Steric Crowding and Redox Reactivity in Platinum(II) and Platinum(IV) Complexes Containing Substituted 1,10-Phenanthrolines

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The effect of the phenanthroline substituents on the structure and reactivity of platinum(II) and platinum(IV) complexes has been investigated. The X-ray crystal structures of the compounds $[PtI_2(4,7\text{-}Ph_2phen)]\cdot CHCl_3$ (**1dz**$\cdot CHCl_3$), $[PtI_4(4,7\text{-}Ph_2phen)]\cdot CHCl_3$ (**2dz**$\cdot CHCl_3$), $[PtI_2(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)]$ (**1fz**), and $[PtI_4(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)]\cdot I_2$ (**2fz**$\cdot I_2$) have shown that complexes **1fz** and **2fz**, containing ortho-substituted phenanthrolines, exhibit a remarkable displacement of the equatorial iodine atoms from the N−Pt−N′ plane (average 0.477(2) and 0.199(2) Å, respectively), a bending of the phenanthroline [angle between outer rings of 19.9(7) and 14.2(7)°, respectively] and a rotation of the N−C−C′−N′ plane with respect to the N−Pt−N′ plane [32.3(10) and 26.5(9)°, respectively]. Comparison between the structures of **1fz** and **2fz**, both having the phenanthroline with methyl substituents in the ortho position, indicates that, in the latter case, because of the presence of the two axial iodine ligands, the displacements of the ligands from the equatorial plane are smaller and find a compensation in a narrowing of the I(1)−Pt−I(1′) angle (5°) and a lengthening of the Pt−N bonds (0.07 Å). The electrochemical behavior of the four-coordinate platinum(II) complexes shows that compounds possessing regular planar geometry have access to the one-electron reduced species, whereas those with distorted coordination geometry are irreversibly reduced by collapsing of the complex geometry. This is in sharp contrast with the behavior of related nickel complexes for which the pseudo-tetrahedral coordination imposed by bulky 2,9-substituents of phenanthroline stabilizes the nickel(I) species. Spectroscopic results allow us to assign a significant Pt(I) character to $[$**1d**$]^-$ monoanions. The electrogenerated, plus one electron, complexes are not indefinitely stable and, because of conjugation with the phen ligand, progressively restore the Pt(II) oxidation state by transferring the electron to the peripheral organic ligand. The latter process can involve multiple electron additions in the macroelectrolysis time scale. The related platinum(IV) complexes $[PtX_4(L)]$ undergo irreversible two-electron reduction accompanied by fast release of the axial ligands and formation of the corresponding platinum(II) species.

Introduction

The steric requirements of a chelating ligand can be modified to increase the selectivity for a specific metal ion. For instance, the introduction of two methyl substituents in the 2,9-positions of 1,10-phenanthroline (phen) leads to a very specific reagent for the analytical determination of copper in the presence of almost any other type of metal ions (neocuproine).[1] The steric requirement of a chelating ligand can also be designed to tune the preference of a particular metal ion for a given coordination geometry and/or oxidation state. For instance, the same $2,9\text{-}Me_2phen$ ligand, because of the steric hindrance created by the two ortho-methyl substituents, stabilizes three-coordinate platinum(0)[2] and five-coordinate platinum(II) and palladium(II) species.[3]

By controlling the coordination geometry of a metal complex, it is also possibile to induce specific and unusual reactivities. For instance the trigonal platinum(0) complex $[Pt(C_2H_4)(2,9\text{-}Me_2phen)]$ easily undergoes oxidative addition of electrophiles (XY) to give the trigonal bipyramidal platinum(II) species $[PtXY(C_2H_4)(2,9\text{-}Me_2phen)]$ without loss of olefin.[2] Halogenation of these very stable five-coordinate platinum(II) species offers an easy route to the unprecedented β-haloalkyl platinum(IV) complexes $[PtX_3(CH_2CH_2X)(2,9\text{-}Me_2phen)]$.[4] Moreover the square planar complexes $[MX_2(2,9\text{-}Me_2phen)]$ (M = Pt, Pd; X = halogen) easily react with an extra ligand (L) to give the addition $[MX_2(L)(2,9\text{-}Me_2phen)]$ rather than the substitution products $[MX(L)(2,9\text{-}Me_2phen)]X$.[3]

The nature and position of the peripheral phenanthroline substituents could also influence the redox properties of the platinum center. In most complexes with aromatic ligands (1,2-diphenyl-1,2-ethenedithiolate,[5] diaminomaleonitrile,[6] 2-phenylpyridine, 2-phenylpyrazole, and 2,2′-bipyridine (bipy),[7−13] 4,7-

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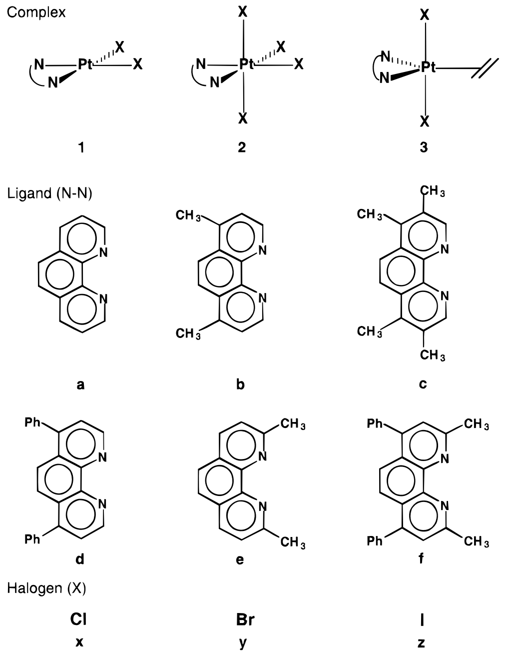
Chart 1



diphenyl-1,10-phenanthroline,[14] and other heterocyclic nitrogen donor ligands[15]) the redox process has been localized on the ligand rather than on the metal. However, in some cases there were also evidences for either an irreversible[8] or a reversible[13,16−18] electron addition process involving a metal-based LUMO level.

In this paper we present a systematic study on the effect of the phenanthroline substituents on the structure and reactivity of platinum(II) and platinum(IV) complexes (Chart 1).

Materials and Methods

Starting Materials. Commercial reagent grade chemicals, 1,10-phenanthroline (phen, **a**), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen, **b**), 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-Me_4phen, **c**), 4,7-diphenyl-1,10-phenanthroline (4,7-Ph_2phen, **d**), 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2phen, **e**), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (2,9-Me_2-4,7-Ph_2phen, **f**) (Aldrich) were used without further purification. $[PtCl_2(DMSO)_2]$ (DMSO = dimethyl sulfoxide) was prepared as already described.[19]

Preparation of Complexes. $[PtCl_2(phen)]$ (1ax), $[PtCl_2(4,7\text{-}Me_2phen)]$ (1bx), $[PtCl_2(3,4,7,8\text{-}Me_4phen)]$ (1cx), and $[PtCl_2(4,7\text{-}Ph_2phen)]$ (1dx). The appropriate phenanthroline ligand (1 mmol) in methanol (5 mL) was added dropwise to a stirred suspension of $[PtCl_2(DMSO)_2]$ (1 mmol) in the same solvent (40 mL). After 12 h of stirring the yellow solid was collected, washed with methanol and diethyl ether, and dried in air; yield, 90%. The elemental analyses are reported in Table S1 of the Supporting Information.

$[PtX_2(4,7\text{-}Ph_2phen)]$ (X = Br, 1dy; I, 1dz). An excess of either tetrabutylammonium bromide or tetrabutylammonium iodide was added with stirring to a suspension of $[PtCl_2(4,7\text{-}Ph_2phen)]$ (**1dz**) (0.5 mmol) in chloroform (200 mL). The reaction mixture was kept in a water bath (40 °C) under stirring for 3 h. The solvent was then evaporated under vacuum and the solid residue washed with methanol to remove excess tetrabutylammonium salt. The deep yellow ($[PtBr_2(4,7\text{-}Ph_2phen)]$, **1dy**) or orange residue ($[PtI_2(4,7\text{-}Ph_2phen)]$, **1dz**) was then washed with diethyl ether and dried in air; yield, 90%. Elemental analyses reported in Table S1 of the Supporting Information.

$[PtX_2(2,9\text{-}Me_2phen)]$ (X = Cl, 1ex; Br, 1ey; I, 1ez) and $[PtX_2(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)]$ (X = Cl, 1fx; Br, 1fy; I, 1fz). Complexes **1ex**−**ez** were prepared by previously reported procedures,[3] and complexes **1fx**−**fz** were prepared in a similar way; the yields were ≥90%. Elemental analyses reported in Table S1 of the Supporting Information.

$[PtX_4(4,7\text{-}Ph_2phen)]$ (X = Cl, 2dx; Br, 2dy; I, 2dz), $[PtX_4(2,9\text{-}Me_2phen)]$ (X = Cl, 2ex; Br, 2ey; I, 2ez), and $[PtX_4(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)]$ (X = Cl, 2fx; Br, 2fy; I, 2fz). An excess of halogen in CCl_4 solution was added with stirring to a suspension of the platinum(II) complex in chloroform (0.5 mmol in 200 mL of solvent). Complexes **2ex** (pale yellow), **2ey** (orange), and **2ez** (black), which have a poor solubility in chloroform, separated from the solution; complexes **2dx** (pale yellow), **2dy** (orange), **2dz** (red), **2fx** (pale yellow), **2fy** (orange), and **2fz** (deep brown) were precipitated by addition of diethyl ether to the reaction solution. The products were collected, washed with diethyl ether, and dried in air. The yields were above 90%. The elemental analyses are reported in Table S1 of the Supporting Information.

$[PtX_2(C_2H_4)(2,9\text{-}Me_2phen)]$ (X = Cl, 3ex; Br, 3ey; I, 3ez) and $[PtX_2(C_2H_4)(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)]$ (X = Cl, 3fx; Br, 3fy; I, 3fz). The five-coordinate complexes **3ex**−**ez** were prepared, as already reported, by direct uptake of ethylene from the corresponding square planar species **1ex**−**ez**. The analogous complexes **3fx**−**fz** were prepared in a similar way starting from **1fx**−**fz** and ethylene. The yields were always greater than 90%. The elemental analyses are reported in Table S1 of the Supporting Information.

Redox Equilibrium of the Pt(IV)/Pt(II) Iodo Species. Platinum(IV) complexes with ortho-substituted phenanthrolines and iodine ligands (**2ez** and **2fz**) are not stable in chloroform solution but undergo halogen dissociation and formation of the corresponding platinum(II) species. The equilibrium constant for dissociation was determined for the more soluble **2fz** species by dissolving a weighed amount of platinum(IV) complex (1.5 mg) in deuteriochloroform (1 mL) and evaluating the Pt(IV)/Pt(II) ratio by integration of the corresponding NMR signals. Addition of iodine shifts the equilibrium toward the platinum(IV) species.

Reaction of Pt(IV) Complexes with Ethylene. The reaction of complexes **2ez** and **2fz** with ethylene was performed in a NMR tube by flowing ethylene gas through a solution (**2fz**) or suspension (**2ez**) of the platinum(IV) complex (5 mg) in $CDCl_3$ (1 mL). A fading of the solution of **2fz** or a complete dissolution of **2ez** took place in a few minutes in accord with the quantitative formation of the corresponding five-coordinate species **3ez** and **3fz**, respectively, and of 1,2-diiodoethane (methylene resonance at δ 3.62 in chloroform solution). In the case of the chloro and bromo species **2fx**,**fy**, 3×10^{-2} mmol of complex was dissolved in 2.5 mL of $CDCl_3$ and the solution was placed in a 40 mL Schlenk tube. Air was removed and the tube connected to a 200 mL rubber ballon filled with ethylene. The tube was then cooled in liquid nitrogen, and after the olefin had passed from the ballon into the tube, the stop-cock was closed. The reaction flask was then allowed to reach room temperature and left under stirring. The conversion was complete for both cases after 1 month. The five-coordinate species (**3fx** and **3fy**, respectively) were precipitated by addition of pentane; the solid was collected and dried. The yield was 60% (**3fx**) and 80% (**3fy**), respectively. Five-coordinate complexes obtained by reaction of the platinum(IV) complexes with ethylene were identical to those obtained from the platinum(II) species by direct uptake of ethylene.

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Table 1. Experimental Data for the X-ray Diffraction Studies

	1dz·$CHCl_3$	**1fz**	**2dz**·$CHCl_3$	**2fz**·I_2
mol formula	$C_{24}H_{16}I_2N_2Pt{\cdot}CHCl_3$	$C_{26}H_{20}I_2N_2Pt$	$C_{24}H_{16}I_4N_2Pt{\cdot}CHCl_3$	$C_{26}H_{20}I_4N_2Pt{\cdot}I_2$
mol wt	900.68	809.36	1154.49	1316.97
cryst syst	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	*Pnma*	$P2_12_12_1$	$C2/c$	*Pnma*
radiation[a]	graphite monochromated	Nb filtered	graphite monochromated	Nb filtered
a, Å	11.151(4)	10.515(2)	36.823(9)	10.631(2)
b, Å	19.647(6)	10.016(2)	8.579(2)	14.834(3)
c, Å	11.448(4)	22.293(4)	20.546(6)	19.357(4)
β, deg			112.38(2)	
V, Å^3	2508(1)	2347.9(8)	6002(3)	3053(1)
Z	4	4	8	4
D_{calcd}, g cm^{-3}	2.385	2.290	2.555	2.866
$F(000)$	1664	1496	4176	2344
θ range, deg	3–25	3–27	3–25	3–25
μ(Mo Kα), cm^{-1}	83.94	86.22	90.76	106.83
unique total data	5304	2920	2285	2818
unique obsd data	1619 [$I > 2\sigma(I)$]	2036 [$I > 2\sigma(I)$]	972 [$I > 2\sigma(I)$]	1460 [$I > 2\sigma(I)$]
no. of variables	95	361	187	167
final R, R_w indices[b]	0.0342, 0.0413	0.0570, 0.0701	0.0368, 0.0428	0.0524, 0.0608

[a] $\lambda = 0.710\,73$ Å. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Crystal Structure Determinations of Complexes 1dz·$CHCl_3$, 2dz·$CHCl_3$, 1fz, and 2fz·I_2. Crystals suitable for the X-ray analyses were obtained by crystallization from chloroform/diethyl ether solutions. Selected crystallographic data for the four compounds are listed in Table 1. Data were collected at room temperature on Philips PW 1100 (**1dz**·$CHCl_3$ and **2dz**·$CHCl_3$) and Siemens AED (**1fz** and **2fz**·I_2) single-crystal diffractometers using the graphite-monochromated (**1dz**·$CHCl_3$ and **2dz**·$CHCl_3$) and niobium-filtered Mo Kα (**1fz** and **2fz**·I_2) radiation. All reflections, having $I > 2\sigma(I)$, were considered observed and used in the analyses. The individual profiles were analyzed following Lehmann and Larsen.[20] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied.[21]

All of the structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares, first with isotropic and then with anisotropic thermal parameters in the last cycles, for all of the non-hydrogen atoms (**1fz** and **2fz**·I_2) or for only the Pt, I, and N atoms of the complex and the C and Cl atoms of the solvation molecule (**1dz**·$CHCl_3$), or for only the Pt and I atoms of the complex and the C and Cl atoms of the solvation molecule (**2dz**·$CHCl_3$). All hydrogen atoms were placed at their calculated positions (C–H = 0.96 Å) and refined "riding" on the corresponding carbon atoms. Since the space group $P2_12_12_1$ leads to a chiral configuration in the structure, an independent final cycle of refinement for **1fz** was carried out using the coordinates $-x$, $-y$, $-z$ for the non-hydrogen atoms. A remarkable increasing of the R value was obtained [$R(+x,+y,+z) = 0.0570$, $R(-x,-y,-z) = 0.0780$]. The former model was selected, and the reported data refer to this model. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref 22. The SHELX-76 and SHELXS-86 systems of computer programs were used.[23] Final atomic coordinates are given in Tables S2 (**1dz**·$CHCl_3$), S3 (**1fz**), S4 (**2dz**·$CHCl_3$), and S5 (**2fz**·I_2) of the Supporting Information. All calculations were carried out on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker AM 300 instrument. IR spectra were recorded as KBr pellets on Perkin-Elmer 283 and FT 1600 spectrophotometers. Materials and apparatus for electrochemistry and coupled EPR measurements are described in ref 24. Potential values are referred to the saturated calomel electrode (SCE). Direct UV–visible spectra on electrolysis solutions were performed with a Perkin-Elmer Lambda 2 fiber optic system.

Results and Discussion

Synthesis of the Complexes. The platinum(II) complexes were synthesized by reaction of $[PtCl_2(DMSO)_2]$ with the appropriate phenanthroline ligand. In the case of phenanthrolines without substituents in the 2,9-positions (**a**–**d** in Chart 1) the reaction was complete in 2–12 h at room temperature and gave quantitative yield of product. In contrast phenanthrolines with substituents in the 2,9-positions (**e** and **f**) required higher temperature (boiling ethanol), longer reaction time (24 h), and chromatographic purification of the crude product.[3] The reactions proceed directly to the formation of the end products $[PtCl_2(N{-}N)]$ (**1ax**–**fx**) without formation of the intermediate cationic species $[PtCl(DMSO)(N{-}N)]Cl$ which, instead, are detected in the case of aliphatic diamines.[25,26] Also the reaction with DMSO of the $[PtCl_2(N{-}N)]$ complexes is different for phenanthrolines and aliphatic diamines. Complexes with aliphatic diamines readily undergo solvolysis with dissociation of one chloride ion.[27] Complexes with phenanthrolines not bearing substituents in the ortho positions, such as **1ax**, in DMSO-d_6 solution remain unchanged over a period of weeks (^{1}H NMR spectra) and do not undergo solvolysis at any appreciable extent. Finally complexes with ortho-substituted phenanthrolines, such as **1ex**–**ez** and **1fx**–**fz**, react readily with DMSO to give addition products ($[PtX_2(DMSO)(2,9\text{-}Me_2phen)]$ and $[PtX_2(DMSO)(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)]$, respectively) in which one molecule of DMSO has displaced one end of the phenanthroline.[3]

The platinum(IV) complexes **2dx**–**dz**, **2ex**–**ez**, and **2fx**–**fz** (Chart 1) were prepared by halogenation of the corresponding platinum(II) species in $CHCl_3$ solution. The stability of the platinum(IV) complexes in organic solvents depends upon the nature of the halogen and of the phenanthroline ligands. The

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Table 2. ^1H NMR Data (δ, Downfield from $SiMe_4$; $CDCl_3$ Solvent) for Phenanthroline Ligands and Platinum(II) and Platinum(IV) Complexes

compd	phen[a]				phen substituents[a]		others
	H(2,9)	H(3,8)	H(4,7)	H(5,6)			
a[b]	9.09 dd (5,1)	7.76 dd (8,5)	8.48 dd (8,1)	7.98			
1ax[b]	9.69 dd (5,1) [40]	8.16 dd (8,5)	9.04 dd (8,1)	8.28			
						Me(4,7)	
b[c]	8.97 d (4)	7.47 dd (1,4)		8.06		2.79 d (1)	
1bx[c]	9.73 d (6) [40]	7.73 dd (6,1)		8.14		2.85 d (1)	
					Me(3,8)	Me(4,7)	
c[c]	8.85			8.06	2.52	2.68	
1cx[c]	9.52 [42]			8.11	2.64	2.72	
						Ph(4,7)	
d	8.23 d (4)	7.58 d (4)		7.84		7.51 m {10}	
1dx	9.97 d (6) [36]	7.82 d (6) [6]		8.05		7.60 m {10}	
1dy	10.19 d (6) [41]	7.79 d (6) [6]		8.04		7.60 m {10}	
1dz	10.66 d (6) [45]	7.83 d (6) [6]		8.03		7.60 m {10}	
2dx	10.00 d (6) [27]	8.09 d (6) [6]		8.21		7.59 m {4}; 7.66 m {6}	
2dy	10.19 d (6) [28]	8.05 d (6) [6]		8.19		7.60 m {4}; 7.65 m {6}	
2dz	10.40 d (6) [30]	8.05 d (6) [6]		8.18		7.64 m {10}	
					Me(2,9)		
e		7.47 d (8)	8.11 d (8)	7.70	2.93		
1ex		7.56 d (8) [16]	8.35 d (8) [4]	7.81	3.25 [7]		
1ey		7.56 d (8) [16]	8.34 d (8) [4]	7.80	3.25 [7]		
1ez		7.57 d (8) [16]	8.34 d (8) [4]	7.80	3.25 [7]		
2ex[c]		7.74 d (8) [11]	8.48 d (8) [3]	7.96	3.61 [6]		
2ey[c]		7.72 d (8) [11]	8.45 d (8) [3]	7.93	3.72 [6]		
2ez[c]		7.69 d (8) [11]	8.42 d (8) [3]	7.89	3.92 [6]		
							C_2H_4
3ex		7.80 d (8) [3]	8.32 d (8)	7.85	3.49 [7]		3.67 [70]
3ey		7.79 d (8) [3]	8.30 d (8)	7.85	3.47 [7]		3.80 [70]
3ez		7.79 d (8) [3]	8.25 d (8)	7.85	3.44 [7]		4.20 [71]
					Me(2,9)	Ph(4,7)	
f		7.43		7.73	2.98	7.50 m {10}	
1fx		7.50		7.79	3.29 [6]	7.56 m {6}; 7.49 m {4}	
1fy		7.50		7.78	3.29 [6]	7.56 m {6}; 7.51 m {4}	
1fz		7.52		7.88	3.29 [6]	7.56 m {6}; 7.52 m {4}	
2fx		7.63 [11]		7.85	3.70 [5]	7.59 m {6}; 7.52 m {4}	
2fy		7.60 [11]		7.81	3.80 [5]	7.59 m {6}; 7.52 m {4}	
2fz		7.58 [11]		7.77	4.00 [5]	7.58 m {6}; 7.53 m {4}	
							C_2H_4
3fx		7.75		7.85	3.54 [7]	7.52 m {10}	3.67 [70]
3fy		7.75		7.85	3.52 [7]	7.53 m {10}	3.79 [68]
3fz		7.75		7.87	3.48 [7]	7.54 m {10}	4.20 [71]

[a] Values of *J*(H−H) (in parentheses) and *J*(Pt−H) [in brackets] are given when assignable. Integral values are given in braces. [b] Solvent = DMSO-d_6. [c] Solvent = CD_2Cl_2.

complexes with phenanthrolines not bearing substituents in the 2,9-positions are stable; in contrast the complexes with ortho-substituted phenanthroline and iodine ligands (**2ez**,**fz**) undergo reductive elimination to platinum(II) species (**1ez**,**fz**) and free iodine ($K = (4 \pm 1) \times 10^{-4}$ mol·L^{-1} for **2fz** in $CDCl_3$ at 25 °C). Although the equilibrium is only slightly shifted to the right, a stream of ethylene through the $CDCl_3$ solution of **2ez**,**fz** causes immediate and complete disappearance of the platinum(IV) complexes and formation of the five-coordinate platinum(II) species [$PtI_2(C_2H_4)$(2,9-Me_2phen)] (**3ez**) and [$PtI_2(C_2H_4)$(2,9-Me_2-4,7-Ph_2phen)] (**3fz**), respectively, and of 1,2-diiodoethane ([PtI_4(L)] + $2C_2H_4 \rightarrow$ [$PtI_2(C_2H_4)$(L)] + $C_2H_4I_2$, L = **e**, **f**). The complexes with ortho-substituted phenanthrolines and either chloro or bromo ligands (**2ex**,**fx** and **2ey**,**fy**) do not undergo detectable reductive elimination of halogen, but they do react with ethylene under pressure to give the five-coordinate platinum(II) species [ca. 15 and 25% conversion for **2fx** and **2fy**, respectively, in $CDCl_3$ solution (3×10^{-2} mmol of complex in 2.5 mL of solvent), 5 atm of C_2H_4, 25 °C, and 108 h reaction time]. The greater tendency of the iodo complexes (**2ez**,**fz**), with respect to the chloro and bromo species (**2ex**,**fx** and **2ey**,**fy**) to undergo reduction and formation of the five-coordinate platinum(II) species when treated with ethylene can be related to both the greater distorsion of the coordination geometry (which increases by increasing the bulk of the halogen atoms) and to the lower redox potential of the halogen (which decreases from Cl_2 to I_2).

^1H NMR data for the free phenanthroline ligands, the four- and five-coordinate platinum(II) species, and the six-coordinate platinum(IV) complexes are reported in Table 2. Comparison of the chemical shifts and ^{195}Pt coupling constants of the ligand protons, among the four-, five-, and six-coordinate complexes, gives useful information about the bonding situation in the three types of complexes. The ^4J- and ^5J(PtH) of the aromatic protons have the greatest values in the square planar platinum(II) species **1ex**−**ez**; slightly smaller values are observed in the octahedral platinum(IV) species **2ex**−**ez**; and much smaller values are observed in the trigonal bipyramidal five-coordinate platinum(II) complexes **3ex**−**ez**. The much smaller ^4J- and ^5J(PtH) couplings observed in the five-coordinate species have already been related to a relevant weakening and lengthening of the Pt−N bonds.[3] In contrast with the aromatic protons, the methyl substituents in ortho positions have almost identical coupling with platinum in the four-, five-, and six-coordinate species (compare values within **1ex**−**ez**−**3ex**−**ez** and within **1fx**−**fz**−**3fx**−**fz**), indicating that this coupling originates mainly from a through-space interaction. Finally, for a given coordination geometry, the presence of methyl substituents in the 2,9-positions of the phenanthroline has the effect of slightly reducing the values of ^4J(PtH) (compare values of **1dx**−**dz** with those

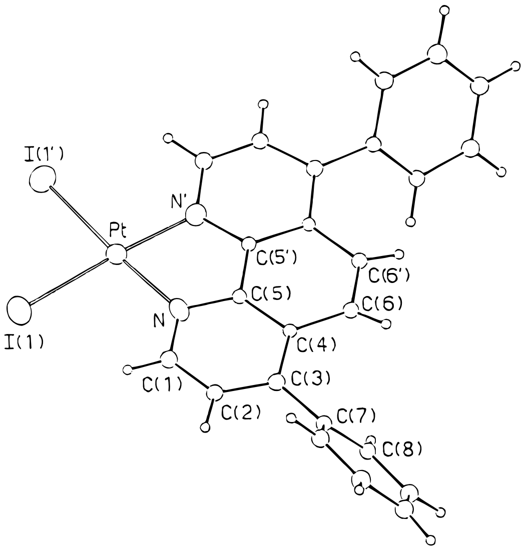

Figure 1. View of the molecular structure of the complex [PtI_2(4,7-Ph_2phen)] (**1dz**) together with the atomic numbering scheme. The ellipsoids enclose 30% probability. The primed atoms are related to the unprimed ones by the transformation *x*, $^1/_2 - y$, *z*.

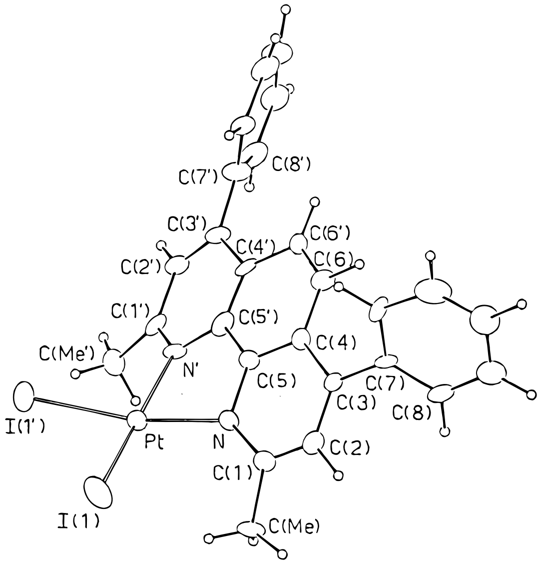

Figure 2. View of the molecular structure of the complex [PtI_2(2,9-Me_2-4,7-Ph_2phen)] (**1fz**) together with the atomic numbering scheme. The ellipsoids enclose 30% probability.

of **1fx**−**fz** and values of **2dx**−**dz** with those of **2fx**−**fz**), which is indicative of a slight weakening of the Pt−N bonds.

Crystal Structures of Compounds 1dz·$CHCl_3$ and 1fz. The crystal structures of two four-coordinate platinum(II) complexes, containing phenanthroline ligands with and without methyl substituents in ortho positions, have been determined. Views of the molecular structures with the atomic numbering schemes are given in Figures 1 and 2. Relevant bond distances and angles are reported in Table 3.

The complex **1dz**·$CHCl_3$ has a crystallographically imposed C_s symmetry; two cis positions of the square planar coordination geometry are occupied by the nitrogen atoms of the 4,7-Ph_2-phen ligand and the other two by iodide ions (Figure 1). The four donor atoms and the central metal are perfectly coplanar. The Pt−I and Pt−N bond distances are 2.558(2) and 2.02(1) Å, respectively, and the I−Pt−I′ and N−Pt−N′ angles 87.3(1) and 78.1(4)°, respectively. The phen moiety exhibits a small bowlike distorsion with a dihedral angle between the outer rings of 5.0(4)°; moreover the plane of the chelating moiety N−C(5)−

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

	1dz·$CHCl_3$[a]	**1fz**	**2dz**·$CHCl_3$	**2fz**·I_2[a]
Pt−I(1)	2.558(2)	2.580(2)	2.606(2)	2.632(2)
Pt−I(1′)		2.574(2)	2.602(2)	
Pt−I(2)			2.655(2)	2.665(3)
Pt−I(3)			2.671(2)	2.674(3)
Pt−N	2.02(1)	2.09(2)	2.09(1)	2.15(2)
Pt−N′		2.07(2)	2.08(2)	
N−C(1)	1.39(2)	1.31(3)	1.32(3)	1.32(2)
N−C(5)	1.35(2)	1.39(3)	1.40(3)	1.40(2)
C(1)−C(2)	1.32(2)	1.34(3)	1.34(3)	1.40(3)
C(2)−C(3)	1.36(2)	1.38(3)	1.38(3)	1.40(3)
C(3)−C(4)	1.44(2)	1.47(3)	1.41(3)	1.40(3)
C(4)−C(5)	1.39(2)	1.41(3)	1.41(2)	1.46(3)
C(5)−C(5′)	1.40(2)	1.36(3)	1.43(3)	1.36(3)
C(4)−C(6)	1.44(2)	1.40(3)	1.43(3)	1.39(3)
C(6)−C(6′)	1.32(2)	1.33(3)	1.35(3)	1.30(3)
C(3)−C(7)	1.45(2)	1.48(3)	1.47(2)	1.50(3)
C(1)−C(Me)		1.50(4)		1.49(3)
N′−C(1′)		1.38(3)	1.31(3)	
N′−C(5′)		1.38(3)	1.40(2)	
C(1′)−C(2′)		1.41(3)	1.36(4)	
C(2′)−C(3′)		1.35(3)	1.36(3)	
C(3′)−C(4′)		1.47(3)	1.39(3)	
C(4′)−C(5′)		1.37(3)	1.40(3)	
C(4′)−C(6′)		1.44(3)	1.42(2)	
C(3′)−C(7′)		1.48(3)	1.42(4)	
C(1′)−C(Me′)		1.52(4)		
N−Pt−N′	78.1(4)	78.8(7)	80.5(6)	78.4(6)
N−Pt−I(1)	97.3(3)	95.2(5)	96.1(5)	99.0(4)
I(1′)−Pt−N′		95.8(5)	95.2(4)	
I(2)−Pt−N			88.6(5)	91.7(4)
I(2)−Pt−N′			89.3(5)	
I(1)−Pt−I(2)			92.3(1)	92.7(1)
I(2)−Pt−I(1′)			90.7(1)	
I(1′)−Pt−I(1)	87.3(1)	88.1(1)	88.2(1)	83.2(1)
I(3)−Pt−N			89.3(5)	88.6(4)
I(3)−Pt−N′			87.9(5)	
I(3)−Pt−I(1)			90.3(1)	87.0(1)
I(3)−Pt−I(1′)			91.3(1)	
Pt−N−C(1)	128(1)	134(1)	129(1)	131(1)
Pt−N−C(5)	116(1)	105(1)	112(1)	108(1)
Pt−N′−C(1′)		133(1)	130(2)	
Pt−N′−C(5′)		108(1)	113(1)	
C(1)−N−C(5)	116(1)	120(2)	119(2)	120(2)
C(5′)−N′−C(1′)		118(2)	116(2)	
N−C(1)−C(Me)		119(2)		123(2)
N−C(1)−C(2)	122(2)	121(2)	124(2)	121(2)
C(2)−C(1)−C(Me)		120(2)		116(2)
C(1)−C(2)−C(3)	124(1)	124(2)	121(2)	122(2)
C(2)−C(3)−C(7)	120(1)	125(2)	119(2)	121(2)
C(2)−C(3)−C(4)	116(1)	114(2)	118(2)	118(2)
C(4)−C(3)−C(7)	124(1)	121(2)	123(2)	
C(3)−C(4)−C(6)	125(1)	124(2)	126(2)	125(2)
C(3)−C(4)−C(5)	118(1)	120(2)	119(2)	117(2)
C(5)−C(4)−C(6)	116(1)	116(2)	114(2)	117(2)
N−C(5)−C(4)	124(1)	118(2)	119(2)	121(2)
C(4)−C(5)−C(5′)	122(1)	121(2)	123(2)	120(2)
N−C(5)−C(5′)	115(1)	120(2)	118(2)	119(2)
C(4)−C(6)−C(6′)	122(1)	124(2)	122(2)	123(2)
C(6)−C(6′)−C(4′)		118(2)	125(2)	
C(6′)−C(4′)−C(3′)		124(2)	127(2)	
C(6′)−C(4′)−C(5′)		119(2)	114(2)	
C(5′)−C(4′)−C(3′)		117(2)	119(2)	
C(5)−C(5′)−C(4′)		121(2)	121(2)	
N′−C(5′)−C(4′)		124(2)	123(2)	
N′−C(5′)−C(5)		115(2)	116(2)	
N′−C(1′)−C(2′)		120(2)	122(2)	
C(1′)−C(2′)−C(3′)		121(2)	124(2)	
C(4′)−C(3′)−C(2′)		119(2)	116(2)	
C(2′)−C(3′)−C(7′)		120(2)	122(2)	
C(4′)−C(3′)−C(7′)		121(2)	122(2)	
N′−C(1′)−C(Me′)		118(2)		
C(2′)−C(1′)−C(Me′)		123(2)		

[a] The primed atoms are related to the unprimed ones by the transformation *x*, $^1/_2 - y$, *z*.

C(5′)−N′ forms a dihedral angle of 3.7(6)° with the N−Pt−N′ plane. An analogous bowlike distorsion of the phenanthroline was observed in the palladium compound [$PdCl_2$(4,7-Ph_2-phen)],[28] while a bending, on opposite directions, of the outer rings with respect to the central ring was found in the bis(phenanthrolinium) cation[29] and in a series of $[M(phen)_2]^{2+}$ complexes (M = Pt and Pd).[7,30]

The structure of **1fz**, with a phenanthroline ligand carrying methyl substituents in the two ortho positions (Figure 2), shows remarkable differences from that of the previously discussed **1dz**. (a) The platinum atom is displaced by 0.222(1) Å from the mean plane through I(1), I(1′), N, and N′ (while it was coplanar with the four donor atoms in **1dz**). (b) The Pt−I [2.574(2) and 2.580(2) Å] and Pt−N bond distances [2.07(2) and 2.09(2) Å] are longer than in **1dz**, the difference is rather small for Pt−I (ca. 0.02 Å) but notably larger for Pt−N (ca. 0.06 Å). (c) The I(1)−Pt−I(1′) and N−Pt−N′ angles [88.1(1) and 78.8(7)°, respectively] remain practically unchanged in the two complexes, but the N···N′ separation is greater in **1fz** [2.64(2) Å] than in **1dz** [2.55(2) Å]. (d) The phen ligand exhibits much greater bowlike distortion [dihedral angles of 19.9(7)° between the mean planes of the outer rings, N−C(1)−C(2)−C(3)−C(4)−C(5) and N′−C(1′)−C(2′)−C(3′)−C(4′)−C(5′)] and rotation with respect to the coordination plane [dihedral angle of 32.3(9)° between the N−C(5)−C(5′)−N′ chelating plane and the N−Pt−N′ coordination plane]. (e) The two iodo ligands are displaced from the N−Pt−N′ plane by 0.508(2) and 0.447(2) Å, respectively (while they were perfectly coplanar with the N−Pt−N′ moiety in **1dz**). The steric interactions between the ortho methyl groups and the cis iodo ligands appear to be responsible for the observed differences.[3ac,30,31]

Crystal Structures of Compounds 2dz·$CHCl_3$ and 2fz·I_2. The X-ray structure analyses of the platinum(IV) complexes **2dz** and **2fz** were also carried on in order to make comparison with those of the corresponding platinum(II) species. The structure of **2dz** is shown in Figure 3; that of **2fz** (which has an imposed C_s symmetry), in Figure 4. Relevant bond distances and angles are reported in Table 3. In both cases the platinum(IV) atom exhibits the expected octahedral coordination involving two nitrogen atoms of the phenanthroline and four iodo anions.

The differences between **2dz** and **2fz** resemble those already described for the corresponding platinum(II) species **1dz** and **1fz**. The presence of methyl substituents in the ortho positions of the phenanthroline causes the following: (a) lengthening of the Pt−I [2.602(2) and 2.606(2) Å in **2dz** and 2.632(2) Å in **2fz**] and Pt−N bond distances [2.08(2) and 2.09(1) Å in **2dz** and 2.15(2) Å in **2fz**], (b) narrowing of the I(1)−Pt−I(1′) [88.20(6) in **2dz** and 83.19(6)° in **2fz**] and N−Pt−N′ bite angles [80.5(6) in **2dz** and 78.4(6)° in **2fz**], (c) bowlike distorsion of the phen ligand [dihedral angle between the outer rings of 1.4(7)° in **2dz** and 14.2(7)° in **2fz**], (d) tilting of the plane of the chelating moiety N−C(5)−C(5′)−N′ with respect to that of coordination N−Pt−N′ [dihedral angle of 3.3(8)° in **2dz** and 26.5(9)° in **2fz**], and (e) displacement of the iodine atoms from the N−Pt−N′ plane [0 in **2dz** and 0.199(2) Å in **2fz**]. The bond lengths of the apical iodines [2.655(2) and 2.671(2) Å in **2dz** and 2.665(3) and 2.674(3) Å in **2fz**] are greater than those of the equatorial ones by ~0.05 Å due to the greater trans influence of iodine with respect to nitrogen atoms.

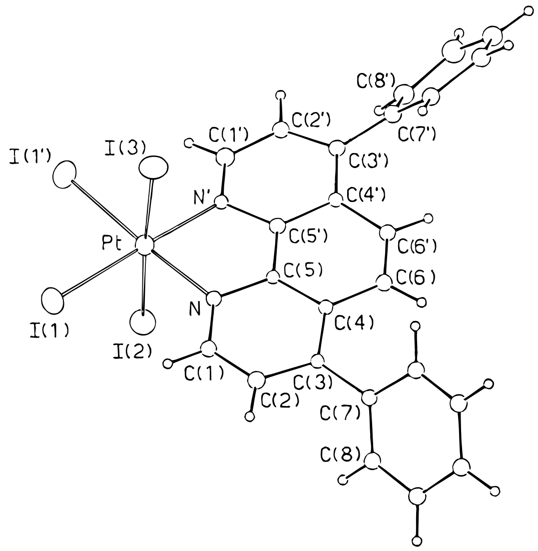

Figure 3. View of the molecular structure of the complex [PtI_4(4,7-Ph_2phen)] (**2dz**) together with the atomic numbering scheme. The ellipsoids enclose 30% probability.

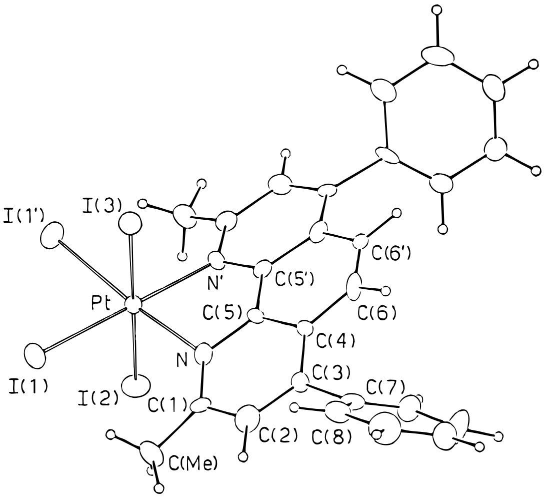

Figure 4. View of the molecular structure of the complex [PtI_4(2,9-Me_2-4,7-Ph_2phen)] (**2fz**) together with the atomic numbering scheme. The ellipsoids enclose 30% probability. The primed atoms are related to the unprimed ones by the transformation x, $1/2 - y$, z.

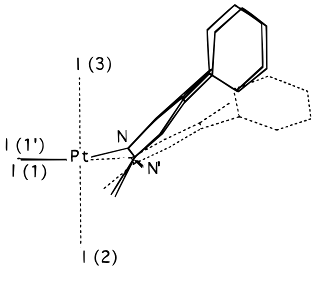

Figure 5. Projection of the structures of complexes **1fz** (solid line) and **2fz** (dashed line) along the N−N′ vector, showing the bending of the phen ligands and their rotation with respect to the platinum equatorial coordination planes.

Comparison between the structures of **1fz** and **2fz** (Figure 5), both having the phenanthroline with methyl substituents in the ortho position, indicates that, in the latter case, because of the presence of the two axial iodine ligands, the displacements of the ligands from the equatorial plane are smaller and find a

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compensation in a narrowing of the I(1)−Pt−I(1′) angle (5°) and a lengthening of the Pt−N bonds (0.07 Å).

Finally comparison between the structures of **1dz**−**fz** and those of **2dz**−**fz** indicates that, on passing from a square planar to an octahedral environment, the equatorial Pt−N and Pt−I bonds become longer (by 0.06 and 0.05 Å, respectively).

In the crystals of **2fz**·I_2 there is one molecule of iodine per molecule of complex. The iodine molecule of solvation [I(4)−I(5)] has an internuclear distance of 2.710(5) Å which is comparable to that found in crystalline I_2 [2.715(6) Å].[32] This molecule interacts with an axial iodine ligand, I(3), and with another I_2 molecule [I(4)···I(3) = 3.634(4) and I(4)···I(5″) = 3.622(5) Å (double primed species = $^1/_2 + x, y, ^3/_2 - z$)]. Both interactions are weaker than those found in crystalline I_2 [I···I = 3.496(6) Å].

Electrochemistry of Platinum(II) Complexes. In dichloromethane solution the cyclic voltammetric response exhibited by **1ax** (unsubstituted phenanthroline) consists of a first reduction process showing features of chemical reversibility (i_{pa}/i_{pc} = 1 at scan rates varying from 0.02 to 10.24 V s^{-1}, $(E°)′ = -1.24$ V)[33] followed by a second cathodic step very close to the solvent discharge. Controlled potential coulometry in correspondence to the first reduction ($E_w = -1.4$ V) quickly consumes 1-electron/molecule, but a residual current, slightly greater than the background current, remains up to the slow consumption of about 4 electrons/molecule. Accordingly, the original lemon-yellow solution turns initially deep blue and then, more slowly, green. This indicates that the reduction process, which involves 1-electron/molecule in the short time of cyclic voltammetry, in the longer time of electrolysis is coupled to a subsequent reaction. Any attempt to identify the final green product by mass spectrometric techniques and NMR spectroscopy failed. The same behavior was displayed in tetrahydrofuran, in which, however, the complex is less soluble.

Complex **1dx** (Ph substituents in the 4,7-positions of phenanthroline) exhibits, in dichloromethane solution, a redox propensity quite similar to that of the previous complex. The one-electron character of the first reduction step in the cyclic voltammetry time scale (Figure 6a) was proved by comparison with the one-electron oxidation of an equimolar amount of ferrocene ($(E°)′ = +0.43$ V). Moreover, as in the case of **1ax**, controlled potential coulometry ($E_w = -1.3$ V) consumes quickly 1-electron/molecule (concomitantly, the pale yellow solution progressively turns blue to emerald green), and then a residual current slowly flows up to the consumption of more than 3 electrons/molecule (the solution turns finally pale green). In tetrahydrofuran solution a second reduction step becomes well-visible that also displays features of chemical reversibility, Figure 6b. In view of the fact that the free ligand **d**, in tetrahydrofuran solution, undergoes a quite irreversible reduction at $E_p = -1.79$ V, we preliminarily assign the two primary cathodic steps to the sequential reductions Pt(II)/Pt(I)/Pt(0).

The other platinum(II) complexes with phenanthrolines not bearing substituents in the 2,9-positions (**b** and **c**) exhibit behavior roughly similar to those of the previous two complexes. In complex **1bx**, the one-electron reduction process is accompanied by a slow chemical reaction even in the short times of cyclic voltammetry and the i_{pa}/i_{pc} ratio reaches unity only at a scan rate greater than 0.2 V s^{-1}. In the case of **1cx**, the reduction process is also not fully reversible and only scan rates greater than 5.0 V s^{-1} allow the anodic-to-cathodic peak−current ratio to reach unity, Figure 7a. In the latter case, the chemical stability of the one-electron reduced species is significantly greater in tetrahydrofuran solution (where complex **1cx** is less soluble) than in dichloromethane and the i_{pa}/i_{pc} ratio is equal to 1 already at a rate of 0.5 V s^{-1}. The free ligand **c**, in tetrahydrofuran solution, undergoes irreversible reduction at $E_p = -2.11$ V.

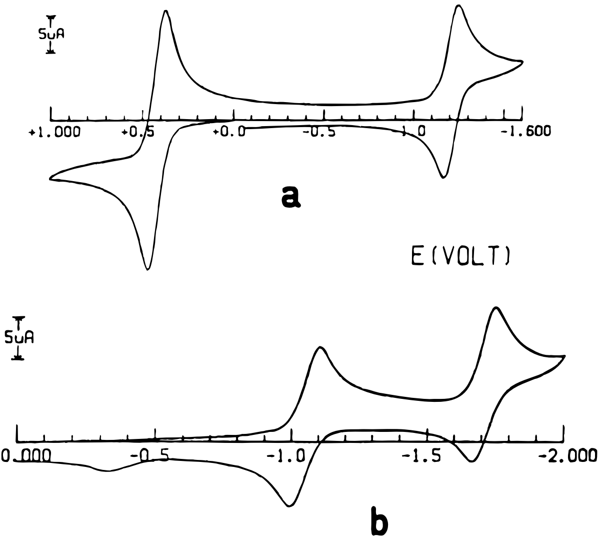

Figure 6. Cyclic voltammetric responses recorded at a platinum electrode on (a) a CH_2Cl_2 solution containing **1dx** (1.24×10^{-3} mol L^{-1}) and $[Fe(C_5H_5)_2]$ (1.29×10^{-3} mol L^{-1}) and (b) THF solution of **1dx** (1.00×10^{-3} mol L^{-1}): $[NBu_4][ClO_4]$ supporting electrolyte, 0.2 mol L^{-1}; scan rate, 0.1 V s^{-1}.

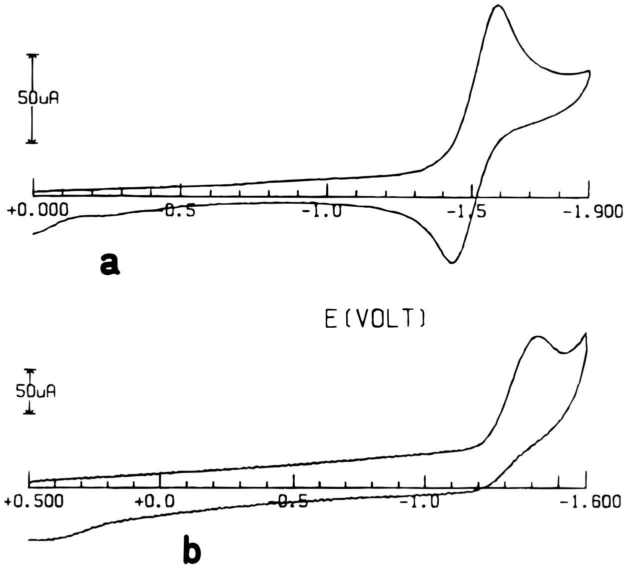

Figure 7. Cyclic voltammograms recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4][ClO_4]$ (0.2 mol L^{-1}) and (a) **1cx** (1.1×10^{-3} mol L^{-1}; scan rate, 5.12 V s^{-1}) and (b) **1fx** (1.0×10^{-3} mol L^{-1}) (scan rate, 20.48 V s^{-1}).

The formal electrode potentials of these redox changes are compiled in Table 4. Comparison of the data indicates that the change from chloride to iodide ligands does not affect appreciably the redox potentials, but it slightly lowers the stability of the reduced species. Also the introduction of electron-releasing substituents (methyl groups) in the phenanthroline ligand (compounds **1b**,**c**) lowers the stability of the reduced species. In contrast, electron-withdrawing substituents (phenyl groups in **1d**) stabilize the reduced species. It is also interesting

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Table 4. Redox Potentials for the Electron Transfers Exhibited by the Platinum(II) Complexes

complex	$(E°)'_{0/-}$[a]	ΔE_p[bc]	$(E°)'_{-/2-}$[a]	ΔE_p[bc]	$E_{p0/2-}$[c]	solvent	ref
1ax	−1.24	76	−1.9[de]	–	–	CH_2Cl_2	*f*
	−1.13	82	−1.92[e]	–	–	THF	*f*
1dx	−1.20	66	−1.80[e]	–	–	CH_2Cl_2	*f*
	−1.05	85	−1.70	75	–	THF	*f*
	−1.20	84	−1.75	–	–	MeCN[g]	*f*
1dy	−1.20	68	−1.80[e]	–	–	CH_2Cl_2	*f*
	−1.04	88	−1.68	144[h]	–	THF	*f*
1dz	−1.20	86[h]	–	–	–	CH_2Cl_2	*f*
	−1.06	82	−1.68[e]	–	–	THF	*f*
1bx	−1.43	80	−2.05[de]	–	–	CH_2Cl_2	*f*
1cx	−1.50	114[i]	–	–	–	CH_2Cl_2	*f*
	−1.33	96	–	–	–	THF	*f*
1ex					−1.27	CH_2Cl_2	*f*
					−1.18	THF	*f*
1ey					−1.14	THF	*f*
1fx					−1.25	CH_2Cl_2	*f*
					−1.15	THF	*f*
1fy					−1.19	CH_2Cl_2	*f*
					−1.08	THF	*f*
1fz					−1.05	THF	*f*
[Pt(bipy)Cl_2]	−1.24	80	–	–	–	MeCN	15
	−1.17	70	−1.82	110	–	DMF	16

[a] In volts vs SCE. [b] In millivolts. [c] Measured at 0.1 V s^{-1}. [d] Difficult to evaluate. [e] Irreversible process. [f] Present work. [g] Very low solubility. [h] Measured at 0.5 V s^{-1}. [i] Measured at 2.0 V s^{-1}.

to note that the first one electron reduction occurs at about the same potential value for [Pt(phen)Cl_2] (**1ax**) and [Pt(bipy)Cl_2].[16,17]

Complexes **1ex**,**fx**, having substituents in the 2,9-positions of the phenanthroline ligand, behave differently from those previously investigated and containing 2,9-unsubstituted phenanthrolines (**1ax**−**dx**). They undergo an irreversible reduction which does not exhibit any directly associated response in the reverse scan, even at a rate of 20.48 V s^{-1}. The cyclic voltammetric profile exhibited by **1fx** is shown in Figure 7b. It is most likely that the same compounds (**1ex**,**fx**) have a remarkably distorted coordination geometry similar to that of compound **1fz** discussed in the crystallographic section.

Therefore the bulk of the data suggests that for platinum(II) complexes the planarity of the platinum center is a prerequisite for the thermodynamic access to the corresponding one-electron reduced species. This is in sharp contrast with the behavior of related [NiCl_2(2,9-substituted-1,10-phen)] complexes, for which the pseudo-tetrahedral coordination imposed by the bulky 2,9-substituents stabilizes the corresponding nickel(I) species.[34]

Electrochemistry of the Platinum(IV) Complexes. The cyclic voltammetric responses exhibited by the platinum(IV) complexes **2dx** and **2fx** are shown in Figure 8. Both complexes display a first irreversible two-electron cathodic step (measured by controlled potential coulometry) followed by a reduction pattern identical to those exhibited by **1dx** and **1fx**, respectively (Figures 6b and 7b). Therefore the platinum(IV) complexes, upon two-electron addition, lose the two axial ligands, affording the corresponding platinum(II) species. Such a behavior was already described by Kochi in the study of the platinum(IV)−cyclobutane complexes [Pt($CH_2CH_2CH_2$)Cl_2(bipy)] and [Pt($CH_2CH_2CH_2$)Cl_2(4,7-Ph_2phen)] (the latter complex contains the same phenanthroline ligand as **2dx**).[15] The values of the electrochemical potentials for the platinum(IV)/platinum(II) reductions are reported in Table 5. Two points are worth noting: (i) the platinum(IV)/platinum(II) reduction is significantly affected by the nature of the halide ligands (this was not the case for the platinum(II)/platinum(I) reduction, which most likely takes place without releasing of halide ions); (ii) the redox-induced removal of the axial halides is notably easier in the actual complexes than in the platinum−cyclobutane complexes (this can be attributed to the greater ability of the equatorial halide ligands, with respect to the hydrocarbon chain, to remove electron density from the platinum center).

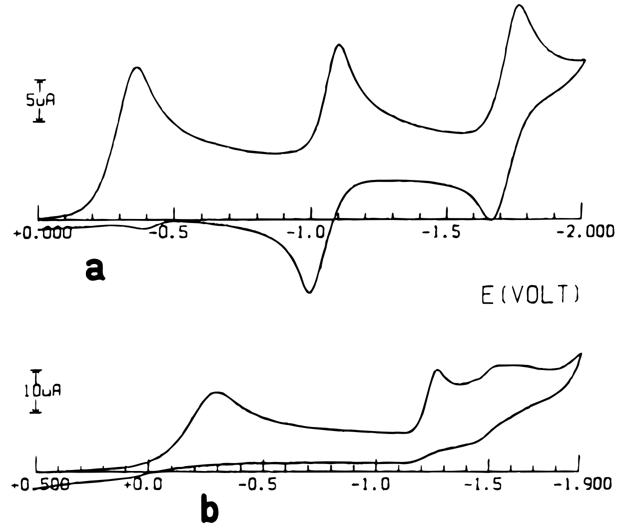

Figure 8. Cyclic voltammograms obtained at a platinum electrode on (a) a THF solution of **2dx** (1.1×10^{-3} mol L^{-1}) and (b) a CH_2Cl_2 solution of **2fx** (9.0×10^{-4} mol L^{-1}): [NBu_4][ClO_4] supporting electrolyte, 0.2 mol L^{-1}; scan rate, 0.2 V s^{-1}.

Table 5. Peak Potential Values (in volts vs SCE) for the Platinum(IV)/Platinum(II) Reduction Process

complex	E_p[a]	solvent	ref
2dx	−0.35	THF	*b*
	−0.29	CH_2Cl_2	*b*
2dy	−0.23	THF	*b*
	−0.18	CH_2Cl_2	*b*
2dz	−0.19	THF	*b*
	+0.11	CH_2Cl_2	*b*
2fx	−0.16	THF	*b*
	−0.22	CH_2Cl_2	*b*
2fy	−0.20	THF	*b*
2fz	−0.23	THF	*b*
[Pt($CH_2CH_2CH_2$)Cl_2(bipy)]	−1.35	MeCN	15
[Pt($CH_2CH_2CH_2$)Cl_2(4,7-Ph_2phen)]	−1.26	MeCN	15

[a] Measured at 0.2 V s^{-1}. [b] Present work.

Spectroscopy of the First Reduction Products of 1ax and 1dx: Visible Spectra. Figure 9 shows the visible spectra recorded at different stages of the controlled potential coulometry of **1dx** ($E_w = -1.3$ V) performed at ambient temperature. In the initial stage of the electrolysis, when the solution is blue colored, a well-shaped absorption at $\lambda_{max} = 633$ nm is predominant (spectrum c); by an increase in the electrolysis time, this band is progressively replaced by two peaks, at 460 and 600 nm, which characterize the multielectron-reduced green solution (spectrum f).

EPR Spectra. The liquid nitrogen X-band EPR spectrum (100 K) recorded at the first stage of the electrolysis of **1dx** performed at 253 K is shown in Figure 10a. The line shape features of the $\lambda_{max} = 633$ nm species are indicative of a $S = {}^1/_2$ paramagnetic system exhibiting a broad axial structure ($g_\parallel > g_\perp > g_e$) with significant orbital contribution: $g_\parallel = 2.055 \pm 0.006$, $g_\perp = 2.005 \pm 0.006$, $\langle g \rangle = 1/3(g_\parallel + 2g_\perp) = 2.022 \pm 0.006$. By considering that the metal d^9 configuration should display typical spectra with $g_\parallel > g_\perp > 2.0023$,[13,17,35] these data

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(34) Masood, M. A.; Hodgson, D. J.; Zacharias, P. S. *Inorg. Chim. Acta* **1994**, *221*, 99−108.

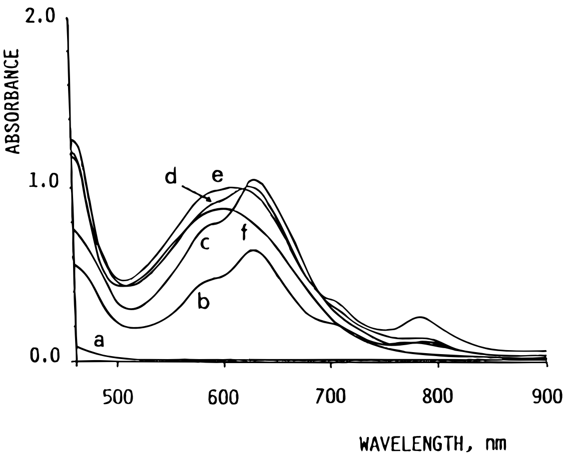

Figure 9. Visible spectra recorded on a CH_2Cl_2 solution of **1dx** (0.8×10^{-3} mol L^{-1}) at different stages of controlled potential electrolysis ($E_w = -1.3$ V): (a) initial and after (b) 0.5, (c) 1.0, (d) 2.0, (e) 2.7, and (f) 3.0 electrons/molecule. $[NBu_4][ClO_4]$ supporting electrolyte, 0.2 mol L^{-1}.

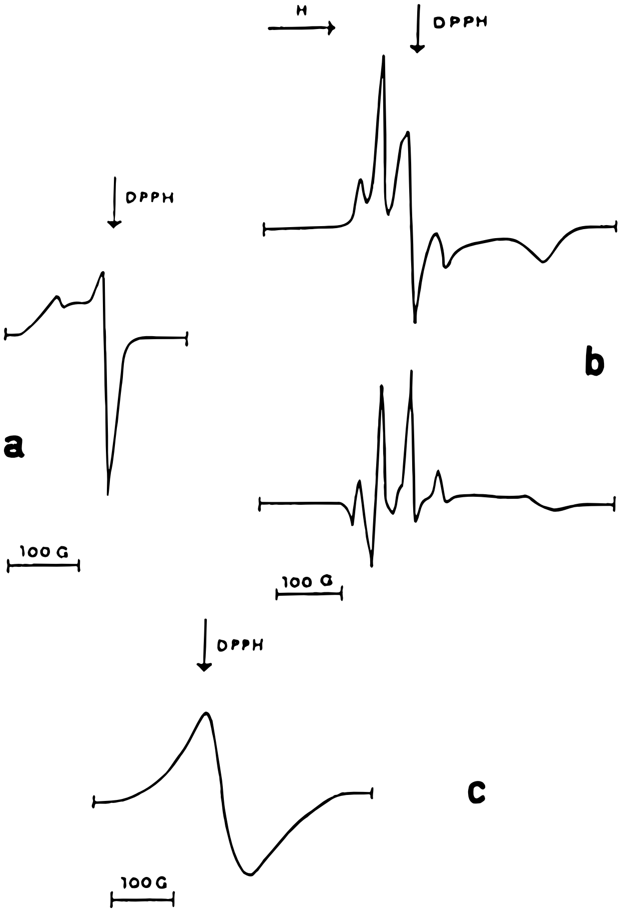

Figure 10. X-band EPR spectra recorded on a CH_2Cl_2 solution of **1dx** (1.9×10^{-3} mol L^{-1}) at different stages of controlled potential electrolysis (performed at 253 K, $E_w = -1.3$ V): (a) after 0.3 electrons/molecule, 100 K; (b) after 2.0 electrons/molecule, 100 K (top, first derivative; bottom, second derivative); (c) after 2.0 electrons/molecule, 300 K. $[NBu_4][ClO_4]$ supporting electrolyte, 0.2 mol L^{-1}.

strongly support a significant metal character for the anionic complex [**1dx**]$^-$ in which the noticeable anisotropic line width overlaps the relevant satellite a_{aniso}(Pt-195) hyperfine features as well as those of the ligands. To the best of our knowledge, within the reduction processes of polypyridine−platinum(II) complexes which are predominantly ligand centered,[14,17] this could constitute EPR evidence for the generation of a platinum having marked Pt(I) character, complexes with inherently Pt(I) character have recently been reported by other authors.[35]

The EPR spectra recorded when the number of electrons/molecule spent in the reduction process is greater than 1 are shown in Figure 10b,c. The liquid nitrogen spectrum (Figure 10b) exhibits a complex spectral pattern, which, at the glassy−fluid transition temperature, converts into a single, relatively broad and isotropic absorption (Figure 10c). These spectral features are reversible on refreezing the solution. A similar absorption was observed in the electrochemical reduction of $[Pt(bipy)Cl_2]$ and was assigned to a ligand centered paramagnetic monoanion $[Pt^{II}(bipy)^*Cl_2]^-$ (asterisk denotes reduced species).[17] The liquid nitrogen line shape analysis can be carried out in terms of a $S = {}^1/_2$ spin Hamiltonian of a paramagnetic species exhibiting a largely structured rhombic symmetry ($g_l > g_m > g_h \neq g_e = 2.0023$) and experiencing a significant metal contribution.[36] The nuclear hyperfine (hpf) splittings ($a_l \neq a_m \neq a_h$) of the Pt-195 satellites are now detectable; they appear well-resolved at low and medium fields but unresolved at higher fields. Second derivative analysis allowed a better characterization of this spectral pattern, which was also confirmed by computer simulation (SIM 14a program).[37] Therefore, in agreement with previous reports,[17,18] the spectra of Figure 10b,c are assigned to a $[Pt^{II}(4,7\text{-}Ph_2phen)^*Cl_2]^{n-}$ species. The fluid parameters fit well the glassy computed ones. Also, in the present case, the lack of the hyperfine isotropic peaks of Pt-195 satellites as well as of the corresponding ligand superhyperfine splittings is attributable to the large isotropic linewidth ΔH_{iso}.

In summary the EPR data indicate that the reduction process of the platinum(II) complex **1dx** generates primarily the corresponding Pt(I) species [**1dx**]$^-$ which, however, because of conjugation with the nonredox innocent phen ligand, progressively restores the Pt(II) oxidation state through internal redox changes based on the peripheral organic ligand. The change of solvent from dichloromethane to tetrahydrofuran causes some variations in the EPR parameters as a consequence of either a line-narrowing or a slightly better hpf resolution.[18] In the case of **1ax**, the EPR spectrum recorded at the first stages of the electrolysis reveals a pattern which can be interpreted as being due to the ovelapping signals of equimolar amounts of rhombic and axial platinum forms, i.e., $[Pt^{II}(phen^*)Cl_2]^-$ and $[Pt^{I}(phen)Cl_2]^-$. Upon exhaustive electrolysis only the Pt^{II} radical survives. Table 6 summarizes the relevant EPR data. Finally, in agreement with the already discussed lower stability of the one-electron reduced complexes [**1bx**]$^-$ and [**1cx**]$^-$, we were unable to detect EPR absorptions for both of them.

Conclusions

Comparison of the X-ray structures of strictly related platinum compounds has allowed an estimate of the distortions caused by the steric interaction between the Me substituents in the ortho position of the phenanthroline and the cis iodo ligands in four- and six-coordinate environments. These involve displacement of the equatorial iodine atoms from the N−Pt−N′ plane [average 0.477(2) and 0.199(2) Å for four- (**1fz**) and six-coordinate complexes (**2fz**), respectively], bending of the phenanthroline (angle between the planes of the outer rings of 19.9(7) and 14.2(7)°, respectively), and rotation of the overall phenanthroline plane with respect to the N−Pt−N′ plane [32.3(10) and 26.5-

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(37) Lozos, J. P.; Hoffman, B. M.; Franz, C. G. *QCPE* **1973**, *11*, 243.

Table 6. X-Band EPR Parameters for the Platinum(I) and Platinum(II) Species Electrogenerated upon Reduction of **1dx** and **1ax** ($g_i \pm 0.006$; $a_i \pm 6$ G)

complex	g_l	g_m	g_h	$\langle g \rangle$	g_{iso}	a_l	a_m	a_h	$\langle a \rangle$	solvent
[**1dx**]$^-$	2.055^{a,b}	2.005^{a,c}		2.022^{a}						CH_2Cl_2
	2.034	2.002	1.902	1.980		56.0	83.0	≤22.0	≤53.0	CH_2Cl_2
	2.034	2.001	1.900	1.979	1.967	57.0	84.0	≤23.0	≤54.0	THF
[**1ax**]$^-$	2.051^{a,b,d}	2.007^{a,c,d}		2.022^{a,d}						CH_2Cl_2
	2.032	2.010	1.907	1.983		58.0	77.0	≤20.0	≤52.0	CH_2Cl_2

[a] Platinum(I) species. [b] $g_{\parallel}$. [c] $g_{\perp}$. [d] Calculated from a complex spectral pattern (see text).

(9)°, respectively]. The smaller deviations imposed by the axial iodo ligands in the six-coordinate complex find a compensation in a narrowing of the I−Pt−I′ angle (5°) and a lengthening of the Pt−N bonds (0.07 Å).

Distortions in the coordination geometries affect the redox properties of these complexes. Species possessing regular square planar geometry afford initially monoanions having Pt(I) character, whereas species with distorted geometry are irreversibly reduced. This is in sharp contrast with the behavior of related nickel complexes for which the tetrahedral distortion imposed by the 2,9-dimethyl substituents of the phenanthroline ligand stabilizes the nickel(I) species. In the long times of macroelectrolysis the instantaneously electrogenerated Pt(I) species convert to the corresponding Pt(II) anion radicals.

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Supporting Information Available: Elemental analyses of the compounds (Table S1); atomic coordinates and isotropic thermal parameters (Tables S2−5), anisotropic thermal parameters (Tables S6−9), and full crystallographic data (Table S10−13) for compounds **1dz**·$CHCl_3$, **1fz**, **2dz**·$CHCl_3$, and **2fz**·I_2, respectively, and experimental data for the X-ray diffraction studies (Table S14) (12 pages). Ordering information is given on any current masthead page.

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