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Synthesis and Structural Characterization of the First Isolated Homoleptic Organoplatinum(IV) Compound: $[Pt(C_6Cl_5)_4]$

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Abstract: The neutral member of the triad $[Pt(C_6Cl_5)_4]^{n-}$ ($n = 0$, 1, or 2) has been synthesized and characterized. Treatment of $[NBu^n_4][Pt^{III}(C_6Cl_5)_4]$ (**2**) with an excess of chlorine in CCl_4 in the presence of $AlCl_3$ gives a high yield (80%) of orange $[Pt^{IV}(C_6Cl_5)_4]$ (**3**) which can also be generated by electrochemical oxidation of **2** in CH_2Cl_2 at 1.8 V. Complex **3** has been characterized by elemental analysis and spectroscopy (IR, mass, ^{13}C and ^{195}Pt NMR, and EXAFS) as well as by electrochemistry and an X-ray crystal structure determination of its toluene solvate. Cyclic voltammetry indicates that the oxidation of **2** to **3** is accompanied by a substantial structural change, a change confirmed by the EXAFS analyses which imply the symmetry of the $[Pt(C_6Cl_5)_4]$ moiety is lowered, with two *o*-chlorine atoms entering the platinum coordination sphere. The X-ray study showed that crystals of $\mathbf{3}\cdot C_6H_5CH_3$ are monoclinic, space group $P2_1/c$, with $a = 11.5972(18)$ Å, $b = 21.213(4)$ Å, $c = 16.838(3)$ Å, $\beta = 102.04(2)°$, $V = 4051.22$ Å^3, and $Z = 4$. The structural study of **3** reveals the Pt center in a distorted octahedral environment; two of the C_6Cl_5 groups behave as conventional σ-bonded ligands, while the other two act as chelating ligands bonded through the *ipso*-C atom and one of the *ortho*-Cl atoms. Crystals of **3** contain the enantiomeric couple (*OC*-6-32-*A*)- and (*OC*-6-32-*C*)-bis(pentachlorophenyl-κC)bis(pentachloro-κCl^2-phenyl-κC)platinum(IV). Complex **3** is diamagnetic and air- and moisture-stable but with limited thermal stability; at room temperature it eliminates $C_6Cl_5-C_6Cl_5$ even in the solid state. It undergoes conproportionation with $[NBu^n_4]_2[Pt^{II}(C_6Cl_5)_4]$ (**1**) yielding **2**.

Introduction

The existence of simple, homoleptic organotransition metal complexes, MR_n, is now well established[1-3] with the subset involving aryl ligands recently receiving renewed attention.[4] As far as we are aware, however, no homoleptic organometallic compound of platinum(IV), $[PtR_4]$, has been described;[5] early reports of the synthesis[6] and characterization[7] of $[PtMe_4]$ were unfounded, the material obtained from $[PtIMe_3]$ and NaMe later being found to contain mainly $[Pt(OH)Me_3]$ and related alkoxides formed by solvolytic processes.[8] Thus the only compounds with the stoichiometry PtX_4 seem to be the binary halides (X = F, Cl, Br, or I),[9] the platinum salt of fluorosulfuric acid (X = SO_3F),[10] and the recently described arylalkyltriazenido complex $[Pt\{C_6H_5NNN(CH_2)_5CH_3\text{-}\kappa N^3\}_4]$.[11]

In the last few years, the homoleptic square-planar platinum(II) compounds $[PtR_4]^{2-}$ (R = C_6F_5[12] or C_6Cl_5[13]) have been synthesized and their chemistry extensively studied.[14] The pentachlorophenyl derivative reacts with Cl_2, Br_2, or I_2 to give[15] the mononuclear, paramagnetic[16] compound $[NBu^n_4][Pt^{III}(C_6Cl_5)_4]$, this one-electron oxidation reaction differing markedly from the well-documented tendency of d^8 square-planar complexes to add halogens oxidatively.[17] Moreover, once formed the d^7 species is inert to subsequent treatment with an excess of chlorine at room temperature, a remarkable observation when

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considering that the most usual oxidation states in platinum chemistry are Pt(II) and Pt(IV). We sought, therefore, to find experimental conditions under which the Pt(III) compound could be further oxidized and now describe the successful synthesis and full characterization of the homoleptic Pt(IV) aryl complex $[Pt(C_6Cl_5)_4]$.

Experimental Section

General Procedures and Materials. The complexes $[NBu^n{}_4]_2[Pt^{II}(C_6Cl_5)_4]$ (**1**),[13] $[NBu^n{}_4][Pt^{III}(C_6Cl_5)_4]$ (**2**),[15] and *cis*-$[Pt(C_6Cl_5)_2(THF)_2]$[18] were prepared by literature methods. Solutions of chlorine were prepared by bubbling a stream of the dry gas through CCl_4 and were titrated by standard redox methods[19] before use. $AlCl_3$ was purchased (Merck) and used as received. Elemental analyses were carried out with a Perkin-Elmer 240-B microanalyzer. IR spectra of Nujol mulls between polyethylene plates were recorded on a Perkin-Elmer 599 spectrophotometer in the range 4000−200 cm^{-1}. NMR spectra were recorded on a Varian Unity-300 spectrometer; a D_2O solution of $Na_2[PtCl_6]$ was used as the reference for ^{195}Pt spectra.[20] Mass spectra were recorded on a VG-Autospec spectrometer using the standard Cs-ion FAB (acceleration voltage: 35 kV). Electrochemical studies were carried out using an EG&G Model 273 potentiostat in conjunction with a three-electrode cell. For cyclic and rotating platinum electrode voltammetry the working electrode was a platinum disc and the auxiliary electrode a platinum wire. For controlled potential electrolysis the working electrode was a platinum basket and the auxiliary a platinum spiral separated from the test compartment by a fine-porosity frit. In all cases, the reference was an aqueous saturated calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were 0.1×10^{-3} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in $[NBu^n{}_4][PF_6]$ as the supporting electrolyte. At the end of each voltammetric experiment, $[Fe(\eta^5\text{-}C_5H_5)_2]$ or $[Fe(\eta^5\text{-}C_5Me_5)_2]$ was added to the solution as an internal standard for potential measurements. Under the conditions used, the $E°$ values for the couples $[Fe(\eta^5\text{-}C_5H_5)_2]^+-[Fe(\eta^5\text{-}C_5H_5)_2]$ and $[Fe(\eta^5\text{-}C_5Me_5)_2]^+-[Fe(\eta^5\text{-}C_5Me_5)_2]$ were 0.47 V and −0.09 V, respectively.

Synthesis of $[Pt(C_6Cl_5)_4]$ (3). Method a. To a solution of **2** (0.6 g, 0.42 mmol) in CH_2Cl_2 (20 cm^3) was added chlorine (0.6 mmol) dissolved in CCl_4, and the mixture was UV-irradiated for 30 min. The initial blue solution became dark wine-red. The solvent was then removed, and the residue was extracted with CCl_4. After filtration, the filtrate was evaporated to dryness. Treatment of the orange residue with acetone gave an orange solid which was removed by filtration and washed with diethyl ether, yield 60 mg (12%).

Method b. To a solution of **2** (1.0 g, 0.7 mmol) in CH_2Cl_2 (30 cm^3) was added $AlCl_3$ (0.2 g, 1.5 mmol) and then Cl_2 (1.5 mmol) dissolved in CCl_4. While stirring the mixture for 20 min, the initial blue solution first became dark red and then deep orange. Removal of the solvent, extraction of the resulting reddish residue with CCl_4 and filtration were then carried out as described above. The filtrate was then evaporated to dryness and treatment of the residue with diethyl ether gave **3** as an orange solid, yield 0.67 g, (80%): IR (Nujol) $\bar{\nu}$ (cm^{-1}) = 1349, 1312, 1288, 1149, 1080, 1072, 834 (X-sensitive),[21] 690, 617 [ν(M−C)];[22] FAB-MS *m/z* 1183 ($C_{24}Cl_{20}Pt^-$), 936 ($C_{18}Cl_{15}Pt^-$), 866 ($C_{18}Cl_{13}Pt^-$). Anal. Found (calcd) for $C_{24}Cl_{20}Pt$: C 24.1 (24.2).

Reaction of $[Pt(C_6Cl_5)_4]$ (3) with $[NBu^n{}_4]_2[Pt(C_6Cl_5)_4]$ (1). The addition of **1** (28 mg, 0.01 mmol) to a solution of **3** (20 mg, 0.01 mmol) in THF (20 cm^3) resulted in an immediate change in color from orange to blue. Removal of the solvent by evaporation and treatment of the residue with *i*-PrOH gave a blue solid identified as **2** by elemental analysis and IR spectroscopy, yield 27 mg (56%).

Synthesis of *cis*-$[Pt(C_6Cl_5)_2(PMe_3)_2]$ (4). To a toluene solution (40 cm^3) of *cis*-$[Pt(C_6Cl_5)_2(THF)_2]$ (323 mg, 0.386 mmol) was added a 1.0 mol dm^{-3} solution of PMe_3 in toluene (Aldrich; 0.8 cm^3, 0.8 mmol). After 1 h of stirring, the solvent was evaporated in vacuo, and the resulting residue was recrystallized in $CHCl_3$/*n*-hexane, rendering eventually **4** as a white solid, yield 0.25 g (76%). IR (Nujol) $\bar{\nu}$ (cm^{-1}) = 1420, 1327, 1319, 1312, 1290, 1218, 1094, 963, 945, 851, 829 (X-sensitive),[21] 672, 617 [ν(M−C)],[22] 364; ^1H NMR ($CDCl_3$, 20 °C) δ = 1.39 [d, $^2J(^{31}P,H)$ = 9 Hz]; ^{31}P NMR ($CDCl_3$, 20 °C) δ = −31.1 [$^1J(^{195}Pt,P)$ = 2245 Hz]; ^{195}Pt NMR ($CDCl_3$, 20 °C) δ = −4445 (t). FAB-MS *m/z* 841 ($C_{18}H_{18}Cl_{10}P_2Pt^+$). Anal. Found (calcd) for $C_{18}H_{18}Cl_{10}P_2Pt$: C 25.34 (25.56), H 2.44 (2.14).

EXAFS Studies. All EXAFS data were collected at the Daresbury synchrotron radiation source (SRS) on station 9.2 in transmission mode, at the Pt L_{III} edge to 20 $Å^{-1}$ in *k*-space. The solid samples were diluted with boron nitride in order to achieve changes in log (I_0/I) in the range 1−1.5 at the absorption edge. Raw data were corrected for dark currents and converted to *k*-space (with EXCALIB[23]), and the background absorption was subtracted (with EXBACK[23]) to yield EXAFS functions $\chi(k)$. These were Fourier filtered to remove features at distances below *ca.* 1.1 Å but not to remove long distance features of the quasi-radial distribution function (*i.e.*, no noise removal was attempted). Model fitting was carried out with EXCURV90,[23] using curved wave theory and allowing for multiple scattering to third order for linear (Pt−C−C−Cl) and near linear (Pt−C−Cl) atom arrangements. Only shells significant at the 95% level were included in the final models, *i.e.*, shells added to the model were only retained if they caused a reduction in the fit index of more than 4% of the previous value.[24] Details of the final models are listed in Table 1, which gives interatomic distances (R), Debye−Waller factors (σ), and the coordination numbers, *i.e.*, the number of atoms in a given shell. *Ab initio* phase shifts and back-scattering factors using spherical wave theory were used throughout.

X-ray Structure Determination. Crystals of $3 \cdot C_6H_5CH_3$ suitable for X-ray diffraction studies were obtained by slow diffusion of a *n*-hexane layer into a saturated toluene solution of **3** at low temperature (−30 °C). Four-circle diffractometer data were taken from a single red crystal of $3 \cdot C_6H_5CH_3$ mounted in lithium grease at the end of a glass fibre. Crystal data and related parameters are given in Table 2. A total of 8169 reflections was measured. A semiempirical absorption correction based on ten complete azimuthal scans was applied. The structure was solved by Patterson and Fourier methods. All calculations were carried out with the SHELXTL-PLUS package.[25] An interstitial toluene molecule (one per asymmetric unit) showed two-fold disorder. The phenyl rings of the two crystallographically independent disordered images of the toluene were treated as rigid groups. The parameters of these groups were correlated and did not converge well, with a maximum shift/esd of 1.1 in the last cycle in which they were refined. For the final least-squares refinement, the parameters of the disordered toluene moieties were fixed. All other atoms were refined anisotropically and the data:variable ratio in the final convergent refinement was 11.4. Final residuals are listed in Table 2.

Results and Discussion

The Electrochemistry of $[Pt^{II}(C_6Cl_5)_4]^{2-}$ and $[Pt^{III}(C_6Cl_5)_4]^-$.

Electrochemical studies of the well characterized redox pair $[Pt^{II}(C_6Cl_5)_4]^{2-}$ and $[Pt^{III}(C_6Cl_5)_4]^-$ have been reported previously,[15a] the dianion showing one, fully reversible, one-electron oxidation wave (and the monoanion a reversible reduction wave) in the cyclic voltammogram (CV). Further studies have now led to the detection of additional redox behavior.

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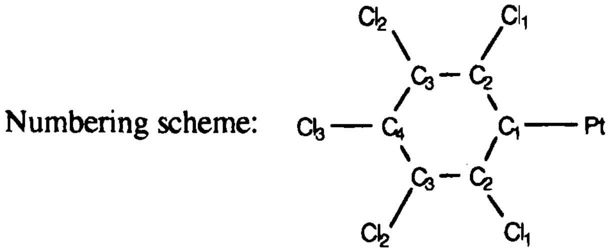
Table 1. Details of EXAFS Data Analysis



	1				2				3			
		EXAFS				EXAFS				EXAFS		
contact	XRD[a] distance	shell occupancy	R (Å)	σ (Å^2)	XRD[a] distance	shell occupancy	R (Å)	σ (Å^2)	XRD distance	contact	R (Å)	σ (Å^2)
C_1	2.09−2.10	4C	2.064(4)[b]	0.0078(8)	2.086	4C	2.083(3)	0.0062(6)	2.04−2.14	4C	2.052(4)	0.0134(8)
C_2	3.05−3.10	8C	3.063(4)	0.0040(6)	3.101	8C	3.044(8)	0.0105(14)	2.71−3.27		not fitted	
Cl_1	3.33−3.42	8Cl	3.359(4)	0.0132(6)	3.405	8Cl	3.317(7)	0.0227(15)	2.56, 2.68	2Cl	2.562(5)	0.0187(11)
									3.28−3.62	4Cl	3.243(19)	0.0486(53)
									3.85, 3.93	2Cl	3.808(18)	0.0247(46)
C_3	4.38−4.45	8C	4.455(11)	0.0042(18)	4.424	8C	4.493(21)	0.0104(42)	4.02−4.51	8C	4.511(16)	0.0182(39)
C_4	4.90−4.95	4C	4.926(20)	0.0100(45)	4.925	4C	4.936(22)	0.0114(50)	4.77−4.99		not fitted	
Cl_2	5.74−5.80	8Cl	5.782(9)	0.0099(16)	5.786	8Cl	5.773(11)	0.0116(20)	5.26−5.97	8Cl	5.720(37)	0.0485(120)
Cl_3	6.45−6.65	4Cl	6.698(9)	0.0148(17)	6.673	4Cl	6.681(8)	0.0130(13)	6.48−6.71	4Cl	6.587(31)	0.0324(80)
correlations between R and $\sigma > 0.50$					$R(C_2)-R(Cl_1) = 0.59$							
k_{max}, Å^{-1}	15.4				17.7				16.1			
R^c (%)	18.0				19.0				15.7			
R' (%)	17.7				18.4				14.3			

[a] XRD values are distances derived from single crystal structure determinations (see ref 15). [b] The estimated standard deviation in the least significant digit as calculated by EXCURV90 model fitting is given in parentheses. Precision is likely to be underestimated, particularly in cases of high correlation between parameters. [c] Residual indices R and R' were calculated as follows: $R = \Sigma_i\{k^3(\chi^{obs}{}_i - \chi^{calc}{}_i)\}^2/\Sigma_i\{k^3\chi^{obs}{}_i\}^2$. R' was calculated as for R, with final model parameters, but with data Fourier filtered with $r_{max} = 7.5$ Å to remove noise.

Table 2. Crystal Data for $[Pt(C_6Cl_5)_4]\cdot C_6H_5CH_3$

formula	$C_{31}H_8Cl_{20}Pt$
fw	1284.5
space group	$P2_1/c$
unit cell parameters	
a, Å	11.597(2)
b, Å	21.213(4)
c, Å	16.838(3)
β, deg	102.04(2)
V, Å^3	4051(2)
Z	4
d_{calcd}, g·cm^{-3}	2.106
cryst size, mm	0.15 × 0.35 × 0.23
μ(Mo Kα), cm^{-1}	48.11
transmissn factors; max, min	1.000/0.5554
data collectn instrument	Siemens-STOE/AED-2
temp, K	200
scan method	$\omega - \theta$
data collectn range, 2θ, deg	4.0−50.0
no. of unique data	7137
no. data with $F > 5.0\sigma(F)$	4650
no. of parameters refined	439
data-to-parameter ratio	10.6:1
R^a	0.0359
$R_w{}^b$	0.0357
S^c	1.05
largest shift/esd, final cycle	0.012
largest peak, e·Å^{-3}	0.70, −0.65

[a] $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. [b] $R_w = [\Sigma\,w(|F_o| - |F_c|)^2/\Sigma\,w|F_o|^2]^{1/2}$; $w = [\sigma^2(F_o) + 0.000258(F_o)^2]^{-1}$. [c] $S = [\Sigma\,w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Figure 1a shows the CV of $[Pt^{III}(C_6Cl_5)_4]^-$, scanned from 1.0 to −1.0 to 2.0 to −1.0 V. On scanning from 1.0 to −1.0 to 1.0 V only the well-defined reduction ($E^\circ = 0.54$ V) of the monoanion to the dianion is observed. However, on continuing the scan to 2.0 V an irreversible oxidation wave [peak potential, $(E_p)_{ox} = 1.85$ V; scan rate = 200 mV s^{-1}] is observed, close to the base electrolyte curve. Furthermore, this wave is accompanied by a decrease in the height of the wave associated with the oxidation of the dianion to the monoanion (0.54 V) and the appearance of an irreversible product reduction wave [$(E_p)_{red} = -0.05$ V], as shown on the partial second scan of Figure 1a.

That the wave at −0.05 V is due to the product of the oxidation of $[Pt^{III}(C_6Cl_5)_4]^-$ is shown by partial electrolysis of the monoanion. Thus, controlled potential oxidation at 1.8 V slowly (50 min) led to a change in color of the solution from deep blue-violet to pale orange red at which stage the CV in Figure 1b was recorded. Though electrolysis was incomplete (the applied potential was slightly negative of the oxidation peak potential and very close to the base electrolyte curve) the wave at 0.54 V due to the couple $[Pt^{II}(C_6Cl_5)_4]^{2-} - [Pt^{III}(C_6Cl_5)_4]^-$ was much diminished in height, and a new irreversible wave at −0.05 V (the product wave in Figure 1a) was observed. On scanning through the wave at −0.05 V a substantial increase in the height of the wave at 0.54 V occurred. Though the number of electrons involved in the oxidation of $[Pt^{III}(C_6Cl_5)_4]^-$ could not be determined accurately the electrolysis experiment provided clear evidence that the monoanion is oxidized to a species which is reconverted to the monoanion on reduction. The implication that the elusive neutral molecule $[Pt^{IV}(C_6Cl_5)_4]$ was the product of oxidation of **2** at *ca.* 1.8 V and that it might be synthesized by treatment of the anion with a strong oxidant was borne out by further chemical studies.

The Synthesis of $[Pt^{IV}(C_6Cl_5)_4]$ (3). Treatment of $[NBu^n{}_4]_2$-$[Pt^{II}(C_6Cl_5)_4]$ with an excess of chlorine in CCl_4 at room temperature[15a] yields only the monoanion $[NBu^n{}_4][Pt^{III}(C_6Cl_5)_4]$. Thus, on the basis of this observation and the electrochemical results noted above, a stronger oxidant is required to generate

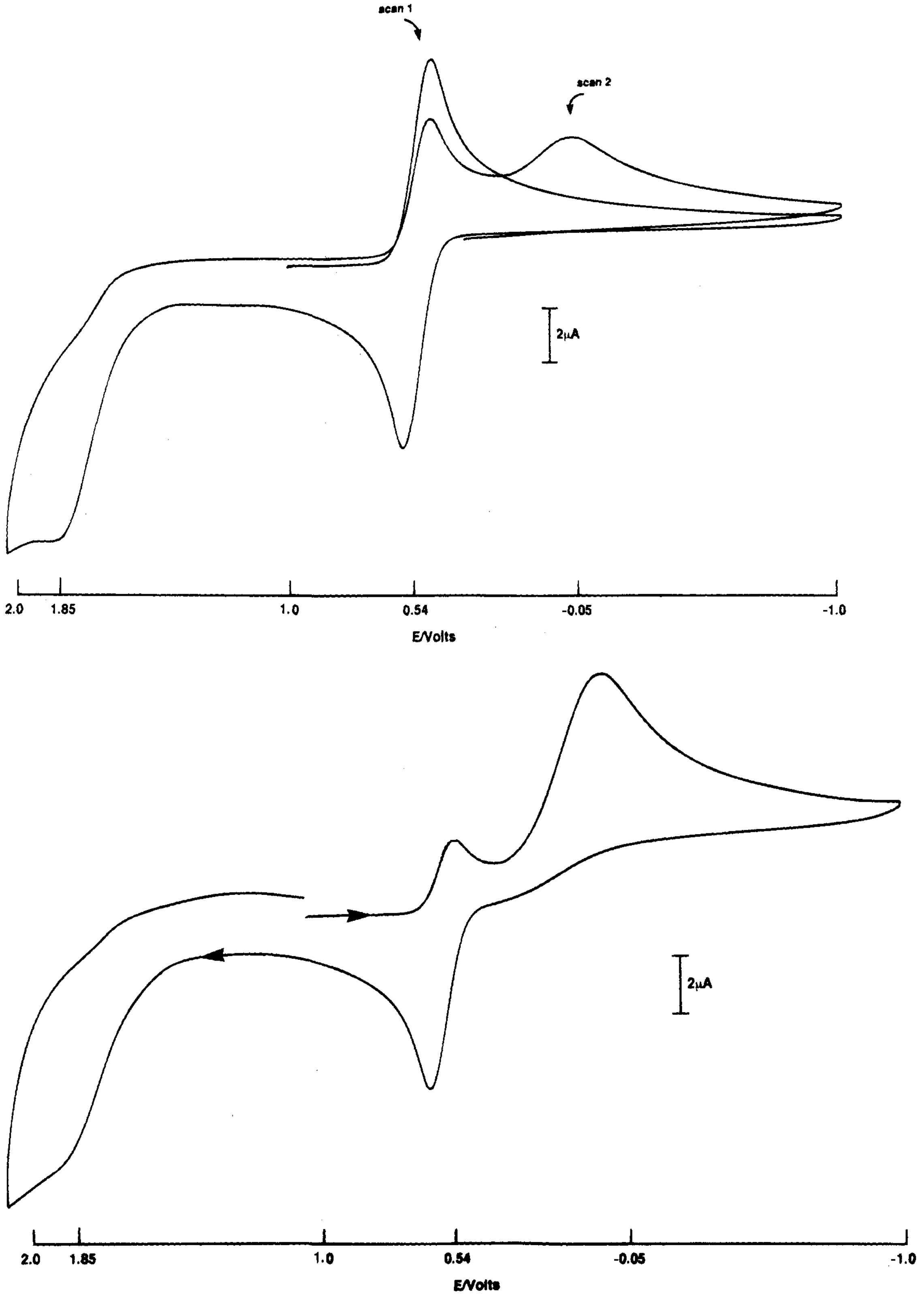


Figure 1. The cyclic voltammogram of **2** (a) from 1.0 to −1.0 to 2.0 to −1.0 V before controlled potential electrolysis at 1.8 V and (b) from 1.0 to −1.0 to 2.0 to 1.0 V after electrolysis.

$[Pt^{IV}(C_6Cl_5)_4]$. Three different methods to enhance the reactivity of molecular chlorine were therefore explored, namely (i) thermal, (ii) photochemical, and (iii) chemical.

The first method proved unsuitable. Passing a slow stream of dry Cl_2 through a refluxing solution of **2** in 1,2-dichloroethane (bp 84 °C) had no perceptible effect and after 1 h only unreacted starting material was recovered, in 86% yield. In a similar experiment 1,1,2,2-tetrachloroethane was used as solvent, and the temperature was slowly raised until a slight color change was noticed. At this stage (146 °C) the temperature was maintained until the initial blue solution had become completely orange. However, only $[NBu^n_4]_2[PtCl_6]$ and C_6Cl_6 could be identified as products. It is apparent, therefore, that chlorine can oxidize **2** at higher temperatures but that oxidation is destructive under these conditions; the nature of the final products implies the breaking of every Pt−C bond.[15a]

Table 3. IR and NMR Spectroscopic Data for Complexes **1−3**

			Complex		
			$[NBu^n_4]_2[Pt^{II}(C_6Cl_5)_4]$ (**1**)	$[NBu^n_4][Pt^{III}(C_6Cl_5)_4]$ (**2**)	$[Pt^{IV}(C_6Cl_5)_4]$ (**3**)
	IR (cm^{-1})	ν (M−C)[a]	590	602	617
		X-sensitive[b]	820	830	834
δ(ppm)	^{13}C NMR[c]	*ipso*-C	168.09 (871)	[d]	[e] (905)
		ortho-C	127.60 (55.0)	[d]	131.32 (56.9)
		meta-C	143.67 (15.1)	[d]	136.29 (26.7)
		para-C	122.40	[d]	133.10 (11.5)
	^{195}Pt NMR[c,f]		−3696 (34.4)	[d]	−546 (46)

[a] See ref 22. [b] See refs 14b and 21. [c] The spectrum of **1** was recorded in $CDCl_3$ at room temperature, and that of **3** was recorded in CCl_2CCl_2:$CDCl_3$ (3:1) at 5 °C. Values of $^nJ(^{195}Pt,C)$ in Hz are given in parentheses. [d] Not observed because of the paramagnetism of the complex. [e] Not observed; the $^1J(^{195}Pt,C)$ value has been taken from the ^{195}Pt NMR spectrum. [f] Values in parentheses refer to $W_{1/2}$ in Hz.

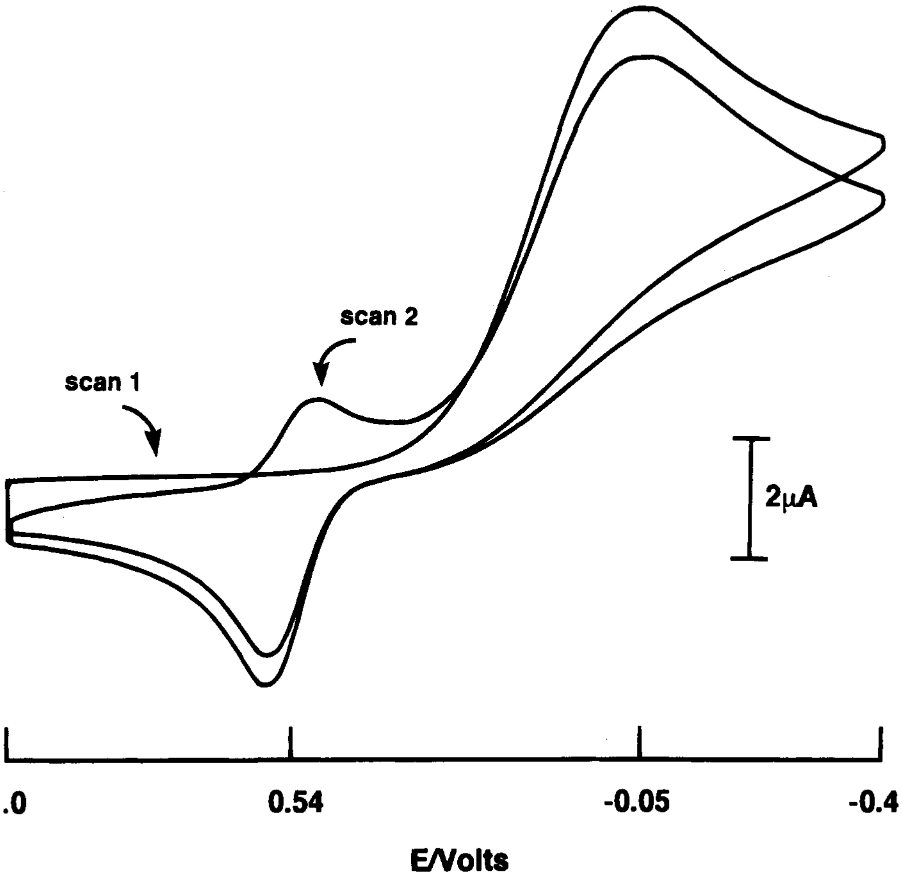
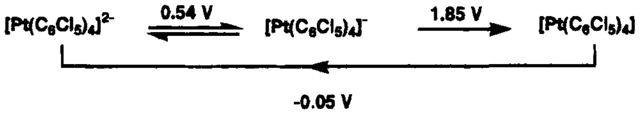


Figure 2. The cyclic voltammogram (two scans) of **3** from 1.0 to −0.4 V.

Scheme 1



UV-irradiation of a suspension of **2** in CCl_4 in the presence of Cl_2 was also unsuccessful, probably because of the insolubility of the ionic starting material in the nonpolar solvent. However, in CH_2Cl_2 reaction takes place in 30 min at room temperature, as shown by the obvious change in color of the solution from blue to dark wine-red. From the reaction mixture, $[Pt^{IV}(C_6Cl_5)_4]$ (**3**) can be isolated but only in 12% yield (eq 1).

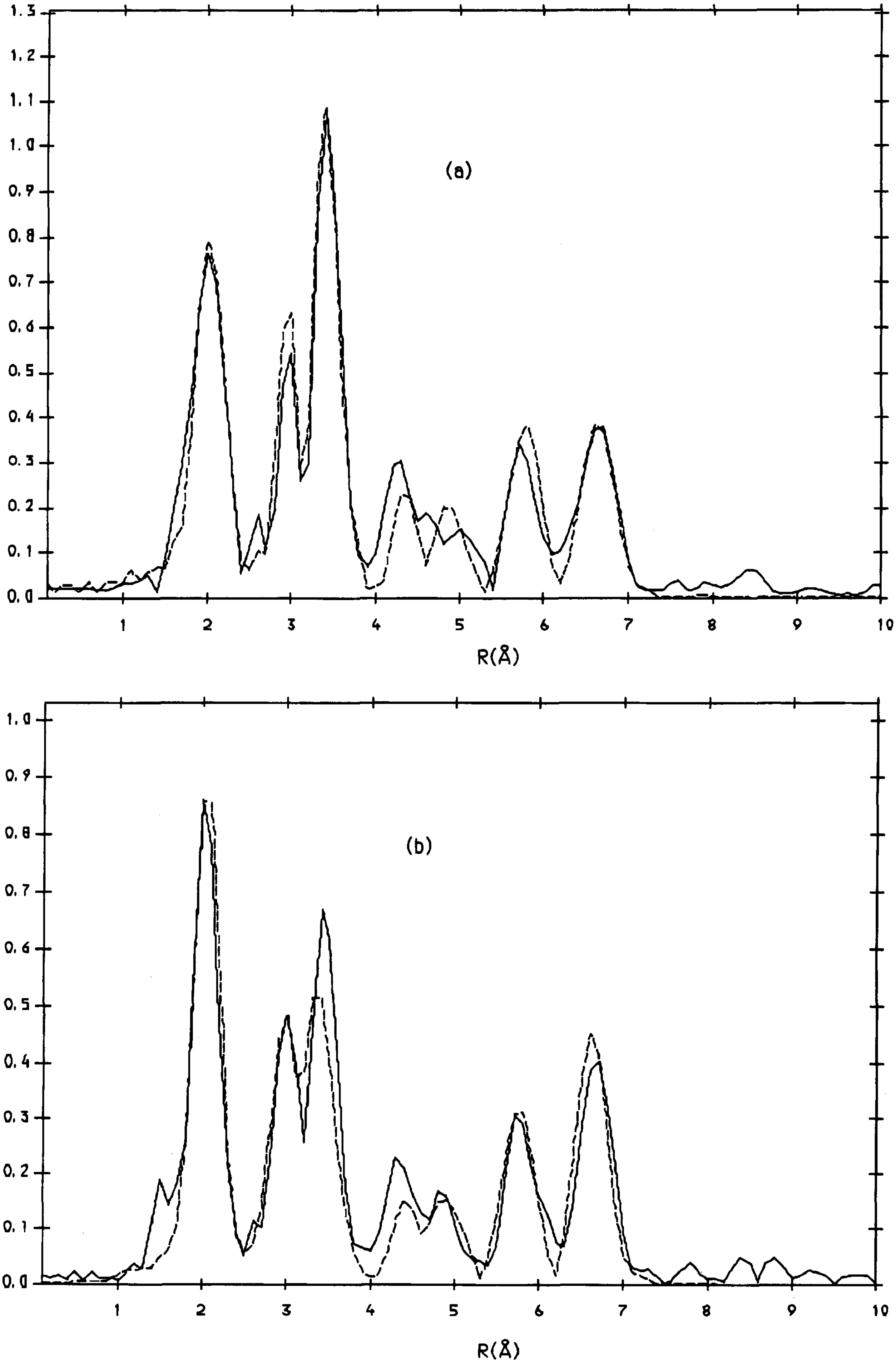
$$[NBu^n_4][Pt^{III}(C_6Cl_5)_4] + {}^1/_2Cl_2 \xrightarrow{h\nu} [Pt^{IV}(C_6Cl_5)_4] + [NBu^n_4]Cl \quad (1)$$

Photochemical activation is a standard method for accomplishing the homolytic cleavage of X−X bonds (X = halogen).[26] Usually, radical reactions are thereby initiated[27] which, if exothermic, are very fast and unselective.[28] The use of CH_2Cl_2 as solvent is therefore a serious drawback because of its potential reactivity toward Cl•, and unwanted side-reactions such as radical transfer (eq 2) may be responsible for the poor yield of **3**. Complex **3** is most conveniently prepared by the room temperature chlorination of **2** in the presence of $AlCl_3$ (eq 3). Thus, treatment of $[NBu^n_4]_2[Pt^{II}(C_6Cl_5)_4]$ in CH_2Cl_2 with $AlCl_3$ and then chlorine in CCl_4 gave a deep orange solution from which solid **3** was isolated in 80% yield.

$$CH_2Cl_2 + Cl\bullet \rightarrow HCl + CHCl_2\bullet \quad (2)$$

$$[NBu^n_4][Pt^{III}(C_6Cl_5)_4] + {}^1/_2Cl_2 + AlCl_3 \rightarrow [Pt^{IV}(C_6Cl_5)_4] + [NBu^n_4][AlCl_4] \quad (3)$$

$AlCl_3$ and other acidic species have been used as efficient "halogen carriers" in the catalyzed electrophilic halogenation of aromatic molecules.[29] Indeed, this type of reaction also occurs at aryl-substituted organometallic substrates.[30] In the


(a)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1
2
3
4
5
6
7
8
9
10
R(Å)
(b)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1
2
3
4
5
6
7
8
9
10
R(Å)

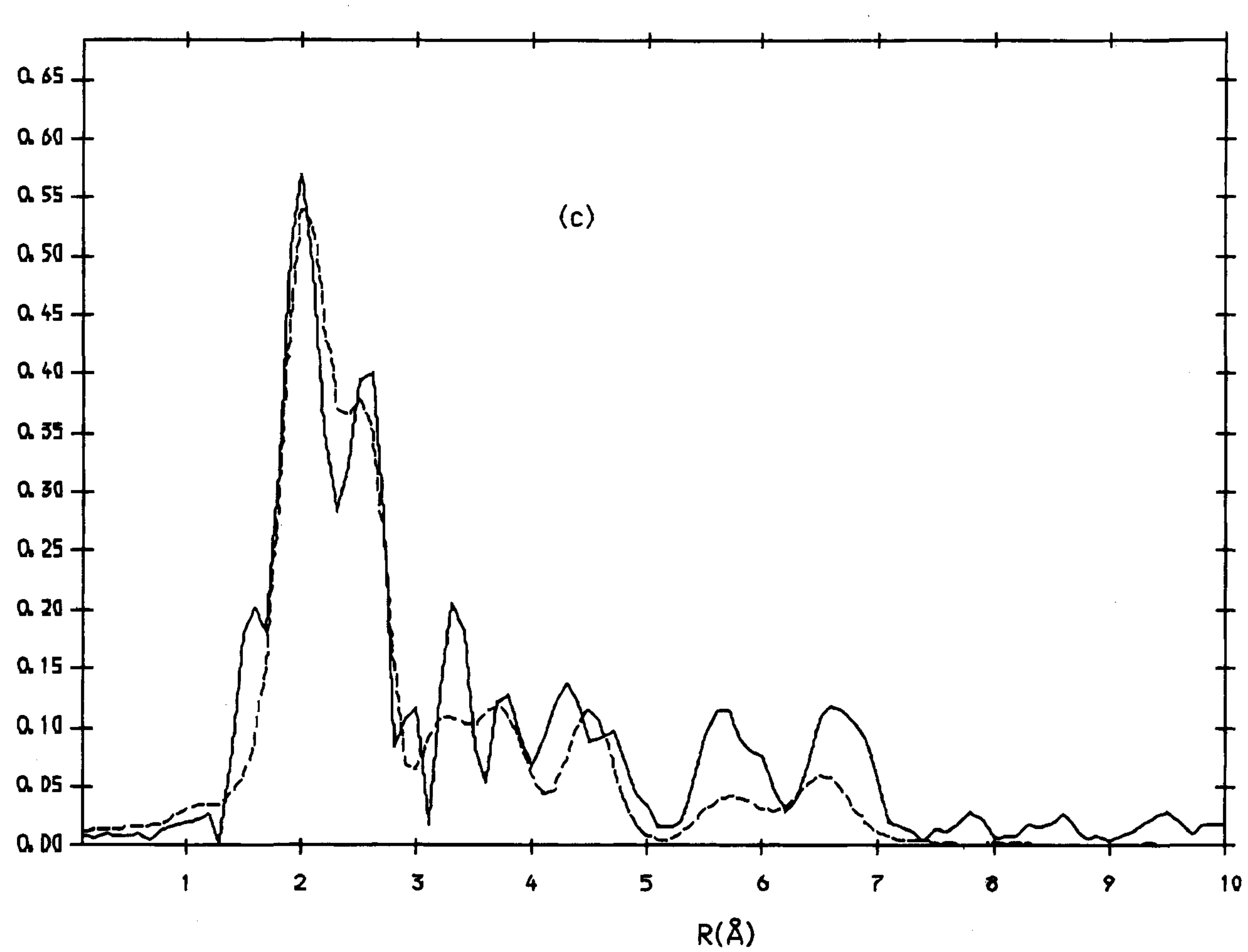


Figure 3. Observed (—) and calculated (— — —) Fourier transform magnitudes (quasi-radial distribution function, in arbitrary units) of the k^3-weighted PtL_{III}-edge EXAFS spectra for solid (a) **1**, (b) **2**, and (c) **3**.

present study, however, such aromatic electrophilic substitution, if operating at all, would have no significant effect as the aryl ligands of **2** are already perchlorinated.

Characterization of 3. Complex **3** is an air- and moisture-stable orange solid. Its thermal stability is, however, rather limited and at room temperature it spontaneously undergoes reductive elimination, slowly losing $C_6Cl_5-C_6Cl_5$ both in solution and in the solid state. On thermolysis in toluene (65 °C) under an atmosphere of CO the "*cis*-$Pt(C_6Cl_5)_2$" fragment is trapped as the stable adduct *cis*-$[Pt(C_6Cl_5)_2(CO)_2]$[18] as required by the stoichiometry shown in eq 4. The stoichiometry of **3**

$$\mathbf{3} \rightarrow \text{``}cis\text{-Pt}(C_6Cl_5)_2\text{''} + C_6Cl_5-C_6Cl_5 \xrightarrow{CO} cis\text{-}[Pt(C_6Cl_5)_2(CO)_2] + C_6C_5-C_6Cl_5 \quad (4)$$

was deduced from elemental analysis (C only) and the mass spectrum which showed a parent ion at *m/z* 1183 with the correct envelope for the formula $[Pt(C_6Cl_5)_4]$. The IR spectrum shows absorptions at 617 and 834 cm^{-1}, which can be assigned to ν(M−C)[22] and the X-sensitive vibration modes of the C_6Cl_5 groups,[21] respectively. These vibrations are sensitive to the oxidation state of the metal center.[14b] Accordingly an increase in wavenumber is observed for both ν(Pt−C) and the X-sensitive modes for **1**−**3** (Table 3) in agreement with the proposed increase in oxidation state from Pt(II) to Pt(IV).

The ^{195}Pt NMR spectrum of **3** consists of a singlet at −546 ppm, shifted by more than 3000 ppm to higher frequency compared with the signal for complex **1** (Table 3). An "oxidation shift" has previously been reported for square-planar Pt(II)/octahedral Pt(IV) systems related by oxidative−addition/reductive−elimination processes.[31] The ^{13}C NMR spectrum of **3** shows only three signals, corresponding to the *o*-, *m*-, and *p*-C atoms of the C_6Cl_5 rings, respectively; the assignment of the signals has been made assuming that the $^{n}J(^{195}\text{Pt},C)$ values decrease as *n* increases. The signal due to the *ipso*-C was not observed (Table 3).

Though the analytical and spectroscopic results noted above are in accord with the formula $[Pt(C_6Cl_5)_4]$, the IR and NMR spectra provide little indication of the structure of **3**. By contrast to the spectroscopic results, electrochemical studies provide a strong indication that a considerable structural change occurs on electron removal from the square-planar monoanion to give **3**. The CV of **3** (Figure 2) shows a completely irreversible reduction wave $[(E_p)_{red} = -0.05$ V] accompanied by a reversible product wave centered at 0.54 V. The first wave coincides with the product wave observed when the monoanion is oxidized at 1.85 V; the wave at 0.54 V corresponds to the dianion/

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monoanion couple. These results confirm the reversibility of the chemical relationship between **1**, **2**, and **3**.

The exact relationship between **3** and the anions is more clearly shown by controlled potential electrolysis and coulometry and by chemical synthesis. Thus, reduction of **3** at −0.2 V, in CH_2Cl_2 at 0 °C, led to the consumption of 1.8 F mol^{-1} ($n = 2$) and the formation of a colorless solution which voltammetry at a rotating platinum electrode showed to contain only the dianion **1**. Moreover, the addition of **1** to **3** in THF immediately gave **2**. A summary of the relationship between the three species is shown in Scheme 1.

Taken together, the electrochemical studies on **1**−**3** show that the oxidation of the monoanion to **3** is chemically reversible but electrochemically irreversible. Moreover, the very large difference (*ca.* 2.0 V) between the potential for the oxidation of the monoanion to **3** and the reduction of **3** (to **1**) indicated a large structural change.[32] An EXAFS spectroscopic study, and ultimately a single crystal structure determination, were therefore carried out on **3**.

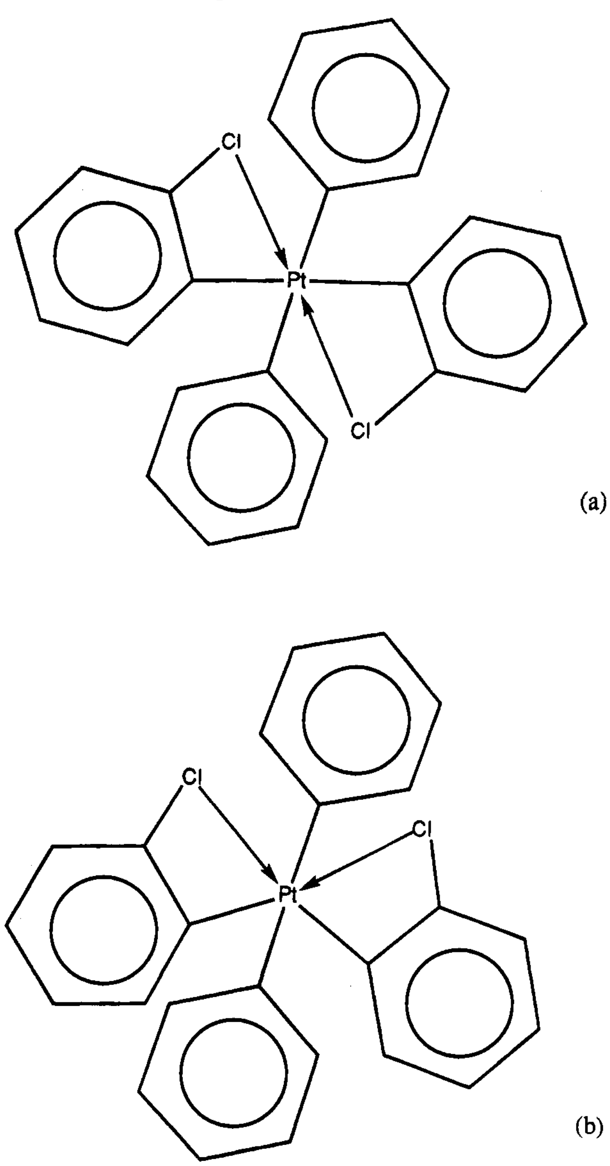
EXAFS Spectroscopy of 1−3. EXAFS data were collected at the Pt L_{III} edge for complexes **1**, **2**, and **3**. Inspection of the Fourier transform (FT, pseudo-radial distribution) functions for **1** and **2** showed very similar gross geometries (Figure 3). The FT has large maxima at *ca.* 2, 3, 3.5, 5.8, and 6.7 Å with subsidiary maxima between 4 and 5 Å. These features are due to $Pt-C_{ipso}$ at 2 Å, $Pt\cdot\cdot\cdot C_{ortho}$ (*ca.* 3 Å), $Pt\cdot\cdot\cdot Cl_{ortho}$ (*ca.* 3.5 Å), $Pt\cdot\cdot\cdot Cl_{meta}$ (*ca.* 5.8 Å), $Pt\cdot\cdot\cdot Cl_{para}$ (*ca.* 6.7 Å). Particularly striking is the presence of the well-defined features between 5 and 7 Å. This indicates both a highly ordered, symmetrical molecular structure and substantial multiple scattering. Both phenomena are to be expected in the light of the crystallographically determined structures of **1** and **2**.[15] Model fitting incorporating multiple scattering led to a detailed description of the structures in good agreement with those determined by X-ray diffraction (Table 1).

The contrast with **3** is striking. As shown in Figure 3c the FT of **3** shows large maxima at *ca.* 2 and 2.5 Å, smaller maxima between 3 and 5 Å, and further features at *ca.* 5.7 and 6.7 Å. The clear implication of these observations is that the structure of the $Pt(C_6Cl_5)_4$ unit in **3** is much less regular and symmetrical than those of **1** and **2**. While the $Pt-C_{ipso}$ contacts appear essentially undisturbed, the feature at 2.5 Å implies new atoms within the Pt coordination sphere. Model fitting confirmed that the feature at *ca.* 2.5 Å in the FT of **3** was due to two chlorine atoms ($Pt\cdot\cdot\cdot Cl$ 2.56 Å by refinement) and that a series of shells consistent with the coordination of *ortho*-chlorine atoms of two aryl ligands could be fitted with final dimensions as listed in Table 1.

Two possible structural models for **3** were therefore indicated as a result of the EXAFS studies. In the first the near D_{4h} symmetry of the platinum coordination in **1** and **2** is lowered to C_{2h} in **3** with a *trans* pair of distorted aryls [(a) in Chart 1]. In the second the symmetry is C_2 and the distorted aryls are mutually *cis* [(b) in Chart 1]. In either case the platinum achieves a distorted octahedral coordination through (rather long) $Pt\cdot\cdot\cdot Cl$ interactions. To confirm this suggestion and to distinguish between the alternative possibilities a crystal structure analysis was carried out on the toluene solvate of **3**.

The X-ray Structure of $\mathbf{3\cdot C_6H_5CH_3}$. After considerable difficulty, a suitable crystal of **3** was prepared for X-ray diffraction. The molecular structure of **3** is shown in Figure 4. Selected bond distances and angles are given in Table 4. As concluded from the EXAFS study, in compound **3** the platinum is six-coordinate but with only four ligands, two of which play a very different structural role from the monodentate C_6Cl_5 groups in the anions of **1** and **2**. In particular the structure adopted is that of the *cis*-distorted isomer [(b) in Chart 1]. Thus the Pt atom is located in a very distorted octahedral environment formed by four Pt−C σ-bonds and two Pt−Cl interactions, in a *cis* arrangement, each involving one of the *ortho*-Cl atoms of a C_6Cl_5 group. The formation of the Pt−Cl bonds on oxidation is most unusual particularly since it leads to two four-membered (Pt−C−C−Cl) rings. Moreover, the asymmetry of the structure in the solid state contrasts with the results of ^{13}C NMR spectroscopy (see above) which therefore suggest that the aryl rings become equivalent by a fluxional process in solution.

Chart 1. *Trans* (a, top) and *Cis* (b, bottom) Isomers of **3**



Two sets of Pt−C distances can be distinguished depending on whether the C atom is *trans* to chlorine [Pt−C(1) 2.038(8), Pt−C(20) 2.043(8) Å] or to a σ-bonded C_6Cl_5 group [Pt−C(10) 2.119(7), Pt−C(30) 2.199(7) Å]. This noticeable difference can be assigned to the different *trans* influence exerted by halogens and organyl groups.[33] The Pt−Cl distances are dissimilar [Pt−Cl(6) 2.559(2), Pt−Cl(15) 2.681(2) Å], but both are longer than standard Pt(IV)−Cl distances.[34] They are also longer than the

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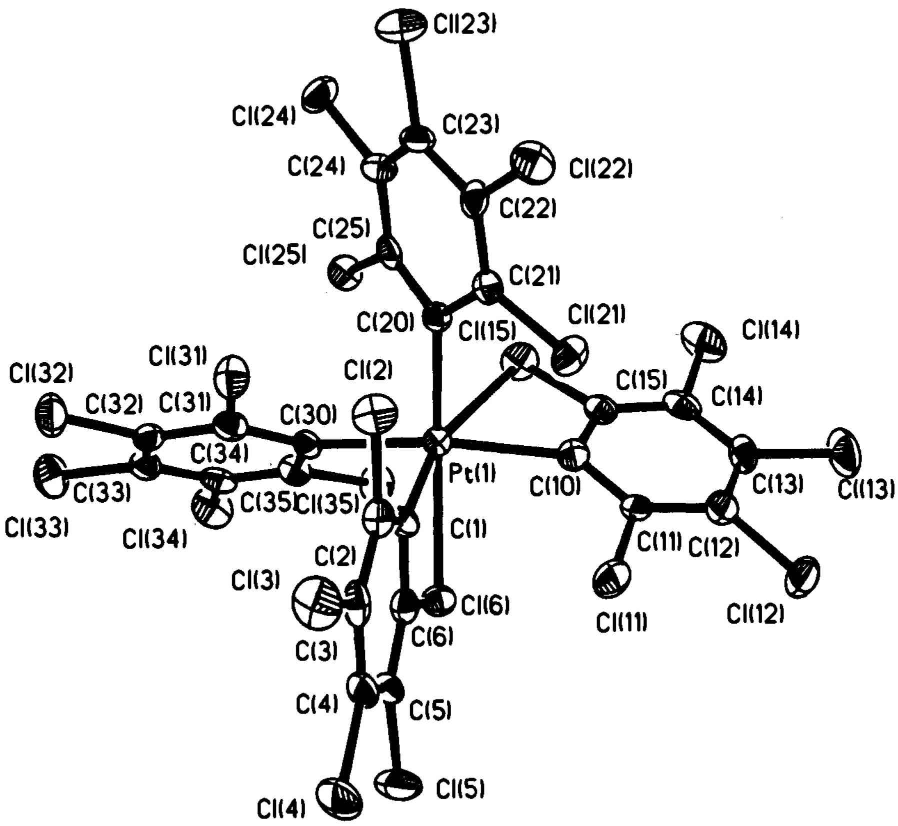

Figure 4. The molecular structure of **3** with ellipsoids drawn to enclose 40% probability density.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for [Pt(C_6Cl_5)$_4$] (**3**)

Pt(1)−C(1)	2.038(8)	Pt(1)−Cl(6)	2.559(2)
Pt(1)−C(10)	2.119(7)	Pt(1)−Cl(15)	2.681(2)
Pt(1)−C(20)	2.043(8)	Pt(1)−C(30)	2.139(7)
C(1)−C(2)	1.390(12)	C(1)−C(6)	1.387(11)
C(2)−Cl(2)	1.722(9)	C(6)−Cl(6)	1.739(9)
C(10)−C(11)	1.383(11)	C(10)−C(15)	1.362(12)
C(11)−Cl(11)	1.734(8)	C(15)−Cl(15)	1.755(8)
C(20)−C(21)	1.399(12)	C(20)−C(25)	1.414(10)
C(21)−Cl(21)	1.718(8)	C(25)−Cl(25)	1.713(9)
C(30)−C(31)	1.403(11)	C(30)−C(35)	1.383(13)
C(31)−Cl(31)	1.723(10)	C(35)−Cl(35)	1.742(8)
C(1)−Pt(1)−Cl(6)	68.2(2)	C(1)−Pt(1)−C(10)	99.9(3)
Cl(6)−Pt(1)−C(10)	84.4(2)	C(1)−Pt(1)−Cl(15)	164.3(2)
Cl(6)−Pt(1)−Cl(15)	106.5(1)	C(10)−Pt(1)−Cl(15)	64.5(2)
C(1)−Pt(1)−C(20)	104.2(3)	Cl(6)−Pt(1)−C(20)	172.0(2)
C(10)−Pt(1)−C(20)	94.8(3)	Cl(15)−Pt(1)−C(20)	80.1(2)
C(1)−Pt(1)−C(30)	88.4(3)	Cl(6)−Pt(1)−C(30)	85.1(2)
C(10)−Pt(1)−C(30)	163.1(3)	Cl(15)−Pt(1)−C(30)	106.2(2)
C(20)−Pt(1)−C(30)	97.5(3)	Pt(1)−C(1)−C(2)	140.0(6)
Pt(1)−C(1)−C(6)	103.1(6)	C(2)−C(1)−C(6)	116.9(7)
C(1)−C(6)−Cl(6)	113.0(6)	Pt(1)−Cl(6)−C(6)	75.6(3)
Pt(1)−C(10)−C(11)	137.0(6)	Pt(1)−C(10)−C(15)	106.6(5)
C(11)−C(10)−C(15)	115.6(7)	C(10)−C(15)−Cl(15)	112.9(6)
Pt(1)−Cl(15)−C(15)	76.0(3)	Pt(1)−C(20)−C(21)	123.9(5)
Pt(1)−C(20)−C(25)	119.8(6)	C(21)−C(20)−C(25)	116.2(7)
Pt(1)−C(30)−C(31)	128.4(6)	Pt(1)−C(30)−C(35)	117.6(5)
C(31)−C(30)−C(35)	114.0(7)		

Pt−Cl distances found in the few reported[35] chlorocarbon derivatives of platinum, [PtMe($Ph_2PCH_2CH_2Cl$-*κP*,*κCl*)($Ph_2PCH_2CH_2Cl$-*κP*)][BF_4] [Pt−Cl 2.425(2) Å] and [PtMe{$Ph_2P(C_6H_4Cl$-2)-*κP*,*κCl*}{$Ph_2P(C_6H_4Cl$-2)-*κP*}][BF_4] [Pt−Cl 2.462(1) Å].

The structure of **3** is remarkably different from the virtually identical square-planar geometries of the anions **1** and **2**.[15] As indicated by the electrochemical studies above, the last step in the sequential oxidation of Pt(II) to Pt(III) to Pt(IV) results in a profound structural change. It has been pointed out[36] that "platinum(IV) has such a pronounced tendency to be six-coordinate that in some of its compounds quite unusual structures are adopted". As far as we are aware, the only square-planar platinum(IV) compound yet reported in the literature[11] is the 14-electron species [Pt{$C_6H_5NNN(CH_2)_5CH_3$-*κN*^{3}}$_4$]. On the other hand, highly electron-deficient metal fragments are known to favor unusual interactions; agostic bonding mainly arises between an aliphatic C−H bond and strongly acidic metal fragments,[37] for example, in [Rh($C_6H_2Me_3$-2,4,6)$_3$], a d^6, 12-electron species which shows agostic interactions with three *ortho*-CH_3 groups, yielding a six-coordinate Rh atom.[38]

Halocarbons, RX, are traditionally considered to be poor ligands, and liquid halocarbon solvents are usually regarded as noncoordinating. However, complexes containing halocarbons as ligands have recently been isolated and characterized.[39] The ease with which such coordination compounds are formed decreases in the order: X = I > Br > Cl. Moreover, intramolecular RX → M coordination modes seem to be favored over intermolecular modes, probably due to chelation. Special stability is associated with the formation of a five-membered metallacyle. Thus, the four-membered platinacycles found upon coordination of two C_6Cl_5 groups as *κC*,*κCl*^{2}-chelating ligands in **3** would be expected to be highly strained and of limited stability. Considerable strain is indeed apparent, shown by the small values of the C(1)−Pt(1)−Cl(6) and C(10)−Pt(1)−Cl(15) angles [68.2(2)° and 64.5(2)°, respectively] and the distortion of the Pt−C_{ipso}−C_{ortho} angles from regularity [Pt(1)−

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C(1)−C(2) 140.0(6), Pt(1)−C(1)−C(6) 103.1(6), Pt(1)−C(10)−C(11) 137.0(6), Pt(1)−C(10)−C(15) 106.6(5)°]. However, the Pt−Cl interactions are not easily broken and **3** neither binds nor even dissolves in coordinating solvents such as acetone, diethyl ether, 1,4-dioxane, acetonitrile, nitromethane, and dimethyl sulfoxide. Similarly, a saturated toluene solution of **3** does not take up CO (0 °C, 30 min, IR). On the other hand, the reaction of **3** with the more basic, small-sized PMe_3 gives *cis*-$[Pt(C_6Cl_5)_2(PMe_3)_2]$ as the only Pt-containing phosphine compound (^{31}P NMR). This Pt(II) derivative forms as the result of reductive elimination of $C_6Cl_5-C_6Cl_5$. Since this process proceeds even at −30 °C, the reduction must be affected by the PMe_3 ligand in contrast to the reaction sequence depicted in eq 4, in which reductive elimination (this time at 65 °C) is believed to occur *previous* to coordination of CO. Complex *cis*-$[Pt(C_6Cl_5)_2(PMe_3)_2]$ (**4**) was prepared more straightforwardly by simple ligand substitution on the adduct *cis*-$[Pt(C_6Cl_5)_2(THF)_2]$.

Conclusions

1. The first isolable, homoleptic organometallic complex of Pt(IV) has been synthesized by one-electron oxidation of the Pt(III) monoanion $[Pt(C_6Cl_5)_4]^-$.

2. Cyclic voltammetry and EXAFS spectroscopy provide evidence for a major structural change on one-electron oxidation of $[Pt(C_6Cl_5)_4]^-$.

3. An X-ray structural study has shown that $[Pt(C_6Cl_5)_4]$ has a distorted octahedral structure including two, mutually *cis*, Pt⋅⋅⋅Cl interactions.

Acknowledgment. We thank the Comisión Interministerial de Ciencia y Tecnología (CICYT, Spain) for financial support (Project PB92-0364) and Degussa for a generous loan of platinum chloride.

Supplementary Material Available: Tables containing bond lengths, bond angles, positional parameters, and thermal parameters for the X-ray structure of $\mathbf{3}\cdot C_6H_5CH_3$ (5 pages); tables of observed and calculated structure factors (26 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, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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