114.5(11)	C(4)–C(5)–C(6)	123.2(9)
C(1)–C(6)–C(5)	123.4(10)	C(3)–C(4)–O	124.2(10)
C(5)–C(4)–O	121.8(11)		

**Figure 2.** Perspective drawing of the anion $[\text{Pt}_2(\mu\text{-C}_6\text{F}_4\text{O})_2(\text{C}_6\text{F}_5)_4]^{2-}$ from the crystal structure of **1**, with the labeling scheme indicated. Primed atoms are related to the corresponding unprimed atoms by a crystallographic inversion center. Atoms of a unique half of the molecule are represented by their 50% probability ellipsoids.**Table 3.** Selected Bond Distances and Angles and Their Estimated Standard Deviations for $[\text{NBu}_4]_2[\text{Pt}_2\{\mu\text{-C}_6\text{F}_4(\text{OME})_2\}_2(\text{C}_6\text{F}_5)_4] \cdot \text{C}_7\text{H}_8$ (2)

Distances, Å			
Pt–Pt'	2.584(1)	Pt–C(1)	2.073(11)
Pt–C(7)	2.074(12)	Pt–C(13)	2.070(10)
Pt'–C(13)	2.060(10)	C(13)–C(14)	1.434(15)
C(14)–C(15)	1.296(19)	C(15)–C(16)	1.521(19)
C(16)–C(17)	1.527(18)	C(17)–C(18)	1.299(19)
C(13)–C(18)	1.467(16)	C(16)–O(1)	1.403(19)
O(1)–C(19)	1.397(19)	C(16)–O(2)	1.380(17)
O(2)–C(20)	1.126(28)		
Angles, deg			
C(1)–Pt–C(7)	85.1(4)	C(1)–Pt–C(13)	87.1(4)
C(1)–Pt–C(13')	168.8(4)	C(7)–Pt–C(13)	168.8(4)
C(7)–Pt–C(13')	85.9(4)	C(13)–Pt–C(13')	102.5(4)
Pt–C(13)–Pt'	76.3(4)	C(14)–C(13)–C(18)	110.8(9)
C(13)–C(14)–C(15)	125.9(11)	C(14)–C(15)–C(16)	125.7(11)
C(15)–C(16)–C(17)	106.7(11)	C(16)–C(17)–C(18)	124.7(11)
C(13)–C(18)–C(17)	125.8(11)	C(15)–C(16)–O(1)	113.3(12)
C(17)–C(16)–O(2)	113.3(12)	O(1)–C(16)–O(2)	104.1(13)
C(16)–O(1)–C(19)	114.3(10)	C(16)–O(2)–C(20)	133.7(15)

mulls between polyethylene sheets. The ^1H and ^{19}F NMR spectra were recorded on a Varian XL-200 or a Unity-300 instrument in CDCl_3 or HDA solutions.

**Figure 3.** Perspective drawing of the anion $[\text{Pt}_2\{\mu\text{-C}_6\text{F}_4(\text{OME})_2\}_2(\text{C}_6\text{F}_5)_4]^{2-}$ from the crystal structure of **2**, with the labeling scheme indicated. Primed atoms are related to the corresponding unprimed atoms by a crystallographic inversion center. Atoms of a unique half of the molecule are represented by 40% probability ellipsoids.

Synthesis of $[\text{NBu}_4]_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_4\text{O})_2(\text{C}_6\text{F}_5)_4]^-$ (1). To an acetone solution (10 mL) of 59.8 μL (0.059 mmol) of NBu_4OH in MeOH (1 N) were added $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5\text{Cl})(\mu\text{-C}_6\text{F}_5)(\text{C}_6\text{F}_5)_4]$ (0.100 g, 0.059 mmol) and 0.1 mL of H_2O . The mixture was stirred at room temperature for 15 min. The resulting solution was evaporated to ca. 2 mL and 10 mL of H_2O was added to afford a dark-red solid. The remaining acetone was evaporated under vacuum and the red solid, **1**, was filtered off. Yield 78%. C, H, N elemental analysis Found (Calc): C, 43.17 (43.64); H, 3.82 (3.88); N, 1.51 (1.50). Δ_M (in acetone, $C = 1 \times 10^{-4}$) 11 178 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (Nujol) $\nu(\text{cm}^{-1})$: 1738 vs, 1721 vs, 1501 vs, 1324 m, 1298 s, 1271 m, 1254 m, 1229 vs, 1119 m, 1057 s, 965 vs, 881 m, 671 w, 461 w; X-sensitive mode 12 814 m, 796 s, 782 m. NMR data: ^{19}F NMR (CD_2Cl_2 , room temperature): $\delta = -98.66$ [m_o , $^3J(^{195}\text{Pt}-\text{F}) = 207$ Hz, 4F, $o\text{-F}$]*, -117.71 [m_o , $^3J(^{195}\text{Pt}-\text{F}) = 351$ Hz, 8F, $o\text{-F}$], -162.59 (t, 4F, $p\text{-F}$), -165.12 (m_o , 8F, $m\text{-F}$), -165.46 (m_o , 4F, $m\text{-F}$)*.

Complex **1** can be also prepared as follows: To a THF or acetone solution (without any drying treatment) (10 mL) of 0.150 g (0.090 mmol) of $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5\text{Cl})(\mu\text{-C}_6\text{F}_5)(\text{C}_6\text{F}_5)_4]$ was added 0.031 g (0.090 mmol) of NBu_4ClO_4 . The mixture was stirred at room temperature for 2 h. The resulting solution was evaporated to dryness and 5 mL of $i\text{PrOH}$ was added giving a dark red solid (**1**) and a red solution. Addition to the solution to 15 mL of H_2O gives an oily product which after washing with OEt_2 (4 mL) affords complex **1**. Total yield 67% (THF), 74% (Me_2CO).

Synthesis of $[\text{NBu}_4]_2[\text{Pt}_2\{\mu\text{-C}_6\text{F}_4(\text{OME})_2\}_2(\text{C}_6\text{F}_5)_4]^-$ (2). To a MeOH solution (10 mL) of 1.197 mL (1.08 mmol) of NBu_4OH in MeOH (0.8 N) was added $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5\text{Cl})(\mu\text{-C}_6\text{F}_5)(\text{C}_6\text{F}_5)_4]$ (0.100 g, 0.059 mmol). The color of the solution turned orange and a pale-orange solid was precipitated. The suspension was stirred at room temperature for 10 min, the MeOH was evaporated to ca. 2 mL, and after addition of $i\text{PrOH}$ (5 mL) the orange solid, **2**, was filtered off and washed with n -hexane. Yield 78%. C, H, N elemental analysis Found (Calc): C, 44.22 (44.04); H, 4.45 (4.31); N, 1.43 (1.43). Δ_M (in acetone, $C = 1 \times 10^{-4}$) 11 162 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (Nujol) $\nu(\text{cm}^{-1})$: 1664 m, 1632 m, 1608 m, 1499 vs, 1296 s, 1270 vs, 1247 s, 1189 w, 1158 w, 1071 vs, 1005 w, 974 s, 961 vs, 875 w, 701 m, 510 m; X-sensitive mode 12 802 s, 793 s, 779 s. NMR data: ^1H NMR (CDCl_3 , room temperature): NBu_4^+ $\delta = 1.01$

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(13) The NMR signals marked with an asterisk are assigned to the bridging ligands.

(t, 24H, δ -H), 1.47 (m, 16H, γ -H), 1.66 (m, 16H, β -H), 3.19 (m, 16H, α -H); OCH₃ δ = 2.67 (s, 12H). ¹⁹F NMR (CDCl₃, room temperature): δ = -113.33 [m_c, ³J(¹⁹⁵Pt-F) = 204 Hz, 4F, α -F]*, -117.32 [m_c, ³J(¹⁹⁵Pt-F) = 383 Hz, 8F, α -F], -164.73 (t, 4F, ρ -F), -165.33 (m_c, 4F, m -F)*, -166.01 (m_c, 8F, m -F).

Synthesis of [NBu₄]₂[Pt₂(μ -C₆F₄(OEt)₂)(C₆F₅)₄] (3). To a EtOH solution (10 mL) of 0.561 mL (0.449 mmol) of NBu₄OH in EtOH (0.8 N) was added [NBu₄]₂[Pt₂(μ -C₆F₃Cl)(μ -C₆F₅)(C₆F₅)₄] (0.150 g, 0.090 mmol). The color of the solution turned pale-orange and a small amount of a yellow solid was precipitated. The suspension was stirred at room temperature for 10 min and evaporated to ca. 5 mL, and the pale-orange solid, 3, was filtered off. Yield 39%. C, H, N elemental analysis Found (Calc): C, 45.04 (45.19); H, 5.02 (4.59); N, 1.50 (1.39). Δ_M (in acetone, $C = 1 \times 10^{-4}$)¹¹ 184 ohm⁻¹ cm² mol⁻¹. IR (Nujol) ν (cm⁻¹): 1668 m, 1652 m, 1633 m, 1608 m, 1500 vs, 1297 s, 1270 vs, 1257 s, 1243 vs, 1180 m, 1153 m, 1115 m, 1060 vs, 1025 s, 1005 s, 991 s, 964 vs, 882 m, 511 m; X-sensitive mode¹² 802 s, 792 s, 778 s. NMR data: ¹H NMR (CDCl₃, room temperature): NBu₄⁺ δ = 1.01 (t, 24H, δ -H), 1.47 (m, 16H, γ -H), 1.66 (m, 16H, β -H), 3.20 (m, 16H, α -H); OCH₂CH₃ δ = 0.96 (t, 12H, β -H), 2.56 (c, 8H, α -H). ¹⁹F NMR (CDCl₃, room temperature): δ = -113.52 [m_c, ³J(¹⁹⁵Pt-F) = 204 Hz, 4F, α -F]*, -117.07 [m_c, ³J(¹⁹⁵Pt-F) = 384 Hz, 8F, α -F], -164.08 (t, 4F, ρ -F), -165.39 (m_c, 4F, m -F)*, -165.97 (m_c, 8F, m -F).

Treatment of [NBu₄]₂[Pt₂(μ -C₆F₄O)₂(C₆F₅)₄] (1) with HCl (1:2). To a solution of 1 (0.100 g, 0.053 mmol) in CH₂Cl₂ (15 mL) was added 0.23 mL (0.106 mmol) of a solution of HCl in MeOH (0.464 N). The mixture was stirred at room temperature for 15 h, but no change in the color of the solution was noted. After evaporation to dryness the dark-red starting material was recovered as a solid and washed with diethyl ether in which it is insoluble. Yield 87%.

Treatment of [NBu₄]₂[Pt₂(μ -C₆F₄O)₂(C₆F₅)₄] (1) with PPh₃ (1:2). To a solution of 1 (0.100 g, 0.053 mmol) in CH₂Cl₂ (20 mL) was added PPh₃ (0.030 g, 0.117 mmol). The mixture was stirred at room temperature for 5 h. No change in the color of the solution took place. After evaporation to dryness the dark-red starting material was recovered as a solid and washed with OEt₂, in which it is insoluble. Yield 88%. The remaining OEt₂ solution was evaporated to dryness and the white solid residue was identified as OPPh₃.

Treatment of [NBu₄]₂[Pt₂(μ -C₆F₄O)₂(C₆F₅)₄] (1) with *p*-CH₃C₆H₄NH₂ (1:5). To a solution of 1 (0.100 g, 0.053 mmol) in CH₂Cl₂ (20 mL) was added PPh₃ (0.028 g, 0.266 mmol). The mixture was stirred at room temperature for 6 h; no change in the color of the solution took place. After evaporation to dryness the dark-red starting material was recovered unchanged after washing with OEt₂. Yield 87%. The remaining OEt₂ solution was evaporated to dryness and the white solid obtained was identified as *p*-CH₃C₆H₄NH₂.

Reaction of [NBu₄]₂[Pt₂(μ -C₆F₄(OMe)₂)(C₆F₅)₄] (2) with HCl or HClO₄ (1:10). To a solution of 2 (0.056 g, 0.029 mmol) in MeOH (5 mL) was added 0.61 mL (0.285 mmol) of a solution of HCl in MeOH (0.464 N) or 3.10 mL (0.285 mmol) of a solution of HClO₄ in MeOH (0.092 N). The color of the solution instantaneously changed from yellow to dark-red. After being stirred at room temperature for 5 min the solution was evaporated to dryness and the residue was treated with toluene (5 mL), affording a dark-red solid which after filtration was washed with OEt₂ and identified as complex 1. Yield 56%.

Reaction of [NBu₄]₂[Pt₂(μ -C₆F₄(OEt)₂)(C₆F₅)₄] (3) with HCl or HClO₄ (1:10). To a solution of 3 (0.055 g, 0.027 mmol) in MeOH (5 mL) was added 0.59 mL (0.272 mmol) of a solution of HCl in MeOH (0.464 N) or 2.96 mL (0.272 mmol) of a solution of HClO₄ in MeOH (0.092 N). The color of the solution instantaneously changed from yellow to dark-red. After being stirred at room temperature for 5 min the solution was evaporated to dryness and the residue was washed with water (10 mL), affording a dark-red solid which after filtration was washed with OEt₂ and identified as complex 1. Yield 61%.

Treatment of [NBu₄]₂[Pt₂(μ -C₆F₄(OMe)₂)(C₆F₅)₄] (2) with PPh₃ (1:2). To a solution of 2 (0.021 g, 0.011 mmol) in CH₂Cl₂ (5 mL) was added PPh₃ (0.006 g, 0.022 mmol). The mixture was stirred at room temperature for 20 h without any change in the color of the solution. After evaporation to dryness the pale-orange starting material was recovered as a solid and washed with OEt₂. Yield 36%. The remaining OEt₂ solution was evaporated to dryness and a white solid was obtained and identified as OPPh₃.

X-ray Structure Analysis of [NBu₄]₂[Pt₂(μ -C₆F₄O)₂(C₆F₅)₄] (1). Crystals of complex 1 were obtained by slow evaporation of a concentrated chloroform solution of the complex at ≈ 4 °C. The dinuclear complex [Pt₂(μ -C₆F₄O)₂(C₆F₅)₄]²⁻ crystallizes as the tetra-*n*-butylammonium salt

in space group $P\bar{1}$ with $Z = 1$. The collection of X-ray diffraction data followed routine procedures which have been described previously.¹⁴ The unit cell dimensions, which had been determined according to normal procedures, were verified by normal-beam oscillation photography. During intensity data collection, the intensities of three monitor reflections were re-measured at regular intervals; they showed no significant variation. Absorption corrections were based on azimuthal scans of 9 reflections.¹⁵

The position of the unique platinum atom was derived from a Patterson map, and the remainder of the structure was developed and refined in an alternating sequence of least-squares refinements and difference Fourier maps. Towards the end of the refinement, we saw evidence of large thermal motion for two of the terminal carbon atoms of the NBu₄⁺ cation. The terminal C-C distances for the two butyl groups involved were shorter than expected, and the anisotropic displacement tensor for one of the terminal carbon atoms, C(22), became non-positive definite. All other atoms were refined with anisotropic displacement parameters. In all, 455 parameters were fitted to 3612 observed data (data:parameter ratio = 7.9). We did not observe significant correlation in the final refinement. In addition, listings of the residuals as functions of $\sin \theta/\lambda$, $|F_o|$, and indices did not show any significant trends.

X-ray Structure Analysis of [NBu₄]₂[Pt₂(μ -C₆F₄(OMe)₂)(C₆F₅)₄]-C₇H₆ (2). Crystals of complex 2 were obtained by slow diffusion of toluene into a dichloromethane solution of the complex at room temperature. The dinuclear complex [Pt₂(μ -C₆F₄(OMe)₂)(C₆F₅)₄]²⁻ crystallizes as the tetra-*n*-butylammonium salt in space group $P2_1/n$ with $Z = 2$. The structure was determined using well-established techniques. An orange parallelepiped crystal, mounted on the tip of a glass fiber with epoxy cement, was used for geometric and intensity data collection. Four-circle diffractometer data were taken at 20 °C. The diffractometer intensity was monitored by means of three reflections measured every 180 min and no decay was observed. An absorption correction was applied, based on 10 complete Ψ -scans of reflections with diffractometer angle χ near 90°. In the final least-squares refinement, 3521 data with $F^2 \geq 3\sigma(F^2)$ were used to fit 498 parameters, for a data-to-parameter ratio of 7.1. Routine computations were performed on VAX/VMS systems with the SHELX-TL-PLUS program package.¹⁶ Table 1 summarizes the crystallographic data and least-squares residuals.

The resolution of the structure revealed the presence of toluene, one of the solvents used to obtain the crystals for diffraction studies. A toluene molecule was found on an inversion center and thus it was only necessary to refine the position of the atoms of half the molecule. The methyl group is disordered over two positions related by the inversion center with an occupancy of 0.5. All the C-C distances have been fixed to 1.39 Å, except for the methyl carbon atom which has been fixed to 1.54 Å. One methyl group of the tetra-*n*-butylammonium cation was also disordered, lying on two positions each one with 0.5 occupancy.

All the non-hydrogen atoms have been refined anisotropically except for the solvent atoms and for the disordered methyl carbon atoms of the cation and the methylene carbon atom bonded to them. Hydrogen atoms have been added at calculated positions and treated as riding atoms, with a single common isotropic displacement parameter for all of them.

The displacement ellipsoids of atoms O(2) and C(20) of one of the methoxy groups are enlarged relative to those of the atoms of the other methoxy group. In particular, atoms O(2) and C(20) have quite large root-mean-square displacements of 0.45 and 0.51 Å, respectively, perpendicular to the O(2)-C(20) bond. (These numbers can be compared, for example, to the analogous root-mean-square displacement of 0.33 and 0.37 Å respectively for O(1) and C(19).) We take these displacements, together with the geometrical parameters of this group (O(2)-C(20) = 1.126(28) Å, C(16)-O(2)-C(20) = 133.7(15)°, as an indication of a dynamic disorder, permitted by weak packing interactions in the surroundings of this group. We did consider the possibility that the large displacement parameters indicated partial occupancy for this group. But since this did not improve the refinement, and since the enlargement of the displacement is markedly anisotropic, and since all chemical and spectroscopic evidence points to a stoichiometry requiring full occupancy, the final crystallographic model assumes full occupancy with significant librational disorder.

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Supplementary Material Available: Listing of atomic coordinates, full tables of bond distances and bond angles, and

anisotropic displacement parameters for **1** and **2** and a stereoplot of the $\{\text{C}_6\text{F}_4(\text{OMe})_2\}$ group of complex **2** showing the atomic thermal ellipsoids at 50% of probability level, which is provided in order to show the significant librational disorder in C(20) and O(2) atoms (17 pages); listing of structure factors for **1** and **2** (45 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.