Synthesis and Reactivity of [NBu4]+[PtIII(C6Cl5)4]-: Molecular Structures of [NBu4]2+[Pt(C6Cl5)4]2-·2CH2Cl2, [NBu4]+[PtIII(C6Cl5)4]-, and [NBu4]+[Pt(C6Cl5)4(NO)]-

Rafael Usón,* Juan Forniés, Milagros Tomás, and Babil Menjón

Departamento de Química Inorgánica, Universidad de Zaragoza, 50009 Zaragoza, Spain

Robert Bau,* Karlheinz Sünkel,† and Estelle Kuwabara

Department of Chemistry, University of Southern California, Los Angeles, California 90089

The synthesis and chemical and spectral characterizations of compounds $[NBu_4]_2^+[Pt(C_6Cl_5)_4]^{2-}$ (1), $[NBu_4]^+[Pt(C_6Cl_5)_4]^-$ (2), $[NBu_4]^+[Pt(C_6Cl_5)_4NO]^-$ (3), and $[NBu_4]^+[Pt(C_6Cl_5)_3(PPh_3)]^-$ (4) are described in this paper. By far the most intriguing complex is 2, the first mononuclear Pt(III) complex ever reported. $[NBu_4]^+[Pt(C_6Cl_5)_4]^-$ (2) can be prepared by reacting $[NBu_4]_2^+[Pt(C_6Cl_5)_4]^{2-}$ (1) with various oxidants such as Cl_2, Br_2, I_2, or $TlCl_3$ and also by the electrochemical oxidation of 1 at 0.7 V in CH_2Cl_2. Compound 2 is stable to air and moisture, shows very limited reactivity, and has magnetic properties consistent with a $^1/_2$ spin system. Complex 2 reacts with NO gas to give the adduct $[NBu_4]^+[Pt(C_6Cl_5)_4(NO)]^-$ (3), which can also be made directly from 1 by reaction with $[NO]^+[ClO_4]^-$ under an atmosphere at NO. Attempts to make the corresponding fluorine analogue of the Pt(III) complex $[NBu_4]^+[Pt(C_6F_5)_4]^-$ were unsuccessful. The X-ray structures of complexes 1–3 have been determined and are also reported in this paper. Complex 3 crystallizes in the tetragonal space group $P4_2/nbc$ (no. 133), with $a = b = 14.948$ (6) Å, $c = 23.488$ (9) Å, $V = 5248$ (3) Å^3, and ρ(calcd) = 1.85 g cm^{-3} for $Z = 4$. The structure has been refined to a final agreement factor of $R = 6.6\%$.

Introduction

Only a few platinum(III) derivatives have been described and authenticated; most of them are binuclear species with at least two bridging ligands and a Pt–Pt bond.[1-14] The so-called "platinum blue" complexes are polynuclear platinum derivatives, with bridging ligands and at least one platinum(III) atom (i.e., they are mixed-valent compounds).[15-20] The preparation of $[Pt(NH_3)(SCN)_2I]$[21] has been reported earlier; on the basis of its ESR spectrum the authors claimed that it could be a mononuclear platinum-(III) derivative, but no other further evidence on this subject has been reported so far. In this paper we describe the synthesis, by several different methods (including electrochemical oxidation), of the deep blue $[NBu_4]^+-[Pt^{III}(C_6Cl_5)_4]^-$, the first mononuclear platinum(III) compound, its structural characterization, and the study of its reactivity. Preliminary results on $[NBu_4]^+[Pt^{III}(C_6Cl_5)_4]^-$ and its precursor, $[NBu_4]_2^+[Pt(C_6Cl_5)_4]^{2-}$, have been reported earlier.[22a]

Results and Discussion

(a) Synthesis of $[NBu_4]^+[Pt^{III}(C_6Cl_5)_4]^-$. When a colorless dichloromethane solution of $[NBu_4]_2^+[Pt-(C_6Cl_5)_4]^{2-}$ (1)[22b] is treated at room temperature with a carbon tetrachloride solution of chlorine or bromine (molar ration 1:1), a dramatic change in the color of the solution to dark blue takes place instantaneously, and $[NBu_4]^+-[Pt^{III}(C_6Cl_5)_4]^-$ (2) (eq 1) (90 and 92% yields, respectively) can be obtained by evaporation to dryness and washing with 2-propanol. Complex 1 reacts with I_2 in CH_2Cl_2

$$[NBu_4)_2^+[Pt(C_6Cl_5)_4]^{2-} + ^1/_2X_2 \rightarrow$$
$$[NBu_4]^+[Pt(C_6Cl_5)_4]^- + [NBu_4]^+X^- \quad (1)$$
$$X = Cl, Br$$
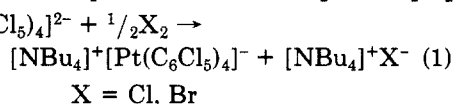
(molar ratio 1:2.5) at reflux temperature, and a deep brown

solution is formed. When the solution is evaporated to dryness and the brown solid washed with $CHCl_3$, complex

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†Present address: Institut für Anorganische Chemie, Universität München, Meiserstrasse 1, D-8000 München 2, West Germany.

Table I. Analytical Results for Compounds 2-4[a]

	color	C	H	N	Cl	M_r	mp, °C
		anal. calcd					
[NBu₄]⁺[Pt(C₆Cl₅)₄]⁻ (2)	blue	33.72 (33.45)	2.83 (2.53)	0.94 (0.97)	49.02 (49.41)	125	210 dec
[NBu₄]⁺[Pt(C₆Cl₅)₄NO]⁻ (3)	red	32.57 (32.71)	2.70 (2.46)	1.96 (1.91)	48.01 (48.40)	88	121 dec
[NBu₄]⁺[Pt(C₆Cl₅)₃PPh₃]⁻ (4)	white	42.89 (43.13)	3.23 (3.53)	1.16 (0.97)	31.07 (31.09)	81	201

[a] Calculated values are given in parentheses.
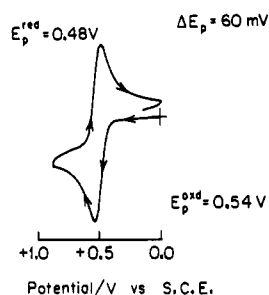
Figure 1. The cyclic voltammogram, at 100 mV s⁻¹, or [NBu₄]₂[Pt(C₆Cl₅)₄] (1) in CH₂Cl₂. Potentials are vs. the SCE with 0.2 mol dm⁻³ [NBu₄][PF₆] as base electrolyte.

Table II. Selected IR Data (in cm⁻¹)

	substituent-sensitive band	ν(MC) band	other bands
[NBu₄]₂⁺[Pt(C₆Cl₅)₄]²⁻ (1)	820	590	
[NBu₄]⁺[Pt(C₆Cl₅)₄]⁻ (2)	830	602	
[NBu₄]⁺[Pt(C₆Cl₅)₄NO]⁻ (3)	827	595	1766[a]
[NBu₄]⁺[Pt(C₆Cl₅)₃PPh₃]⁻ (4)	827	615, 600, 594	532, 511, 492[b]

[a] ν(NO). [b] PPh₃.

2 (61% yield) (almost insoluble in CHCl₃) is obtained. However, if equimolar amounts of both reactants (1 and I₂) are used (like in eq 1), not only 2 is obtained but also some unreacted starting material 1 is obtained. An excess of I₂ is necessary in this case, probably because of the formation of polyiodides [NBu₄]⁺[Iₓ]⁻ instead of I⁻ as reduction products.

On the other hand, complex 2 can also be prepared from complex 1 by using TlCl₃ (in CH₂Cl₂) as oxidant. If a 1:1 molar ratio is used, some unreacted starting material 1 can also be recovered, but the reaction is complete for a molar ratio of 2:3 (Pt:Tl). The TlCl formed in this process can be easily eliminated by filtration, and from the resulting solution, complex 2 (52% yield) and [NBu₄]⁺[TlCl₄]⁻ can be isolated (eq 2). It can be seen from eq 2 that the Cl⁻

$$2[NBu_4]_2^+[Pt(C_6Cl_5)_4]^{2-} + 3TlCl_3 \rightarrow$$
$$TlCl + [NBu_4]^+[TlCl_4]^- + 2[NBu_4]^+[Pt^{III}(C_6Cl_5)_4]^- \quad (2)$$
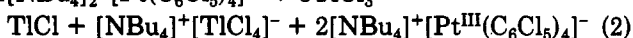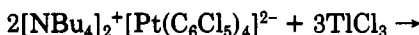
which is formed is eliminated as [TlCl₄]⁻, and this is the reason why a molar ratio of 2:3 (Pt:Tl) is necessary to complete the reaction. Finally, the treatment of complex 1 with the mild one-electron oxidant [p-CH₃C₆H₄N₂]⁺[BF₄]⁻ (molar ratio 1:1) in CH₂Cl₂ gives rise to the formation of complex 2 in 81% yield.

The oxidation of complex 1 to give complex 2 can also be achieved electrochemically. When an increasing voltage (0–1 V) is applied to a colorless solution of 1 in CH₂Cl₂ (0.1V·s⁻¹), an oxidation wave was observed at 0.54 V, with a strong change in the color of the solution to deep blue. The reduction peak (see Figure 1) was at 0.48 V. The value of [E_p(ox.) − E_p(red.)] is 0.06 V, showing that it is reversible one-electron process. The electrolysis of [Pt(C₆Cl₅)₄]²⁻ at fixed voltage (0.7 V) uses 1 faraday for 1 mol of Pt as expected.

Complex 2 is air- and moisture-stable not only in the solid state but also in solution and shows very limited reactivity, as will be discussed later. C, H, N, and Cl analyses, melting points, and conductivity data in solution (acetone, approximately 5 × 10⁻⁴M, 1:1 electrolyte) are summarized in Table I. Some relevant IR data are listed in Table II. The monomeric nature of the anion in complex 2 and its structural disposition has been established by an X-ray structural determination and will be discussed later. This is in agreement with measured values of its magnetic susceptibility. The monomeric nature of complex 2 can also be inferred from measurements[23a] of its magnetic

susceptibility: μ_{eff} = 2.57 and 2.42 μ_B at 260 and 80 K, respectively, which is consistent with a ¹/₂ spin system with a large orbital contribution from the low-lying excited states, as has been observed in other d⁷ square-planar complexes.[23b]

(b) Reactivity. Complex 2, containing a d⁷ Pt(III) atom, is a 15-electron compound and reacts with three-electron donors such as NO. Thus, when NO is bubbled through a dichloromethane solution of complex 2, the color of the solution changes to deep red and [NBu₄]⁺[Pt-(C₆Cl₅)₄(NO)]⁻ (3) (an 18-electron complex) is obtained (eq 3). Complex 3 is stable in the solid state at room tem-

$$[NBu_4]^+[Pt(C_6Cl_5)_4]^- + NO \rightarrow$$
$$[NBu_4]^+[Pt(C_6Cl_5)_4(NO)]^- \quad (3)$$
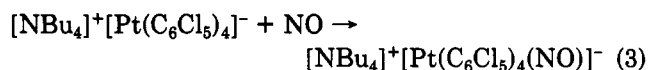
perature under air and moisture. When 3 is heated at 121 °C, it loses NO with the formation of complex 2; in a CH₂Cl₂ or (CH₃)₂CO solution, NO is lost even at room temperature, and from the resulting blue solution, complex 2 can be isolated.

On the other hand, complex 3 can also be obtained by reacting a dichloromethane solution of complex 1 with [NO]⁺[ClO₄]⁻ (molar ratio 1:1) in the presence of NO (eq 4). The presence of NO prevents the decomposition of

$$[NBu_4]_2^+[Pt(C_6Cl_5)_4]^{2-} + [NO]^+[ClO_4]^- \xrightarrow{NO}$$
$$[NBu_4]^+[Pt(C_6Cl_5)_4(NO)]^- + [NBu_4]^+[ClO_4]^- \quad (4)$$
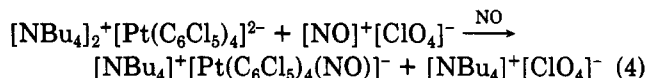
complex 3 to complex 2 but no reaction occurs directly between complex 1 and NO. Analytical results, decomposition points and conductivity data in solution (acetone, approximately 5 × 10⁻⁴M, 1:1 electrolyte) are summarized in Table I. Some relevant IR data for complex 3 are shown in Table II. The structure of [NBu₄]⁺[Pt(C₆Cl₅)₄(NO)]⁻ has been established by X-ray crystallography and will also be discussed later.

On the other hand, complex 2 in dichloromethane does not react with an excess of chlorine, neither at room nor at reflux temperature. Moreover, bubbling Cl₂ for 1 h through a refluxing solution of 2 in a higher boiling solvent such as 1,2-dichloroethane (84 °C) still leaves complex 2 unaffected. However, under similar conditions but in a

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Table III. Summary of Crystal Parameters and Data Collections for Compounds 1-3

	[NBu$_4$]$_2$$^+$[Pt(C$_6Cl_5$)$_4$]$^{2-}$·2CH$_2Cl_2$ (1)	[NBu$_4$]$^+$[Pt-(C$_6$Cl$_5$)$_4$]$^-$ (2)	[NBu$_4$]$^+$[Pt(C$_6$Cl$_5$)$_4$(NO)]$^-$ (3)
crystal color	pale yellow	deep blue	deep red
space group	*P4/nnc* (no. 126)	*P*1̄ (no. 2)	*P4$_2$/nbc* (no. 133)
unit-cell type	tetragonal	triclinic	tetragonal
unit-cell parameters			
a, Å	14.407 (6)	9.747 (8)	14.948 (6)
b, Å	14.407 (6)	16.170 (8)	14.948 (6)
c, Å	19.929 (8)	17.675 (8)	23.488 (9)
α, deg		104.95 (3)	
β, deg		92.09 (5)	
γ, deg		77.67 (5)	
V, Å^3	4135 (3)	2629 (2)	5248 (3)
molecules/unit cell, *Z*	2	2	4
d(calcd), g cm^{-1}	1.49	1.81	1.85
M$_r$	1845.26	1433.46	1463.46
wavelength used in data collection	0.710 69 (Mo Kα)	0.710 69 (Mo Kα)	0.710 69 (Mo Kα)
s in λ/θ limit, Å^{-1}	0.5385	0.5385	0.5385
no. of reflctns used in structure analysis	951	4786	913
final agreement factors, *R*	0.046	0.033	0.066

1,1,2,2-tetrachloroethane solution (146 °C), an orange solution is obtained. From this, C$_6$Cl$_6$ and [NBu$_4$]$_2$$^+$[PtCl$_6$]$^{2-}$ are produced, indicating that all the Pt–C bonds in complex 2 have been broken at these higher temperatures, and an oxidative addition reaction of Cl$_2$ to form a Pt(IV) complex has taken place. The stability of complex 2 against oxidation processes with chlorine is noteworthy, since it is known that Pt(IV) complexes can easily be prepared by treatment of chlorine with Pt(II) compounds.[24]

We have recently described[22,25] that the treatment of [M(C$_6$X$_5$)$_4$]$^{2-}$ (M = Pd, Pt; X = F, Cl) with a methanolic solution of HCl (molar ratio 1:2) gives rise to the formation of [M$_2$(μ-Cl)$_2$(C$_6$X$_5$)$_4$]$^{2-}$. However, the reaction of complex 2 with HCl (molar ratio 1:2) does not produces any binuclear Pt(III) compound. In this case, from the reaction mixture, some [NBu$_4$]$^+$[Pt(C$_6$Cl$_5$)$_4$]$^-$ (2) is obtained (25% yield) and also C$_6$Cl$_5$H and [NBu$_4$]$_2$$^+$[Pt$_2$(μ-Cl)$_2$(C$_6Cl_5$)$_4$]$^{2-}$ are isolated. These indicate that not only Pt–C bonds have been broken but also reduction from Pt(III) to Pt(II) has taken place.

Complex 2 reacts with PPh$_3$ (molar ratio 1:3) in dichloromethane. The color of the solution changes from blue to pale yellow, and the Pt(II) complexes [NBu$_4$]$_2$$^+$-[Pt(C$_6Cl_5$)$_4$]$^{2-}$ (1) (21% yield) and [NBu$_4$]$^+$[Pt(C$_6$Cl$_5$)$_3$-(PPh$_3$)]$^-$ (4) (40% yield) are obtained. Analytical results, melting points and conductivity data (in approximately 5 × 10^{-4} M acetone solution, 1:1 electrolyte) for complex 4, described in this paper for the first time, are collected in Table I.

(c) Attempts To Obtain Other Pt(III) Compounds. [NBu$_4$]$_2$$^+$[Pt(C$_6F_5$)$_4$]$^{2-}$ [26] reacts with chlorine but in a different way than [NBu$_4$]$_2$$^+$[Pt(C$_6Cl_5$)$_4$]$^{2-}$ does. When a solution of chlorine in CCl$_4$ is added dropwise to [NBu$_4$]$_2$$^+$[Pt(C$_6F_5$)$_4$]$^{2-}$ in CH$_2$Cl$_2$ (molar ratio 1:1), the color of the solution goes from colorless to orange and then immediately to yellow. From the solution a yellow solid which seems to be a mixture of products is obtained. The IR spectrum of the solid shows only a single absorption at 950 cm^{-1}. This band is assigned to the C$_6$F$_5$ group, and its position is related to the oxidation state of the metal:[27]

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Table IV. Selected Bond Distances and Angles in [NBu$_4$]$_2$$^+$[Pt(C$_6Cl_5$)$_4$]$^{2-}$ • 2CH$_2$Cl$_2$ (1)

(A) Bond Distances (Å)

Pt(1)–C(1)	2.086 (14)	N(1)–C(1)	1.61 (2)^a
C–C	1.393 (16)^a	C(1)–C(2)	1.53 (3)^a
C–Cl	1.731 (12)^a	C(2)–C(3)	1.61 (3)^a
		C(3)–C(4)	1.53 (5)^a
		Cl–C	1.72 (6)^a

(B) Bond Angles (deg)

C–Pt–C	180 (trans)	C(1)–N(1)–C(1)	109.3 (10)^a
C–Pt–C	90 (cis)	C(2)–C(1)–N(1)	109.6 (15)^a
C(2)–C(1)–Pt(1)	123.4 (9)	C(3)–C(2)–C(1)	103.8 (20)^a
C–C–C	119.3 (10)^a	C(4)–C(3)–C(3)	106.3 (25)^a
Cl–C–C	119.3 (8)^a	Cl–C–Cl	111(3)^a

^{a} Average values.

Table V. Selected Bond Distances and Angles in [NBu$_4$]$^+$[Pt(C$_6$Cl$_5$)$_4$]$^-$ (2)

(A) Bond Distances (Å)

Pt(1)–C(11)	2.092 (9)	N(1)–C(1)	1.555 (14)^a
Pt(1)–C(21)	2.095 (8)	C(1)–C(2)	1.553 (18)^a
Pt(1)–C(31)	2.097 (7)	C(2)–C(3)	1.583 (22)^a
Pt(1)–C(41)	2.090 (8)	C(3)–C(4)	1.286 (26)^a
C–C	1.388 (12)^a		
C–Cl	1.725 (9)^a		

(B) Bond Angles (deg)

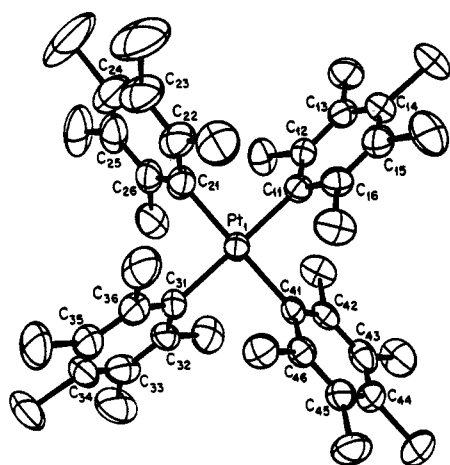|			
C(21)–Pt(1)–C(11)	90.5 (3)	C–C–C	120.0 (8)^a
C(31)–Pt(1)–C(11)	178.2 (3)	Cl–C–C	119.4 (7)^a
C(41)–Pt(1)–C(11)	88.2 (3)	C(1)–N(1)–C(1)	109.4 (7)^a
C(31)–Pt(1)–C(21)	90.2 (2)	C(2)–C(1)–N(1)	114.1 (9)^a
C(41)–Pt(1)–C(21)	178.8 (3)	C(3)–C(2)–C(1)	105.2 (10)^a
C(41)–Pt(1)–C(31)	90.9 (2)	C(4)–C(3)–C(2)	105.8 (12)^a
C(2)–C(1)–Pt(1)	122.1 (5)^a		
C(6)–C(1)–Pt(1)	122.9 (5)^a		

in this case, it clearly shows that only Pt(II) complexes are present.[27a] Also, absorption peaks assignable to ν(PtCl) are observed. Several processes of oxidative addition of chlorine followed by reductive elimination of C$_6$F$_5$Cl could have been responsible of the presence of Pt(II)–chlorine complexes in the reaction product.[28] Such reductive elimination processes take place even at –78 °C. The similar solubilities of these anionic species, even in different solvents, preclude their separation.

On the other hand, [NBu$_4$]$_2$$^+$[Pt(C$_6F_5$)$_4$]$^{2-}$ reacts with I$_2$ (molar ratio 1:1) in dichloromethane at –60 °C giving

(28) Reductive elimination of C$_6$F$_5$Cl is often observed in our systems. However, no effort was made to detect the compound in this case.

Figure 2. The molecular geometry of the [Pt(C₆Cl₅)₄]²⁻ anion in the Pt(II) complex [NBu₄]₂⁺[Pt(C₆Cl₅)₄]²⁻ (1). Average Pt–C, C–C, and C–Cl distances in this anion are 2.086 (14), 1.393 (16), and 1.731 (12) Å, respectively.

Figure 3. The molecular geometry of the [Pt(C₆Cl₅)₄]⁻ anion in the Pt(III) complex [NBu₄]⁺[Pt(C₆Cl₅)₄]⁻ (2). Average Pt–C, C–C, and C–Cl distances in the anion are 2.094 (8), 1.388 (12), and 1.725 (9) Å, respectively.

[NBu₄]₂⁺[Pt(C₆F₅)₃I]²⁻ [25] (60% yield), while with use of more I₂ (molar ratio 1:2.5) at room temperature, [NBu₄]₂⁺[Pt₂(μ-I)₂(C₆F₅)₄]²⁻ [25] (80% yield) is obtained.

(d) Structures. The structures of the new complexes **2** and **3** have been solved by single-crystal X-ray crystallography. General crystallographic information is reported in Table III. In order to establish the relationship between the Pt(III) derivative [NBu₄]⁺[Pt(C₆Cl₅)₄]⁻ (**2**) and its Pt(II) precursor [NBu₄]⁺[Pt(C₆Cl₅)₄]²⁻ (**1**), the structure of the latter compound, which crystallizes as [NBu₄]₂⁺[Pt(C₆Cl₅)₄]²⁻·2Cl₂CH₂, has also been determined. Selected bond distances and angles of compounds **1** and **2** are given in Tables IV and V, respectively.

The structures of [Pt(C₆Cl₅)₄]²⁻ and [Pt(C₆Cl₅)₄]⁻ are shown in Figures 2 and 3, respectively. As it can be seen from these figures, both compounds show an almost identical square-planar geometry. In compound **1**, the Pt atom is situated on a site of D_{4d} symmetry, while in compound **2**, no crystallographic constraints are imposed on the Pt atom (in other words, in compound **2**, the Pt atom is situated on a general position). Table VII presents a comparison of the average Pt–C, C–C, and C–Cl distances for these complexes, as well as the interatomic angles that are almost the same within experimental error. Even the torsion angle (θ) between the C₆Cl₅ rings and the central PtC₄ plane is basically the same (Table VII). The [Pt(C₆Cl₅)]⁻ anions are quite far away from each other in both

Table VI. Selected Bond Distances and Angles in [NBu₄]⁺[Pt(C₆Cl₅)₄NO]⁻ (3)

(A) Bond Distances (Å)

Pt(1)–N(1)	2.22 (6)	N(2)–C(20)	1.59 (6)
Pt(1)–C(1)	2.12 (2)	C(20)–C(21)	1.38 (8)
N(1)–O(10)	1.04 (9)	C(21)–C(22)	1.59 (7)
C–C	1.38 (3)ᵃ	C(22)–C(23)	1.58 (4)
C–Cl	1.73 (2)ᵃ		

(B) Bond Angles (deg)

C(1)–Pt(1)–C(1)′	91.0 (9)	C–C–Pt(1)	123 (2)ᵃ
C(1)′–Pt(1)–C(1)″	89.5 (9)	C–C–C	120 (2)ᵃ
C(1)–Pt(1)–C(1)″	172.5 (9)	C–C–Cl	119 (2)ᵃ
C(1)–Pt(1)–N(1)	86 (2)		
C(1)′–Pt(1)–N(1)	94 (2)	C(2)–N(2)–C(2)	110(3)ᵃ
C(1)″–Pt(1)–N(1)	86 (2)	C(21)–C(20)–N(2)	126 (4)
C(1)‴–Pt(1)–N(1)	94 (2)	C(22)–C(21)–C(20)	108 (4)
O(10)–N(1)–Pt(1)	180	C(23)–C(22)–C(21)	106 (3)

ᵃ Average values.

Table VII. Comparison of Average Distances and Angles for Compounds 1-3

	[Pt(C₆Cl₅)₄]²⁻ (1)	[Pt(C₆Cl₅)₄]⁻ (2)	[Pt(C₆Cl₅)₄NO]⁻ (3)
d(Pt–C), Å	2.086 (14)	2.094 (8)	2.12 (2)
d(C–C), Å	1.393 (16)	1.388 (12)	1.382 (34)
d(C–Cl), Å	1.731 (12)	1.725 (9)	1.726 (22)
tortion angle,ᵃ deg	63.1	63.0	52.4

ᵃ The average dihedral angle between each C₆Cl₅ ligand and the central PtC₄ plane.

Figure 4. The molecular geometry of the [Pt(C₆Cl₅)₄NO]⁻ anion in the Pt(II) complex [NBu₄]⁺[Pt(C₆Cl₅)₄NO]⁻ (3). Average Pt–C, C–C, and C–Cl distances in the anion are 2.12 (2), 1.382 (24), and 1.726 (22) Å, respectively.

crystal structures (the shortest nonbonding Pt⋯Pt distance is 9.7 Å). This fact excludes any possibility of linear stacking interactions of these units or the formation of Pt–Pt bonds between any two metallic centers. Selected bond distances and angles for complex **3** are given in Table VI. The final atomic coordinates and thermal parameters are deposited as supplementary material.[34]

The crystal structure of the anion [Pt(C₆Cl₅)₄(NO)]⁻ is shown in figure 4. The anion can be thought as a slightly distorted tetragonal pyramid. The Pt–NO group is linear, and the Pt atom resides on a site of D₂d symmetry, thus making the NO ligand disordered (half "up", half "down"); refinement with half-occupancy factors assigned to the NO group proceeded satisfactorily. The central PtC₄ unit displays a slight deviation from planarity. If we consider the four Pt–C bonds, it can be seen that two of the C atoms

in trans positions are 0.14 Å over the Pt plane, while the other two are 0.14 Å below it in accordance with the fact that the Pt atom lies on a D_{2d} site.

Angles and bond distances for the Pt environment in complex 3 are compared with those of its precursors (complexes 1 and 2), also given in Table VII. As it can be seen, no significant variations exist in the Pt–C, C–C, and C–Cl distances. The Pt–N and N–O distances in 3 are 2.2 (6) and 1.04 (9) Å, respectively. The structure of complex 3 is remarkable since according to ref 29 and 30, it would be expected that for {PtNO}[8] there would be a bent nitrosyl group (C_s symmetry) or a trigonal bipyramid with a nitrosyl ligand in a equatorial position and Pt–NO in a linear disposition. However, in complex 3, the Pt–NO is found to be linear with the platinum in an almost square-planar pyramidal environment.

Experimental Section

C, H, and N analyses and conductance and melting point determinations were performed as described elsewhere.[25] Quantitative Cl analysis were made as described by White,[31] utilizing a few miligrams of sucrose being added to facilitate combustion.[32] Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrophotometer.

$[NBu_4]_2^+[Pt(C_6Cl_5)_4]^{2-}$ (1) was prepared by a previously reported method.[22b]

$[NBu_4]^+[Pt(C_6Cl_5)_4]^-$ (2). (a) Reaction with Cl$_2$ or Br$_2$. Cl$_2$ (50 mmol) in CCl$_4$ (10 mL of a 0.05 M solution) was added to a colorless solution 0.8 g (0.477 mmol) of 1 in 100 mL of CH$_2$Cl$_2$. The color of the solution immediately turned into deep blue. After being stirred for 15 min, the solution was evaporated to dryness, and the dark blue residue was washed with 10 mL of 2-propanol which dissolved the [NBu$_4$]Cl formed in the reaction, leaving behind 0.61 g of complex 2 (90% yield). Complex 1 reacts with Br$_2$ under similar conditions to give rise to complex 2 (92% yield).

(b) Reaction with I$_2$. I$_2$ (0.095 g, 0.37 mmol) was added to solution of 0.25 g (0.15 mmol) of complex 1 in 50 mL of CH$_2$Cl$_2$ at room temperature. The solution immediately turned into a deep brown color. After 3 h of refluxing, the solution did not show any further change. The CH$_2$Cl$_2$ solvent was then removed, and a dark brown solid was obtained. The treatment of this residue with 15 mL of CHCl$_3$ produced a brown solution and a blue compound (2) (0.13 g and 61% yield), which was separated by filtration.

(c) Reaction with TlCl$_3$. To 0.5 g (0.298 mmol) of 1 in 60 mL of CH$_2$Cl$_2$ was added 0.14 g (0.46 mmol) of TlCl$_3$.[33] The color of the mixture slowly changed from colorless to deep blue. After 24 h of stirring at room temperature, the TlCl formed was separated by centrifugation. The blue solution was evaporated to dryness, and the blue residue was washed with 15 mL of MeOH. The solid thus obtained is complex 2 (0.224 g and 92% yield). The mother liquor contained a mixture of 2 and [NBu$_4$]$^+$[TlCl$_4$]$^-$.

(d) Reaction with $[p$-CH$_3$C$_6$H$_4$N$_2]^+$[BF$_4]^-$. To a solution of 0.3 g (0.13 mmol) of 1 in 40 mL of CH$_2$Cl$_2$ was added 0.037 g (0.18 mmol) of $[p$-CH$_3$C$_6$H$_4$N$_2]^+$[BF$_4]^-$, and the mixture was stirred at room temperature for 30 min. The solution was then evaporated

to dryness, and the blue solid was washed with 5 mL of MeOH. This produced 0.21 g (81% yield) of 2.

$[NBu_4]^+[Pt(C_6Cl_5)_4(NO)]^-$ (3). (a) From $[NBu_4]^+[Pt-(C_6Cl_5)_4]^-$. NO gas was bubbled for 10 min through a solution of 2 (0.2 g, 0.14 mmol) in 20 mL of CH$_2$Cl$_2$. The color of the solution changed from deep blue to deep red. The solution was evaporated to dryness. The brown solid residue was washed four times with 3-mL portions of CHCl$_3$ at –30 °C, giving a blue solution of 2 and 0.12 g (58% yield) of complex 3. This complex is stable at room temperature in the solid state and decomposes in solution to give complex 2 (approximately 1 h in CH$_2$Cl$_2$ and 15 min in Me$_2$CO).

(b) From $[NBu_4]_2^+[Pt(C_6Cl_5)_4]^{2-}$. To a NO-saturated, colorless solution of 0.3 g (0.18 mmol) of [NBu$_4$]$_2^+$[Pt(C$_6$Cl$_5$)$_4$]$^{2-}$ in 20 mL of CH$_2$Cl$_2$ was added 0.046 g (0.36 mmol) of [NO]$^+$[ClO$_4$]$^-$ under a NO stream. The solution became deep red, and it was kept stirring for 20 min. Solvent was removed until approximately 5 mL of solution was left, and then 10 mL of CHCl$_3$ was added. When some more solvent was removed, 0.13 g (49% yield) of 3 was obtained.

Reactivity of $[NBu_4]^+[Pt(C_6Cl_5)_4]^-$ (2). (a) Toward HCl (1:1). To a solution of 0.2 g (0.14 mmol) of 2 in 20 mL of Me$_2$CO was added 0.3 mL (0.14 mmol) of a methanolic solution of HCl (0.464 M). After 20 min, the solution was evaporated to dryness, and the blue residue was washed with Et$_2$O. C$_6$Cl$_5$H crystallized from the diethyl ether solution. Once the residue was washed and dried, it was treated with 10 mL of CHCl$_3$, producing a solution and a solid. This solid was complex 2 (0.050 g, 25% of the starting product). From the solution, 0.050 g of [NBu$_4$]$_2^+$-[Pt$_2(\mu$-Cl)$_2$(C$_6$Cl$_5$)$_4$]$^{2-}$ (37% yield) was obtained upon addition of 2-propanol.

(b) With PPh$_3$. PPh$_3$ (0.11 g, 0.42 mmol) was added to a solution of 0.2 g (0.14 mmol) of [NBu$_4$]$^+$[Pt(C$_6$Cl$_5$)$_4$]$^-$ in 30 mL of CH$_2$Cl$_2$, and the resulting mixture was stirred for 4 h at room temperature. Meanwhile, the color of the solution changed from blue to pale yellow, and a small amount of solid appeared simultaneously. The resulting solution was filtered and evaporated to dryness. The residue was washed with 15 mL of Et$_2$O and then with 5 mL of CHCl$_3$. The remaining solid consisted of 0.050 g 21% yield) of 1. If the CHCl$_3$ (that was used to wash the solid) is evaporated to dryness, an oily substance is obtained which, after washing with 10 mL of Et$_2$O, produces 0.080 g (40% yield) of [NBu$_4$]$^+$[Pt(C$_6$Cl$_5$)$_3$(PPh$_3$)]$^-$ (4).

Preparation of Crystals for X-ray Structure Determination. Crystals of complex 1, [NBu$_4$]$_2^+$[Pt(C$_6$Cl$_5$)$_4$]$^{2-}$ (pale yellow), were obtained by slow diffusion of cyclohexane into a dichloromethane solution of the complex at room temperature. Crystals of complex 2, [NBu$_4$]$^+$[Pt(C$_6$Cl$_5$)$_4$]$^-$ (blue), were obtained by slow diffusion of n-hexane into a solution of the complex in dichloromethane at –30 °C. Crystals of complex 3, [NBu$_4$]$^+$-[Pt(C$_6$Cl$_5$)$_4$(NO)]$^-$ (red), were obtained by the same method as described in the previous sentence. In this case, a very small amount of crystals of complex 2 was also obtained. The crystals of 2 and 3 can easily be separated because of the difference in color.

X-ray Structure Determination. In all three cases (complexes 1–3), X-ray diffraction data were collected on crystals mounted in thin-walled glass capillaries, using a system P2$_1$ diffractometer with Mo Kα radiation. The $\theta/2\theta$ data collection mode was used, with 2θ varying between 3.5 and 45.0°. The structures were solved by standard Patterson/heavy atom methods, and a summary of data collection and refinement details is given in Table IV. In addition to selected bond distances for the three compounds listed in Tables IV–VI, Supplementary material giving the final atomic coordinates and thermal parameters (Tables A–F) and structure factors (Table G) are also available.[34]

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Synthesis and Reactivity of Cis and Trans Dicarbonyl Derivatives of Platinum(II)

Rafael Usón,* Juan Forniés, Milagros Tomás, and Babil Menjón

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Direct carbonylation of *cis*-[Pt(C$_6$X$_5$)$_2$(OC$_4$H$_8$)$_2$] (X = F (1), Cl (2)) with CO (room temperature, P_{CO} $\approx$ 1 atm) gives *cis*-[Pt(C$_6$X$_5$)$_2$(CO)$_2$] (X = F (3), Cl (4)) as white, stable solids. The synthesis of *trans*-[Pt(C$_6$F$_5$)$_2$(CO)$_2$] (5) by carbonylation of (NBu$_4$)[*trans*-Pt(C$_6$F$_5$)$_2$Cl(CO)] in the presence of AgClO$_4$ is also described. Addition of neutral or anionic ligands to dichloromethane solutions of 3, 4, or 5 results in substitution of one CO group and affords *cis*- or *trans*-[Pt(C$_6$X$_5$)$_2$L(CO)]$^{n-}$ (n = 0, 1).

Introduction

Although the chemistry of the Pt(II) carbonyl derivatives has been fairly well developed and a wide range of compounds has been prepared and studied,[1] only a few Pt(II) dicarbonyls have been described, i.e., *cis*-[PtX′$_2$(CO)$_2$] (X′ = Cl,[2a–f] Br,[2d] I[2d]), which are usually synthesized by high-pressure (40–210 atm) carbonylation of different substrates and *trans*-[PtCl$_2$(CO)$_2$][3] (prepared at –80 °C and normal pressure). Only the cis dichloro derivative has been studied in detail.[4]
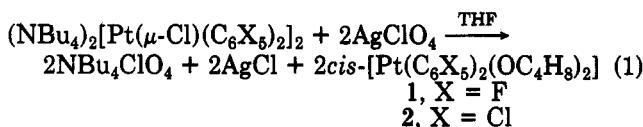
In this paper, we report the syntheses of *cis*-[Pt(C$_6$X$_5$)$_2$(CO)$_2$] (X = F, Cl) and *trans*-[Pt(C$_6$F$_5$)$_2$(CO)$_2$], at room temperature and normal pressure, as well as their reactions with both neutral and anionic ligands, which lead to two series of cis or trans monocarbonyl platinum(II) derivatives.

The synthesis of the *cis*-[Pt(C$_6$X$_5$)$_2$(CO)$_2$] has already been briefly communicated.[5]

Results and Discussion

(a) Synthesis of *cis*-[Pt(C$_6$X$_5$)$_2$(OC$_4$H$_8$)$_2$] (X = F (1), Cl (2)). Our aim has been to synthesize suitable precursors

containing *two* readily displaceable ligands, thus allowing the simultaneous entrance of two groups of our choice under very mild reaction conditions. Since platinum(II) is a class b cation, an O-donor ligand would be ideal.[6] We attempted the preparation of compounds of the type PtR$_2$(O-donor)$_2$, which could be achieved by halide abstraction from the binuclear (NBu$_4$)$_2$[Pt(μ-Cl)(C$_6$X$_5$)$_2$]$_2$ complex (X = F,[7] Cl[8]), according to eq 1.

$$(NBu_4)_2[Pt(\mu\text{-Cl})(C_6X_5)_2]_2 + 2AgClO_4 \xrightarrow{\text{THF}}$$
$$2NBu_4ClO_4 + 2AgCl + 2cis\text{-}[Pt(C_6X_5)_2(OC_4H_8)_2] \quad (1)$$
$$\begin{array}{c} \textbf{1, X = F} \\ \textbf{2, X = Cl} \end{array}$$

For our purposes, it was sufficient to obtain stable solutions of the precursors; notwithstanding, both complexes 1 and 2 can be isolated in 93% and 50% yields, respectively, in the form of white, air- and moisture-stable solids, at room temperature. This is fortunate, since solutions in any solvent of our choice can be prepared. At present we are engaged in a general study of the reactivity of both complexes.

(b) Synthesis of *cis*-[Pt(C$_6$X$_5$)$_2$(CO)$_2$] (X = (3), Cl (4)). Bubbling CO, at room temperature and normal pressure, through dichloromethane solutions of 1 or 2 causes the substitution of two CO groups for the THF ligands, according to eq 2.

$$cis\text{-}[Pt(C_6X_5)_2(OC_4H_8)_2] \xrightarrow{\text{CO}}$$
$$cis\text{-}[Pt(C_6X_5)_2(CO)_2] + 2OC_4H_8 \quad (2)$$
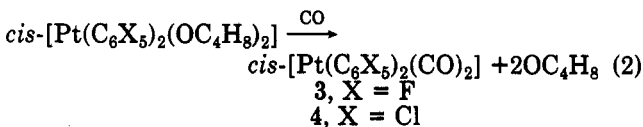$$\begin{array}{c} \textbf{3, X = F} \\ \textbf{4, X = Cl} \end{array}$$

Table I gives analytical and other data for both dicarbonyl complexes 3 and 4, which are indefinitely air- and moisture-stable white solids as are their solutions in noncoordinating solvents. Even recrystallization from diethyl

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