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On the Question of Mixed-Valent States in Ligand-Bridged Dinuclear Organoplatinum Compounds $[R_kPt(\mu\text{-L})PtR_k]^n$, $k = 2$ or 4†

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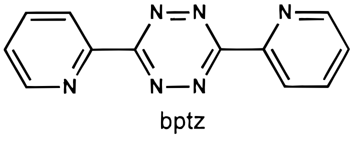
Symmetrically dinuclear complexes between the bis-bidentate bridging ligands μ-L (μ-L = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) or 2,5-bis(1-phenyliminoethyl)pyrazine (bpip)) and the organoplatinum fragments $PtMes_2$ (Mes = mesityl), $PtMe_2$, or $PtMe_4$ were synthesized as deeply colored compounds. Low-energy charge-transfer transitions from metal d orbitals (Pt^{II}) or metal−carbon σ bond combinations (Pt^{IV}) to low-lying π^* orbitals of the π acceptor ligands are responsible for long-wavelength absorption maxima $\lambda_{max}(CT) > 700$ nm. UV/Vis and EPR spectroelectrochemical results for reversible reduction processes indicate the formation of $[Pt^{IV}]_2(\mu\text{-L}^{\bullet-})$ and $[Pt^{II}]_2(\mu\text{-L}^{\bullet-})$ species, however, the latter exhibit a significant metal contribution according to a Pt^{II}/Pt^{I} formulation. Cyclic voltammetry reveals that the remarkable system $[Mes_2Pt(\mu\text{-bptz})PtMes_2]^n$ forms an enormously stabilized radical anion ($n = 1-$) with $\Delta E_{1/2} = 1250$ V and $K_c = 10^{21.2}$ and a Pt^{III}/Pt^{II} mixed-valent state ($n = 1+$) with $\Delta E_{1/2} = 80$ mV and $K_c = 23$. This small K_c value is attributed to the predominantly d_σ orbital character of the redox orbitals on the Pt(II) centers.

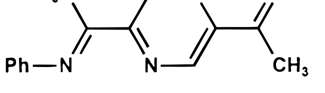
Introduction

Electrochemical, spectroscopic, and reactivity studies[1−3] of platinum(II) and -(IV) complexes with unsaturated nitrogen-donor-containing ligands are of current interest due to the photoemissive,[2] C−H-activating or catalytic[4] and pharmacological[5] relevance of such species. Instead of π-accepting monochelate ligands such as aromatic 2,2′-bipyridine[1b,c,f] and 1,10-phenanthrolines[1g] or non-aromatic α-diimines such as 1,4-diaza-1,3-butadienes,[1e,n] we have recently[6] used the conventional bridging ligand 2,2′-bipyrimidine[7] (bpym) to form compounds $[R_kPt(\mu\text{-bpym})PtR_k]^n$, $k = 2$ or 4. Absorption spectra, calculations, a structure determination, and spectroelectrochemical and EPR studies of generated paramagnetic species were described.[6] In the following, we present results for dinuclear complexes $[R_kPt(\mu\text{-L})PtR_k]^n$, $k = 2$ or 4, with two special bis-bidentate bridging ligands μ-L, μ-L = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) and 2,5-bis(1-phenyliminoethyl)pyrazine (bpip).

$[Mes_2Pt(\mu\text{-bptz})PtMes_2]^n = \mathbf{1}^n$ $[Mes_2Pt(\mu\text{-bpip})PtMes_2]^n = \mathbf{4}^n$
$[Me_2Pt(\mu\text{-bptz})PtMe_2]^n = \mathbf{2}^n$ $[Me_2Pt(\mu\text{-bpip})PtMe_2]^n = \mathbf{5}^n$
$[Me_4Pt(\mu\text{-bptz})PtMe_4]^n = \mathbf{3}^n$ $[Me_4Pt(\mu\text{-bpip})PtMe_4]^n = \mathbf{6}^n$
$[Me_4Pt(bpip)]^n = \mathbf{7}^n$



bptz



bpip

The ligand bptz was found to have a very low-lying tetrazine-localized π^* orbital[8a] and to form very stable anion radical complexes;[8b] on the other hand, it induced a very large comproportionation constant $K_c = 10^{15.0}$ for

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† Dedicated to Prof. Heinrich Nöth on the occasion of his 70th birthday.

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the Ru^{III}/Ru^{II} mixed-valent state $[(H_3N)_4Ru(\mu\text{-bptz})Ru(NH_3)_4]^{5+}$.[8c] The ligand bpip is a rather new bis(α-diimine) ligand which, like the monochelating 2-pyridinecarbaldimines,[10] acts through two different chelate donors, one imine and one azine nitrogen atom per metal center. The ligand bpip was found to be a stronger π acceptor than the related 2,5-bis(2-pyridyl)pyrazine.[9a,d] A Rh^{II}/Rh^{I} mixed-valent intermediate $[(C_5Me_5)Rh(\mu\text{-bpip})Rh(C_5Me_5)]^+$ was recently identified through typical intervalence transfer (IT) transitions in the near-infrared region.[9c]

Concerning the co-ligands, the methyl group (Me) was used as the most simple organic substituent and the axially protecting mesityl (Mes = 2,4,6-trimethylphenyl) substituent was chosen to avoid the undesired addition of nucleophiles to the one-electron-oxidized monomeric platinum(III) states, as shown for several mononuclear species $[PtMes_2(\alpha\text{-diimine})]^+$.[1c,f,g] The corresponding Pt^{III}/Pt^{II} half-wave potentials can then be used to correlate optical data (absorption or emission energies) with electrochemical results. However, the dinuclear system $[Mes_2Pt(\mu\text{-bpym})PtMes_2]^n$ showed no separated redox features for the oxidation of the two individual metal centers; the nonobservability of a Pt^{III}/Pt^{II} mixed-valent state was attributed to insufficient orbital overlap between the π system of the organic bridge and the d_σ redox orbitals on platinum.[6] The methods used to study the electronic structures of compounds **1**−**7** were absorption spectroscopy of the neutral precursors and cyclic voltammetry in combination with EPR or UV/Vis spectroscopy (spectroelectrochemistry).

Experimental Section

Materials and Procedures. The ligands bptz[8] and bpip[9] and the platinum precursor complexes $(DMSO)_2PtMes_2$,[10] $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$,[11] and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$[12] were obtained following literature procedures. All preparations and physical measurements were carried out in dried solvents under an argon atmosphere, using Schlenk techniques. Furthermore, the tetramethylplatinum(IV) compounds had to be prepared and studied in the absence of intense light.

Bis(dimesitylplatinum) Complexes (μ-L)[PtMes$_2$]$_2$: 1 (L = bptz) and 4 (L = bpip). In a typical reaction, 295 mg (0.5 mmol) of dimesitylbis(dimethylsulfoxido)platinum(II) was suspended together with 0.25 mmol of the bridging ligand in 70 mL of toluene and heated under reflux for 5 days. The sulfoxide vibration ν(S=O) at 1130 cm^{-1} of the platinum precursor complex[13] had by then disappeared. At the end of the reaction, the temperature was lowered within another day to accomplish slow precipitation of the products. The solids were collected on a microporous frit and washed with diethyl ether. We thus obtained a poorly soluble blue-black powder for the bptz complex **1** in a 224 mg (81%) yield. Anal. Calcd for $C_{48}H_{52}N_6Pt_2$: C, 52.26; H, 4.75; N, 7.62. Found: C, 52.50; H, 4.82, N, 7.74. In the case of the bpip complex **2**, we obtained greenish-black microcrystals in a 243 mg (82%) yield. Anal. Calcd for $C_{56}H_{66}N_4Pt_2$: C, 56.74; H, 5.61; N, 4.73. Found: C, 56.41; H, 5.58; N, 4.74.

(μ-bptz)[PtMe$_2$]$_2$, 2. A solution of 0.063 g (0.11 mmol) of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and 0.027 g (0.11 mmol) of bptz in a mixture of 15 mL of toluene and 5 mL of diethyl ether was stirred overnight at ambient temperature to yield a black microcrystalline precipitate. After filtration, the virtually insoluble solid was washed with diethyl ether and toluene (66 mg, 87%). Anal. Calcd for $C_{16}H_{20}N_6Pt_2$: C, 27.99; H, 2.94; N, 12.24. Found: C, 28.95; H, 3.06; N, 11.39. The very poor solubility in all common solvents precluded further investigation.

(μ-bptz)[PtMe$_4$]$_2$, 3. A solution of 0.063 g (0.11 mmol) of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and 0.027 g (0.11 mmol) of bptz in a mixture of 15 mL of toluene and 5 mL of diethyl ether was stirred overnight at ambient temperature in the dark. The poorly soluble precipitate was filtered and washed with diethyl ether and toluene to yield 66 mg (87%) of a black microcrystalline solid. Anal. Calcd for $C_{16}H_{20}N_6Pt_2$: C, 27.99; H, 2.94; N, 12.24. Found: C, 28.95; H, 3.06; N, 11.39. The virtual insolubility in all common solvents precluded further investigation.

(μ-bpip)[PtMe$_2$]$_2$, 5. A solution of 0.063 g (0.11 mmol) of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and 0.031 g (0.031 mmol) of bpip in 15 mL of benzene and 10 mL of diethyl ether was stirred overnight at ambient temperature to produce a dark-green precipitate. After removal of the solvent mixture, the residue was washed with 10 mL of diethyl ether, filtered, and dried in vacuo. A greenish-black microcrystalline powder was obtained in a

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Table 1. ^{1}H NMR Data[a] of bpip and Its Organoplatinum Complexes

	Pt−CH$_3$		bpip		
compound	C*H*$_3$^{ax}	C*H*$_3$^{eq}	C*H*$_3$[b]	H$_{(pyrazine)}$	H$_{(phenyl)}$
bpip			2.36	9.43	6.84,[c] 7.15,[d] 7.42[e]
4[f]			2.34 (6.8)	8.65	6.76,[c] 7.08,[d] 7.18[e]
5[g]		1.12 (86.5), 1.89 (87.2)	1.97	9.71 (19.0)	7.08,[c] 7.37,[d] 7.57[e]
6	−0.41 (45.3)	0.47 (74.1), 0.92 (72.9)	2.82 (7.2)	9.68 (12.6)	7.01,[c] 7.37,[d] 7.57[e]
6[h]	−0.37 (45.0)	0.49 (73.8), 0.96 (72.4)	2.68 (7.5)	9.58 (13.0)	6.97,[c] 7.33,[d] 7.53[e]
7	−0.47 (44.9)	0.40 (73.8), 0.86 (72.7)	2.44	9.66[i]	6.95,[c] 7.18,[d] 7.44[e]
			2.70 (7.0)	9.78[i] (7.4)	7.01,[c] 7.43,[d] 7.54[e]

[a] Measured in acetone-d_6 at room temperature unless noted otherwise; chemical shifts δ in ppm, $J(^{195}Pt/^1H)$ coupling constants in hertz (in parentheses). [b] Iminoethyl group. [c] *ortho*-H, dd, $^3J_{HH} \cong 8.4$ Hz, $^4J_{HH} \cong 1.1$ Hz. [d] *para*-H, tt, $^3J_{HH} \cong 7.5$ Hz, $^4J_{HH} \cong 1.1$ Hz. [e] *meta*-H, m, $^3J_{HH} \cong 8.4$ Hz. [f] Further signals at $\delta = 6.27$ (*m*−H), 2.54 (*o*-CH$_3$), 2.12 (*p*-CH$_3$). [g] In CD_2Cl_2. [h] In THF-d_8. [i] $^5J_{HH} = 1.2$ Hz.

0.034 g yield (66%). Anal. Calcd for $C_{24}H_{30}N_4Pt_2$: C, 37.7; H, 5.13; N, 6.79. Found: C, 37.23; H, 4.98; N, 6.77.

(μ-bpip)[PtMe$_4$]$_2$, 6. A solution of 0.127 g (0.2 mmol) of [Pt$_2$Me$_8$(μ-SMe$_2$)$_2$] and 0.063 g (0.2 mmol) of bpip was stirred in 25 mL of diethyl ether at ambient temperature over 10 h in the dark. Removal of the solvent lead to a black residue, which was washed with 10 mL of diethyl ether, filtered, and dried in vacuo to yield a black microcrystalline powder. Yield: 0.089 g (68%). Anal. Calcd for $C_{28}H_{42}N_4Pt_2$: C, 40.77; H, 5.13; N, 6.69. Found: C, 40.27; H, 4.98; N, 6.77.

(bpip)PtMe$_4$, 7. A solution of 0.127 g (0.2 mmol) of [Pt$_2$Me$_8$-(μ-SMe$_2$)$_2$] and 0.129 g (0.41 mmol) of the bpip ligand was stirred in 25 mL of diethyl ether at ambient temperature over 10 h in the dark. Removal of one-half of the solvent, addition of 15 mL of *n*-hexane, and leaving this mixture at −30 °C overnight lead to precipitation of a green-black solid. This was collected on a microporous glass frit, washed with 10 mL of diethyl ether, and dried in vacuo. Yield: 0.120 g (51%). Anal. Calcd for $C_{24}H_{30}N_4Pt$: C, 50.61; H, 5.31; N, 9.84. Found: C, 50.46; H, 5.09; N, 9.54.

Instrumentation. EPR spectra were recorded in the X band on a Bruker ESP 300 system equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. ^{1}H NMR spectra were taken on a Bruker AC 250 spectrometer; infrared spectra were recorded with a Perkin-Elmer 283 instrument. UV/Vis/NIR-absorption spectra were recorded on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry and differential pulse voltammetry were carried out using a three-electrode configuration (glassy carbon working electrode, platinum counter-electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator with PAR M270/250 software. As an internal standard, the ferrocene/ferrocenium couple was used. Cyclic voltammograms were simulated with the help of the program DigiSim 2.1 (BAS). Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell[14] for UV/Vis/NIR spectra, a platinum two-electrode capillary for EPR studies,[9a] and a Bank Elektronik Potentioscan Wenking POS 73 potentiostat and function generator equipped with an XY-plotter PAR RE 0089.

Results and Discussion

Synthesis and Structure. The mono- and dinuclear organoplatinum(II) and -(IV) compounds were obtained according to established procedures[1c,e,f,11,12] as thermally stable species. However, special care had to be taken regarding the light-sensitive tetraalkylplatinum(IV) complexes.[1m,n] The identity of the compounds was confirmed by elemental analysis and, except for poorly soluble (**1**) or virtually insoluble compounds (**2** and **3**), by ^{1}H NMR spectroscopy (Table 1).

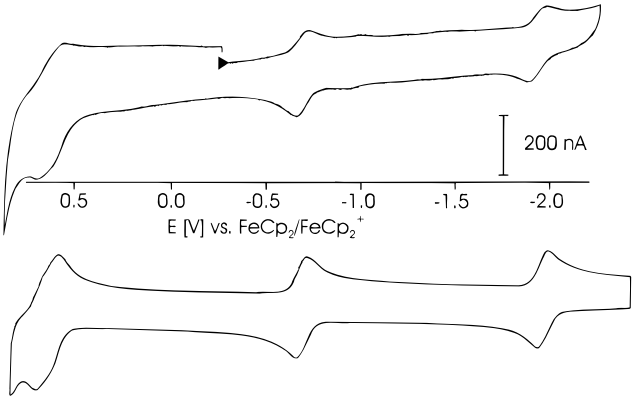

Figure 1. Cyclic voltammogram of **1** in THF/0.1 M Bu$_4$NPF$_6$ at 100 mV/s scan rate (top); simulated cyclic voltammogram of **1** (bottom). The low solubility of **1** causes a more soluble impurity to become detectable at about −1.0 V.

Dimesitylplatinum(II) complexes of aromatic α-diimines had been structurally characterized[1c,g] with approximately square-planar metal configurations and sterically protected axial positions; we therefore assume a similar situation for the compounds Mes$_2$Pt(μ-L)-PtMes$_2$. The structures of mono- and dinuclear tetramethylplatinum(IV) complexes of α-diimines have also been characterized before,[1e,6] illustrating significantly longer metal-to-carbon bonds to the axial methyl groups (ca. 2.13 Å) than to the equatorial CH$_3$ substituents (ca. 2.04 Å). In the NMR spectra of the PtMe$_4$ species, the asymmetric chelate coordination is reflected by distinctly different chemical shifts of the two nonequivalent equatorial methyl groups.

Electrochemistry. All soluble dinuclear compounds **1** and **4**−**6** exhibit two reversible one-electron reduction processes in THF/0.1 M Bu$_4$NPF$_6$ (Figure 1, Table 2). Whereas the soluble methylplatinum complexes are oxidized in an electrochemically irreversible fashion, compounds **1** and **4** with the axially shielding mesityl groups exhibit reversible oxidation waves (Figure 1, Table 2).

Both the Pt(II) and Pt(IV) species are believed to have the π^*(L) orbital, supported by d_{xz}(Pt), as the lowest unoccupied MO (LUMO).[1n] On the other hand, the HOMO is primarily a metal-centered d orbital for the diorganoplatinum(II) compounds but an antisymmetric Pt−C$_{ax}$ σ orbital combination with some p_x(Pt) contributions for PtMe$_4$(L) species. These calculation results have been supported by experimental evidence.[1m,n,6]

As noted for the mononuclear species PtMe$_n$(RN=CH−CH=NR),[1e,n] the cyclic voltammograms for com-

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Table 2. Electrochemical Data[a] of bpip and bptz and Their Organoplatinum Complexes

compound	E_{pa}oxII[b]	$E_{1/2}$oxI (ΔE_p)[c]	$E_{1/2}$redI (ΔE_p)[c]	$E_{1/2}$redII (ΔE_p)[c]
bptz			−1.33 (59)	−2.34[d]
1[e]	0.66 (60)	0.58 (60)[f]	−0.69 (60)	−1.94 (75)
bpip			−2.05 (80)	−2.39[d]
4		0.53 (60)[f]	−0.93 (63)	−1.75 (75)
5		0.64[b]	−1.11 (84)	−1.76 (78)
6		0.40[b]	−1.06 (90)	−1.94 (75)
7[e]		0.40[b]	−1.46 (85)	

[a] From cyclic voltammetry in 0.1 M Bu_4NPF_6/THF solutions at 100 mV/s scan rate. Potentials in volts vs the ferrocene/ferrocenium couple. No cyclovoltammograms could be obtained for $Me_2Pt(bptz)PtMe_2$ and $Me_4Pt(bptz)PtMe_4$ due to very poor solubility. [b] Anodic peak potentials E_{pa} for irreversible oxidation steps. [c] Half-wave potentials $E_{1/2}$; peak potential differences $\Delta E_p = E_{pa} - E_{pc}$ in millivolts in parentheses. [d] Cathodic peak potentials E_{pc} for irreversible reduction steps. [e] Further irreversible reduction occurs at −2.64 V. [f] Two-electron process.

pounds $n = 2$ (**5**) and 4 (**6**) look very much alike. A reversible ligand-centered reduction and an irreversible oxidation, either of the metals (Pt^{II} compounds) or of the $Pt-C_{ax}$ σ bonds (Pt^{IV} complexes), occur at very similar potentials (Table 2). Obviously, the binding of two additional methyl carbanions compensates almost exactly for the effect of the higher metal oxidation state.

As expected,[6,8] the dinuclear complex **6** is reduced at less negative potentials than the mononuclear analogue **7**, reflecting the stepwise polarization of the ligand bpip through successive metal coordination. The potentials in the bpip ligand series also show that the bis(dimesitylplatinum) system **4** is reduced easier than the analogous dimethylmetal compound **5**, which reflects the stronger electron-donating effect of alkyl vs aryl groups.

The splitting of the redox potentials neighboring the monooxidized and monoreduced paramagnetic states merits particular attention. The bptz-bridged state $\mathbf{1}^{\bullet-}$ exhibits an enormous potential range (Figure 1) and comproportionation constant $K_c = 10^{21.2}$, calculated according to eq 1. This value is significantly higher than

$$K_c = 10^{\Delta E/59\text{mV}} = [M^{(n-1)}]^2/[M][M^{(n-2)}] \qquad (1)$$

$$M + M^{(n-2)} \rightleftharpoons 2M^{(n-1)}$$

the $K_c = 10^{13.3}$ value found for $\{(bptz)[Ru(NH_3)_4]_2\}^{3+}$;[8c] it supports previous suggestions[8] concerning the generally very large stability constants of tetrazine anion radicals which, however, were often deduced from less reversible second reduction features. Obviously, the introduction of mesityl substituents does not only protect the oxidized metal center from nucleophilic attack[1c,f,g] but also the doubly reduced ligand from degradation through electrophiles. We assume that $\mathbf{1}^{\bullet-}$ exhibits a K_c value more typical of tetrazine redox systems; the lower value found for $\{(bptz)[Ru(NH_3)_4]_2\}^{3+}$ [8c] probably indicates[15] strong metal/ligand orbital mixing as is also evident from the very rapid EPR relaxation behavior of that species.[8c]

The dinuclear bpip complexes $\mathbf{4}^{\bullet-}$, $\mathbf{5}^{\bullet-}$, and $\mathbf{6}^{\bullet-}$ exhibit smaller but still rather large redox potential ranges and K_c values of $10^{13.9}$, $10^{11.0}$, and $10^{14.9}$, respectively. The significantly lower number for $\mathbf{5}^{\bullet-}$ is in agreement with the EPR spectroscopically detectable[1e,m] higher degree of mixing between the metal centers and the singly occupied ligand-centered orbital (cf. below). The established[1c,f,g] stabilization of the Pt^{III} state through dimesityl substitution has allowed us to quantitatively assess, for the first time, the extent of metal−metal interaction in a compound $[R_kPt^{II}(\mu\text{-}L)Pt^{III}R_k]^+$. Previous studies of $[Mes_2Pt(\mu\text{-bpym})PtMes_2]^n$ [6] and the similar observation of one two-electron oxidation process for **4** to $\mathbf{4}^{2+}$ (Table 2) have only indicated that such a "communication" must be very small. The capacity of the bptz bridging ligand to effect extremely high K_c values not only for the ligand-reduced form but also for the mixed-valent metal states has previously been demonstrated for $\{(bptz)[Ru(NH_3)_4]_2\}^{5+}$, for which $K_c = 10^{15.0}$.[8c] On oxidation, the corresponding diplatinum complex **1** does indeed show a small but detectable splitting between the waves for the $\mathbf{1}/\mathbf{1}^+$ and $\mathbf{1}^+/\mathbf{1}^{2+}$ couples (Figure 1). The potential difference of 80 mV, as extracted from simulation (Figure 1), translates to $K_c = 23$ for the $Pt^{II}-Pt^{III}$ mixed-valent intermediate. This small value confirms the weak coupling of the d^7/d^8 pair through the bridging π system, in agreement with the notion of a singly occupied σ-type orbital (d_{z^2}) in the Pt^{III} state. In contrast, the numerous d^5/d^6 mixed valent systems[16] exhibit a much stronger metal−metal interaction in such situations due to the involvement of π-type orbitals in both the bridging ligand and at the metal oxidation sites.[16] In any case, the superior capacity of the bptz bridging ligand in stabilizing odd-electron intermediates is confirmed for both the one-electron oxidized and the one-electron reduced forms of compound **1**.

Absorption Spectroscopy. Platinum(II) and tetraorganoplatinum(IV) complexes of π-acceptor ligands are distinguished by low-lying solvatochromic charge-transfer transitions, either from metal d orbitals (Pt^{II}) or from $Pt-C$ σ bond combinations (Pt^{IV}) to low-lying π^* orbitals.[1n,17] Since bpip and especially bptz have very low-lying acceptor MOs,[8,9] it is not surprising that the compounds presented here display particularly long-wavelength absorptions (Figure 2, Table 3), extending into the near-infrared region.

Chelating acceptor ligands such as bpip[9] or bptz[8] are generally distinguished by several low-lying π^* orbitals of either Ψ or χ local symmetry.[1g,18] The three lowest-lying π^* MOs are of a_u, a_u (2Ψ), and b_g (2Ψ) symmetry for bptz[8] and of a_u (2Ψ), a_u (2χ), and b_g (2Ψ) symmetry for bpip (each in the C_{2h} conformation; 2 indicates the number of corresponding chelate sites), Chart 1.[9d]

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[15] (a) Kaim, W.; Kasack, V. *Inorg. Chem.* **1990**, *29*, 4696. (b) Kasack, V.; Kaim, W.; Binder, H.; Jordanov, J.; Roth, E. *Inorg. Chem.* **1995**, *34*, 1924.

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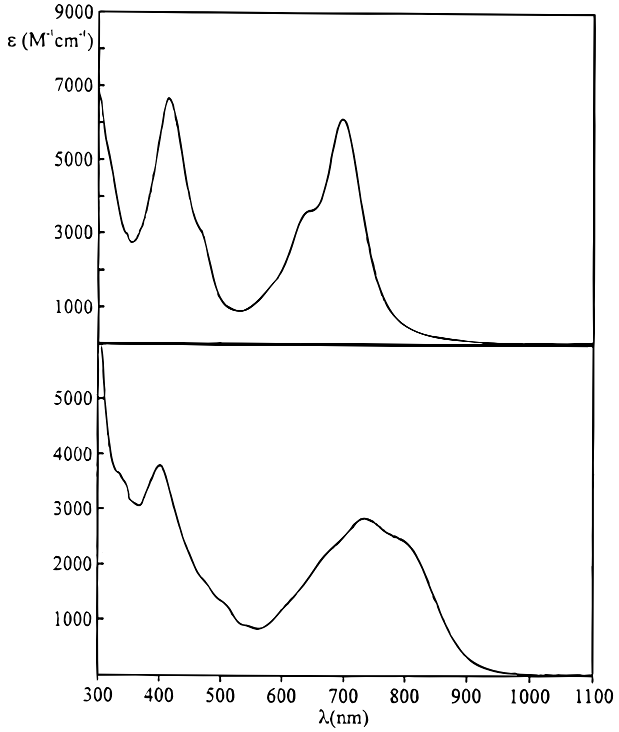


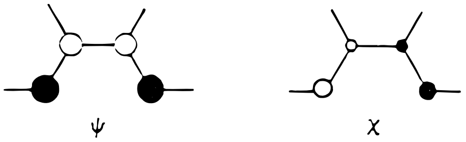
Figure 2. Absorption spectra of compounds **5** (top) and **6** (bottom) in dichloromethane.

Table 3. Long-Wavelength Absorption Data[a] of Mono- and Dinuclear Organoplatinum Complexes

complex	λ_3	λ_2	λ_1
1	440[b]	690[b]	852[b]
4	418	557, 603, 654	765
5	414 (6.7)	465sh	588sh, 641sh, 702 (6.15)
6	400 (3.8)	510sh	670sh, 734 (2.85), 805sh
7	388	503	612sh, 671sh, 731, 796sh

[a] Wavelengths, λ, of maxima in nanometers (extinction coefficients, ϵ, in 10^3 M^{-1} cm^{-1}); measurements in CH_2Cl_2. For assignments of transitions, see text. [b] Values in THF: 421 (2.99), 639 (3.45), and 782 (3.02) nm.

Chart 1



Several intense (allowed) charge-transfer transitions are thus expected and observed in the visible region (Figure 2).

We have previously pointed out that the d^8 configuration of square-planar Pt^{II} typically results in a situation where the allowed transitions from the stabilized d_{xz} to $\pi^*(\Psi)$ orbital and from the less stabilized d_{xy} orbital to the $\pi^*(\chi)$ MO come to lie in comparable energy ranges, the frequent result being an overlap of several often vibrationally structured band systems.[1c,f] Such a situation is also observed here for compounds **1**, **4**, and **5**, however, an exact assignment cannot be made yet with reasonable confidence. The platinum(IV) compounds **6** and **7** also exhibit long-wavelength charge-transfer bands which we assign to transitions from Pt−C σ bond combinations to low-lying π^* orbitals of appropriate symmetry.[1e,f,n,17] Vibrational structuring of the typical[1f,19] magnitude 1300 ± 150 cm^{-1}, could only be observed for the complexes with bpip (Figure 2, Table 3). The lack of such features for bptz compound **1** is attributed to strong band broadening on MLCT excitation involving tetrazine π^* orbitals; 1,2,4,5-tetrazines exhibit extensive structural reorganization on π^* orbital occupation.[20] As Figure 2 illustrates, the spectral resolution is better for the Pt^{II} compound **5** than for the Pt^{IV} analogue **6** with more degrees of geometrical freedom.

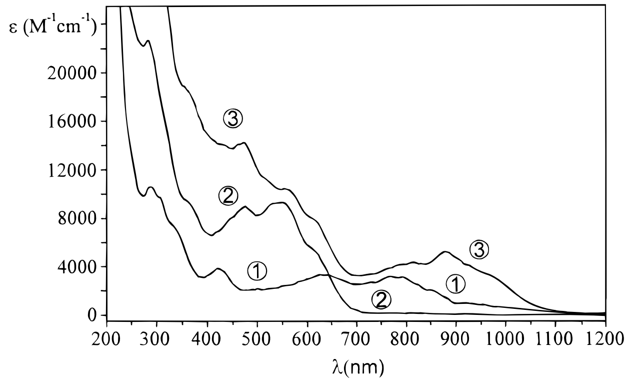


Figure 3. Absorption spectra of (1) **1**, (2) $\mathbf{1}^{\bullet-}$, and (3) $\mathbf{1}^{2-}$ from spectroelectrochemistry in THF/0.1 M Bu_4NPF_6.

Table 4. Parameters[a] of Linear Regressions $\tilde{\nu} = A + B \times E^*_{\mathrm{MLCT}}$[b] for the Solvatochromism of Long-Wavelength Absorption Maxima

compound	band	A	B	r	n[d]
4	λ_1	12 280	1790	0.820	6
4	λ_2	14 450	1830	0.940	6
5	λ_1[c]	13 060	1880	0.999	4
5	λ_2[c]	22 530	2450	0.996	4
6	λ_1	12 540	1980	0.828	6
6	λ_2	23 860	2170	0.913	6

[a] A and B in cm^{-1}; r is the correlation coefficient. [b] Solvent parameters E^*_{MLCT} from ref 21a. [c] Main features of corresponding band system (see Table 3). [d] Number of solvents used for correlation.

The charge-transfer bands of organoplatinum compounds with π-acceptor ligands are usually solvent dependent (solvatochromism).[1b,c,f,n,2] The long-wavelength absorption maxima of the centrosymmetric compounds **4**−**6** were thus measured (Table S1, Supporting Information) in various solvents. For the less soluble complex **1**, the database was too small to extract meaningful correlations with solvent parameters. The complexes of bpip exhibit the typical negative solvatochromism,[21] i.e., hypsochromic shifts with increasing solvent polarity. Correlations with the established[8a,21a,b] solvent parameter E^*_{MLCT}[21a] were only partly satisfactory in terms of a linear regression (Table 4); the sensitivity B from the equation $\nu = A + B \times E^*_{\mathrm{MLCT}}$

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Table 5. Spectroelectrochemical Data:[a] UV/Vis/NIR-Absorption Maxima, λ, of Ionic Dinuclear Organoplatinum Complexes

complex	λ
1	421 (2.99), 639 (3.45), 782 (3.02)
$\mathbf{1}^{\bullet-}$	553 (9.6), 613sh (5.1)
$\mathbf{1}^{2-}$	555 (18.0), 878 (11.4)
4	406 (10.73), 639 (7.07), 728 (6.13)
$\mathbf{4}^{\bullet-}$	313 (13.0), 540 (13.65), 611sh (6.92), 1056 (0.4)
$\mathbf{4}^{2-}$	280 (18.8), 542 (25.0), 577 (27.1)
$\mathbf{5}^{\bullet-}$	325, 375, 468, 596, 735, 840
6	394, 711
$\mathbf{6}^{\bullet-}$	398, 475, 575, 630
$\mathbf{6}^{2-}$	585 br
$\mathbf{1}^{2+\,b}$	1390 (0.13)
$\mathbf{4}^{2+\,b}$	922 (0.78), 1335sh (0.45), 1427 (0.54)

[a] Wavelengths, λ, in nanometers (extinction coefficients in 10^3 M^{-1} cm^{-1}) from measurements following in situ electrolysis in THF/0.1 M Bu_4NPF_6 at ambient temperatures. [b] Ligand-field transitions of low-spin d^7 system.

exhibits typical values for “normal” MLCT absorption bands.[21,22a]

The availability of half-wave potentials $E_{1/2}$ from reversible processes for both oxidation and reduction of bis(dimesitylplatinum) compounds **1** and **4** allowed us to estimate the Franck−Condon contributions χ_{FC} from intra- and intermolecular reorganization after long-wavelength CT excitation (E_{op}).[1f,n,22] Using the approximation given in eq 2 and the data from Tables 2, 3, and S1, we arrive at values of 0.27 eV for **1** in THF; compound **4** yields 0.25 eV in THF and 0.18 eV in dichloromethane. Despite the dinuclear composition,

$$\chi_{FC} = E_{op}\,[\text{eV}] - (E_{1/2}\,\text{oxI} - E_{1/2}\,\text{redI})\,[\text{V}] \qquad (2)$$

$$(1\ \text{eV} = 8065.5\ \text{cm}^{-1})$$

the numbers for χ_{FC} are still rather small and only slightly higher than those of mononuclear species with α-diimine ligands,[1f,n] which supports the notion of little structural change[1n] and largely independent metal/ligand interfaces.[21c]

Spectroelectrochemical data of the dinuclear compounds, as obtained with an OTTLE cell,[14] are summarized in Table 5. A corresponding spectrum is shown for the system $\mathbf{1}^{0/1-/2-}$ in Figure 3.

The reversibility of the electron-transfer processes was confirmed in the spectroelectrochemistry experiments. The data for the reduction processes show no particular long-wavelength shifts, presumably due to the stabilization of the π^* orbital occupied by one or two electrons. More detailed assignments of the transitions will require high-level open-shell calculations and spectroelectrochemical data for the ligands and more simple complexes.

The weak long-wavelength bands detected above 900 nm for the dicationic species $\mathbf{1}^{2+}$ and $\mathbf{4}^{+}$ (Table 5) are readily assigned to d→d (ligand-field) transitions in a low-spin d^7 configuration (Pt^{III}).[1f] Up to three such weak, low-energy bands may be observed[1f,23] from doubly occupied d orbitals to the singly occupied level.

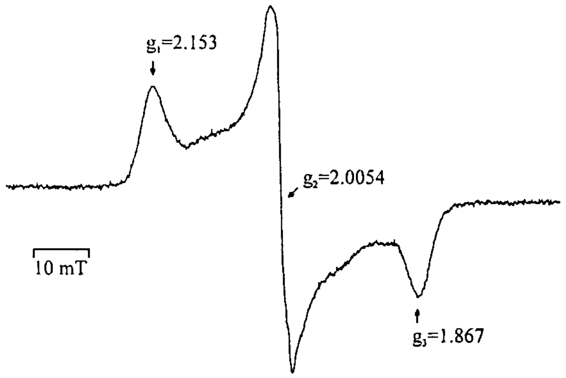

Figure 4. EPR spectrum (110 K) of electrogenerated $\mathbf{5}^{\bullet-}$ in THF/0.1 M Bu_4NPF_6.

Special features of the mixed-valent monocation $\mathbf{1}^{+}$ could not be discerned as a consequence of the small K_c value of 23.

EPR Spectroscopy. The stability of several kinds of odd-electron dinuclear organoplatinum species has stimulated our efforts in characterization through EPR spectroscopy. Recent results of paramagnetic platinum complexes with α-diimine and related ligands[1a−m,24,25] have led to different formulations of the proper oxidation states involved. Dinuclear platinum compounds[26] are of particular interest in that respect because of possible mixed-valency contributions.

As observed previously,[1c,f,g] the persistent oxidized species containing Mes_2Pt^{III} centers remained EPR silent even at 3.5 K. (There is no indication for Pt^{III} dimer formation, which would be hindered by the mesityl groups.) The very rapid relaxation is attributed to the presence of close-lying d orbitals for the single-electron and to correspondingly close-lying paramagnetic states. The high spin−orbit coupling constant[27] of the 5d element adds to the EPR line broadening. On the other hand, the monoanionic states, obtained through in situ one-electron reduction in a two-electrode cell, exhibit partially resolved EPR spectra (Figures 4 and 5); data analysis yielded the results summarized in Table 6.

All dinuclear anions $[R_kPt(\mu\text{-}L)PtR_k]^-$ exhibit a rhombic g factor pattern. The total g anisotropy $\Delta g = g_1 - g_3$ is smallest for the reduced diplatinum(IV) compound $\mathbf{6}^{\bullet-}$ and highest for the related $\mathbf{5}^{\bullet-}$. In the series of

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[22] (a) Kober, E. M.; Goldsby, K. A.; Narayana, D. N. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4303. (b) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1985**, *119*, 61; **1986**, *124*, 152.

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[24] See also paramagnetic dithiolene platinum complexes formulated with “Pt^{III}” ($g_1 \approx 2.2$, $g_2 \approx 2.07$, $g_3 \approx 1.84$): Möller, E.; Kirmse, R. *Inorg. Chim. Acta* **1997**, *257*, 273.

[25] Pt^{I} species are postulated in the following: Fanizzi, F. P.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1996**, *35*, 3173.

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[27] Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*; Wiley: New York, 1994.

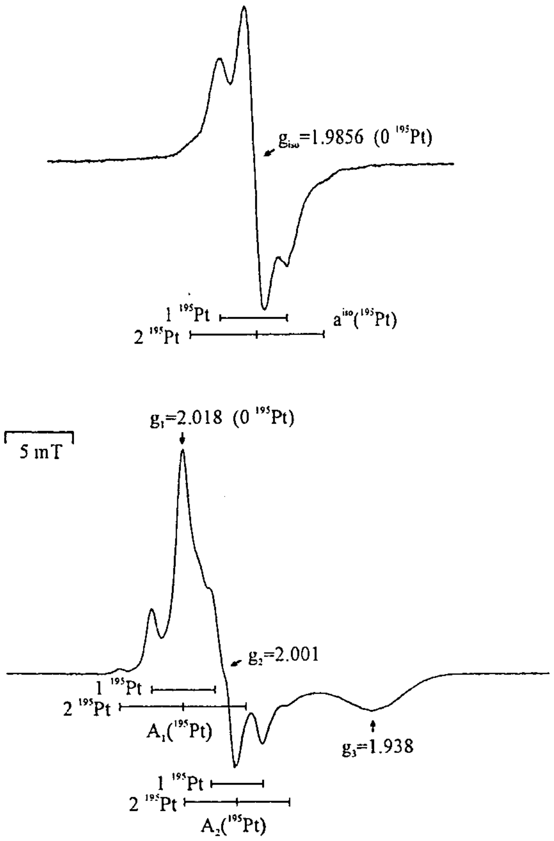

Figure 5. EPR spectra at 300 (top) and 110 K (bottom) of electrogenerated $\mathbf{6}^{\bullet-}$ in THF/0.1 M Bu_4NPF_6.

Table 6. ESR Data[a] of Anionic Dinuclear Organoplatinum Complexes

anion[b]	g_{iso}	a_{Pt}[c]	g_1	g_2	g_3	Δg[d]	solvent
$\mathbf{1}^{\bullet-}$	2.0264	n.o.	2.0824	2.0244[e]	1.9727	0.109	DCE
$\mathbf{4}^{\bullet-}$	2.0090	n.o.	2.1083	2.0062	1.9033	0.205	CH_2Cl_2
$\mathbf{4}^{\bullet-}$	2.0053	n.o.	2.1110	2.0059	1.9150	0.196	THF
$\mathbf{5}^{\bullet-}$	2.0080	n.o.	2.153	2.0054	1.867	0.286	THF
$\mathbf{6}^{\bullet-}$	1.9856	4.8	2.018[f]	2.001[g]	1.938	0.080	THF

[a] Coupling constants *a* in mT (1T = 10^4 Gauss). [b] Generated by in situ electrolysis at ambient temperatures in 0.1 M Bu_4NPF_6 solvent systems. g_{iso} measured at room temperature, anisotropic *g* factors at 110 K. [c] ^{195}Pt, $I = 1/2$, 33.8% natural abundance. [d] $\Delta g = g_1 - g_3$. [e] a_2 (^{195}Pt) = 3.0 mT. [f] a_1(^{195}Pt) = 4.7 mT. [g] a_2(^{195}Pt) = 3.8 mT.

dimesitylplatinum systems, the bptz complex $\mathbf{1}^{\bullet-}$ exhibits a distinctly smaller *g* anisotropy than $\mathbf{4}^{\bullet-}$. Since the large spin−orbit coupling contributions from platinum[27] are a major factor in influencing *g* values,[1a−m,24] we conclude that the metal participation at the SOMO is lower in $\mathbf{1}^{\bullet-}$ than in $\mathbf{4}^{\bullet-}$ (due to a lower lying π^* orbital of bptz) and in $\mathbf{6}^{\bullet-}$ relative to $\mathbf{5}^{\bullet-}$. Previous studies on mononuclear systems have similarly revealed that reduced diorganoplatinum(II) species exhibit a higher degree of metal contribution to the spin distribution than tetraorganoplatinum(IV) analogues.[1e,m] Incidentally, the isotropic values g_{iso} do not reflect these details; however, they indicate that the reduced $(Pt^{IV})_2$ systems differ from the reduced $(Pt^{II})_2$ species by the sign of the *g* factor deviation from the free electron value of $g_e = 2.0023$. The deviation $g > g_e$ for the latter radicals reflects the closeness of occupied d orbitals to the SOMO.[7a,28]

^{195}Pt metal hyperfine coupling was only observed for $\mathbf{1}^{\bullet-}$ (a_2) and $\mathbf{6}^{\bullet-}$ (a_{iso}, a_1, a_2).[1p] The parameters lie in the typical range for other known platinum complexes of α-diimine anion radicals.[1a−m]

Summary. The results presented in this study not only confirm that double metal coordination to the good π-accepting bridging ligands bpip and bptz causes facilitated reduction and low-energy charge transfer absorptions, they also illustrate the superior capacity of bptz, particularly, to stabilize odd-electron intermediates, both for the reduced and oxidized forms of the compounds $[R_kPt(\mu\text{-}L)PtR_k]$.

(i) Starting from $R_2Pt^{II}(\mu\text{-}L)Pt^{II}R_2$, the persistent and stable ($K_c > 10^{11}$) one-electron reduced form is predominantly formulated as $[R_2Pt^{II}(\mu\text{-}L^{-I})Pt^{II}R_2]^-$ with only slight but detectable contributions from a metal mixed-valent form $[R_2Pt^{II}(\mu\text{-}L^0)Pt^{I}R_2]^-$ (alternatively $[R_2Pt^{III}(\mu\text{-}L^{-II})Pt^{II}R_2]^-$).

(ii) If sterically protected as in system **1**, it may even be possible to observe the mixed-valent intermediate in the comproportionation equilibrium

$$[R_2Pt^{II}(\mu\text{-}L)Pt^{II}R_2] + [R_2Pt^{III}(\mu\text{-}L)Pt^{III}R_2]^{2+} \rightleftharpoons 2[R_2Pt^{III}(\mu\text{-}L)Pt^{II}R_2]^+$$

However, the metal−metal interaction across the π ligands is much smaller for these d^7/d^8 systems than for d^5/d^6 species.

(iii) Finally, reduction of $R_4Pt^{IV}(\mu\text{-}L)Pt^{IV}R_4$ yields $[R_4Pt^{IV}(\mu\text{-}L^{-I})Pt^{IV}R_4]^-$ with negligible contributions from $[R_4Pt^{IV}(\mu\text{-}L^0)Pt^{III}R_4]^-$.

Acknowledgment. We thank the Volkswagenstiftung and Deutsche Forschungsgemeinschaft for financial support.

Supporting Information Available: Table S1, giving absorption spectral data of complexes **1** and **4**−**6** in various solvents (1 page). Ordering information is given on any current masthead page.

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