Inorg. Chem. **2007**, *46*, 5562–5566

Reversibly Reducible *cis*-Dichloroplatinum(II) and *cis*-Dichloropalladium(II) Complexes of Bis(1-methylimidazol-2-yl)glyoxal

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Received January 31, 2007

Complexes *cis*-MCl_2(big), big = bis(1-methylimidazol-2-yl)glyoxal, M = Pt, Pd, were prepared and characterized through electrochemistry, spectroscopy, and for M = Pt, by X-ray structure analysis. The seven-membered chelate ring formed through N,N′ coordination of the ligand big shows a boat conformation in agreement with density functional theory (DFT) calculation results. No significant intermolecular interactions were observed for the platinum compound. Both the Pd^{II} and Pt^{II} complexes undergo reversible one-electron reduction in CH_2Cl_2/0.1 M Bu_4NPF_6; the reduced palladium compound disintegrates above −30 °C. Electron paramagnetic resonance (EPR), UV–vis, and IR spectroelectrochemistry studies were employed to study the monoanions. The anion radical complex [*cis*-$PtCl_2$(big)]$^{\bullet-}$ exhibits a well-resolved EPR spectrum with small but well-detectable *g* anisotropy and an isotropic ^{195}Pt hyperfine coupling of 12.2 G. DFT calculations confirm the spin concentration in the α-semidione part of the radical complex with small delocalization to the bis(imidazolyl)metal section. The results show that EPR and electroactive moieties can be linked to the *cis*-dichloroplatinum(II) group via imidazole coordination.

cis-Dichloroplatinum complexes with nitrogen co-ligands have been studied for various reasons. A major incentive has been the success of certain compounds *cis*-$PtCl_2$(N)(N) in the therapy of tumors.[1] Although much is already known about the molecular mechanism of action, there is still a need to explore new classes of compounds to extend the therapeutic scope of those metalladrugs. Complexes of *cis*-$PdCl_2$ and *cis*-$PtCl_2$ were also studied as precursors for water reduction catalysis.[2] In yet a further area of research, the propensity of such planar platinum(II) compounds for intense luminescence in the solid state and/or in solution has instigated several studies to clarify the correlation between structure and spectroscopic behavior.[3,4] The potential for stacking of planar Pt^{II} complexes and for Pt−Pt interaction has raised particular interest. Finally, the possible one-electron-transfer reactivity of such compounds has been studied, regarding either the oxidation to Pt^{III}-involving species[5] or the reduction to formally "platinum(I)" compounds.[5−7] Spectroelectrochemical and electron paramagnetic resonanance (EPR) studies have established that reduction generally involves the ligands, leading to anion radical complexes of platinum(II).[5−7] Typical examples are [*cis*-

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10.1021/ic070185b CCC: $37.00
Published on Web 06/16/2007

$PtCl_2(N\hat{}N)]^{\bullet-}$, N^N = 2,2′-bipyridine or 2,2-bipyrimidine,[6a,b,7a] which have been identified as paramagnetic molecules with only minor amounts (ca. 5%) of spin density on the Cl_2Pt moiety.

Using bis(1-methylimidazol-2-yl)glyoxal (big) as a coordinatively variable, reversibly reducible, and biochemically relevant imidazole-containing ligand,[8−10] we have now obtained complexes *cis*-MCl_2(big), M = Pt, Pd, and studied their electron-transfer behavior. Although Pd analogues of the platinum systems mentioned above have not been studied as extensively, probably due to their lower stability, the pervasive use of palladium compounds in organic synthesis justifies their investigation.

The frequent occurrence of two histidine binding sites for metal centers in proteins[11] has prompted the development of many bis(imidazole)-containing chelate ligands for purposes of active-site modeling.[12] Among these ligands, bis(1-methyl-2-imidazolyl)ketone (bik)[13] and its reduced forms have been employed, also in connection with platinum.[13,14] The related tetradentate (N,O,O′,N′) big[8−10] contains an α-diketo moiety, providing a low-lying π^* orbital in the coplanar conformation, which makes this ligand far more easily reducible than bik. Complexes of big with copper(II),[9] rhodium(III),[9] iridium(III),[9] and rhenium(I)[10] have been described. In addition to the interesting electronic situation, the structural alternatives of the big ligand are manifold and not easy to predict;[15] only few experimental structures have been established so far.[9,10] Recently, a computational study of big as a free molecule (neutral, one-electron reduced, and oxidized forms) and as a ligand with different coordination modes in complexes was reported.[15]

Imidazole-containing chelate ligands are not only used in the modeling of metalloprotein active-site structures[11,12,14] but have also found application in systems for asymmetric catalysis and for the separation and detection of biomolecules.[16]

Experimental Section

Instrumentation. EPR spectra in the X band were recorded with a Bruker System ESP 300 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 obtained using a Perkin-Elmer FTIR 684 instrument. UV−vis−NIR (NIR = near-infrared) absorption spectra were recorded on a J&M TIDAS spectrophotometer, and the emission was studied using a Perkin-Elmer LS50-B instrument. Cyclic voltammetry was carried out in 0.1 M Bu_4NPF_6 and approximately 10^{-3} M sample solutions using a three-electrode configuration (glassy-carbon working electrode with 3 mm diameter, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc^+) couple served as an internal reference. A two-electrode capillary was used in radical complex generation for X-band EPR studies.[17]

Preparation of $PtCl_2$(big). To a solution of 95 mg (0.43 mmol) big[8−10] in 15 mL acetonitrile was added 375 mg (0.88 mmol) of $PtCl_2(DMSO)_2$[18] in 10 mL acetonitrile, and the reaction mixture was refluxed for 48 h. Upon cooling to room temperature, an orange solid precipitated, which was filtered to give 110 mg (52.9%) of $PtCl_2$(big) after drying. Single crystals for X-ray diffraction were grown from acetonitrile solution by slow evaporation. Anal. Calcd for $C_{10}H_{10}Cl_2N_4O_2Pt$ (484.21): C, 24.81; H, 2.08; N, 11.57. Found: C, 24.68; H, 1.96; N, 11.47. ^{1}H NMR (in acetone-d_6): δ 7.58 (s, 2H, im) 7.38 (m, 2H, im), 3.86 (s, 6H, NCH_3). Poor solubility of the complex precluded the observation of ^{195}Pt coupling in the ^{1}H NMR spectrum. IR (KBr): 1679 cm^{-1}. Cyclic voltammetry at 100 mV in CH_2Cl_2/0.1 M Bu_4NPF_6 gave a reversible wave with $E_{1/2} = -0.79$ V vs $Fc^{+/0}$, $\Delta E = 88$ mV.

Preparation of $PdCl_2$(big). To a solution of 50.4 mg (0.23 mmol) of big in 10 mL acetonitrile was added 771 mg (0.23 mmol) of $PdCl_2(DMSO)_2$[18] in 12 mL acetonitrile at 25 °C, and the reaction mixture was stirred for 5 h. The filtration of the yellow solid gave

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Table 1. Crystallographic Data for $PtCl_2$(big)

empirical formula	$C_{10}H_{10}Cl_2N_4O_2Pt$
fw	484.21
T (K)	100(2)
space group	$I\bar{4}$
a (Å)	17.4566(6)
c (Å)	9.0567(3)
V (Å^3)	2759.9(2)
Z	8
D_{calc} (g cm^{-3})	2.331
μ (mm^{-1})	10.56
R_{int}	0.059
R_1	0.031
R_2	0.062
Flack x	−0.026

41 mg of the product after drying (45%). Anal. Calcd for $C_{10}H_{10}Cl_2N_4O_2Pd$ (395.52): C, 30.37; H, 2.55; N, 14.17. Found: C, 30.60; H, 2.24; N, 14.09. ^{1}H NMR (acetone-d_6): 7.56 (s, 2H, im), 7.43 (s, 2H, im), 3.86 (s, 6H, NCH_3). ^{1}H NMR (CD_3CN): δ 7.43 (d, 2H, im), 7.36 (d, 2H, im), 3.81 (s, 6H, NCH_3). IR (KBr): 1678 cm^{-1}. Cyclic voltammetry at −30 °C (200 mV/s scan rate) in CH_2Cl_2/0.1 M Bu_4NPF_6 showed a reversible wave with $E_{1/2} = -0.74$ V vs $Fc^{+/0}$, $\Delta E = 76$ mV.

Crystallography. Single crystals of $PtCl_2$(big) were obtained by slow evaporation from saturated solution. Data were collected from a selected specimen (yellow platelet, 0.1 × 0.1 × 0.04 mm) with a NONIUS Kappa CCD diffractometer at 100 K. Additional crystallographic information is given in Table 1. The structure was solved using direct methods with refinement by full-matrix least-squares of F^2, employing the program system *SHELXL 97* in connection with absorption correction.[19] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were introduced at appropriate positions.

DFT Calculations. Density functional (DFT) calculations were carried out using the program package *Gaussian 98*.[20] The hybrid functional B3LYP with the LANL2DZ basis set was employed. Open-shell calculations were carried out with the unrestricted UB3LYP functional. Atomic spin densities were also calculated utilizing this functional.

Results and Discussion

Although both complexes *cis*-MCl_2(big), M = Pt, Pd, were obtained by a straightforward route from bis(dimethylsulfoxide) precursors, the palladium compound is markedly less stable in solution. The ligand big is known to exhibit additional reactivity in connection with metal coordination, including hydroxide addition to one of the electrophilic carbonyl functions[9] or the loss of 1 equiv of CO to form bik.[21] The formation of dinuclear compounds with various

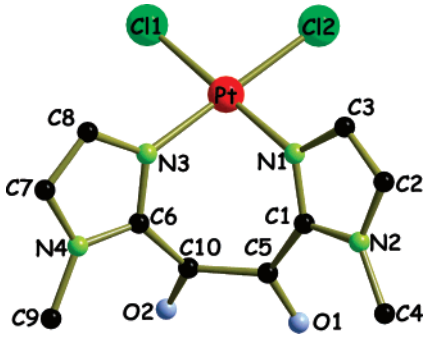

Figure 1. Molecular structure of $PtCl_2$(big) in the crystal with atom numbering.

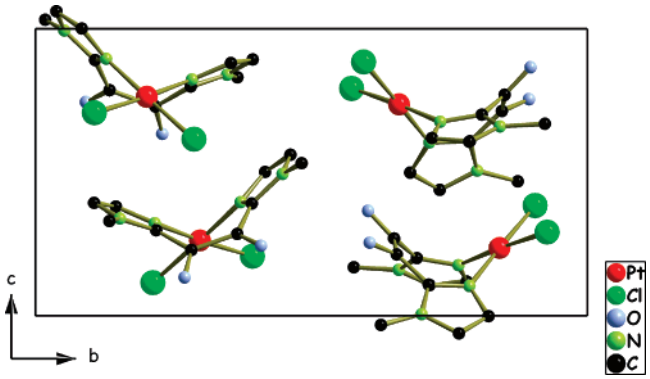

Figure 2. Arrangement of $PtCl_2$(big) molecules in the crystal.

different coordination alternatives[15] is also possible,[10] as is reduction to a radical anion ligand (cf. below). Although a 2:1 ratio of platinum precursor and big was used for optimum yield, there was no indication for the formation of dinuclear species under the conditions described in the Experimental Section. We attribute this finding to the stability of Pt−N(imine) over Pt−O(carbonyl) bonds.

The X-ray structure determination of the platinum complex (Table 1) revealed metal binding via the imidazole-imine donor atoms to form a boat-shaped seven-membered chelate ring (Figures 1 and 2). Such a conformation had been observed previously for the mononuclear complexes [RhCl(C_5Me_5)(big)]$^+$ [9] and *fac*-Re(CO)$_3$Cl(big).[10] The structure of *cis*-$PtCl_2$(big) is well-reproduced by DFT (Table 2), and the subsequently performed calculation of the reduced form [*cis*-$PtCl_2$(big)]$^{\bullet-}$ shows the typical[15,22] CO bond lengthening and (O)C−C(O) bond contraction in connection with flattening, which is usually associated with α-semidione formation (Table 2). The overall conformation was retained on reduction. No significant intermolecular interactions were found (Figure 2), and the shortest Pt−Pt distance is 5.78 Å.

Although *cis*-$PtCl_2$(big) exhibits an absorption band at 318 nm, there was no detectable emission of the solid. This is in contrast to what is observed in many related complexes of *cis*-$PtCl_2$(N)(N)[3,4] and may be attributed to the nonplanarity, absence of stacking, and the presence of methyl groups, all of which provide pathways for radiationless energy conversion involving low-energy molecular motions.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[PtCl_2(big)]^{0/\bullet-}$

	exp[a]	DFT[a]	DFT[b]
	bond lengths		
Pt−N3	2.009(6)	2.034	2.030
Pt−N1	2.003(6)	2.034	2.030
Pt−Cl1	2.297(2)	2.403	2.431
Pt−Cl2	2.294(2)	2.398	2.431
N3−C6	1.334(9)	1.369	1.361
N1−C1	1.333(10)	1.354	1.361
C5−C10	1.536(9)	1.553	1.456
C5−C1	1.463(10)	1.478	1.490
C5−O1	1.199(9)	1.247	1.298
N4−C9	1.462(9)	1.479	1.469
N2−C4	1.460(10)	1.476	1.469
C10−O2	1.213(9)	1.259	1.298
	bond angles		
N1−Pt−N3	89.2(2)	93.4	89.8
Cl1−Pt−N1	178.73(19)	177.9	177.5
Cl2−Pt−N3	176.94(18)	178.1	177.5
Cl1−Pt−N3	90.68(17)	88.3	89.2
Cl2−Pt−N1	88.86(17)	87.2	89.2
Cl1−Pt−Cl2	91.20(6)	91.1	91.7
	torsional angles		
Pt−N1−C1−C5	1.0(1)	−13.7	6.4
Pt−N3−C6−C10	3.0(1)	−0.5	−6.3

[a] For $PtCl_2(big)$. [b] For $[PtCl_2(big)]^{\bullet-}$.

Like other complexes of big,[9,10] the compounds *cis*-MCl_2(big) could be reduced reversibly in cyclic voltammetry experiments (Figure 3). For the palladium complex, the temperature had to be kept below −30 °C. In relation to the free ligand (−1.68 V) and the previously reported mononuclear rhenium(I) complex of big (−0.95 V),[10] the reduction potentials for *cis*-$PdCl_2$(big) (−0.74 V) and *cis*-$PtCl_2$(big) (−0.79 V, $E_{1/2}$ values against $Fc^{+/0}$ in CH_2Cl_2/0.1 M Bu_4NPF_6) are less negative, illustrating the strongly polarizing acceptor effect of $PdCl_2$ and $PtCl_2$ groups.[7] On the other hand, a comparison with, e.g., $[cis\text{-}PtCl_2(bpym)]^{0/\bullet-}$ (−1.28 V)[7a] illustrates the more facile reduction of the α-diketone ligand big in relation to an aromatic α-diimine ligand such as 2,2′-bipyrimidine (bpym).

The site of reduction can be probed by spectroelectrochemistry (UV−vis−NIR, IR, EPR). Previously studied $[RhCl(C_5Me_5)(big)]^{\bullet}$ [9] and $[fac\text{-}Re(CO)_3Cl(big)]^{\bullet-}$ [10] were recognized as radical complexes containing the $big^{\bullet-}$ anion.

The electrochemically generated complexes $[cis\text{-}PdCl_2(big)]^{\bullet-}$ and $[cis\text{-}PtCl_2(big)]^{\bullet-}$ exhibit EPR signals (Pd) and even resolved spectra (Pt) near $g = 2.00$ in agreement with a low-spin d^8/radical formulation $M^{II}(big^{\bullet-})$. In contrast to the labile $[cis\text{-}PdCl_2(big)]^{\bullet-}$ with an insufficiently resolved EPR signal ($\Delta H_{pp} = 7.5$ G) at $g_{iso} = 2.0053$, the anion radical complex $[cis\text{-}PtCl_2(big)]^{\bullet-}$ is persistent at room temperature ($g_{iso} = 2.0117$) and shows well-resolved EPR hyperfine splitting (Figure 4) from ^1H, ^{14}N, and ^{195}Pt nuclei ($I = {}^1/_2$, 33.8% natural abundance[22]). The ligand values lie in a similar range as those of free $big^{\bullet-}$ [10] while the metal isotope coupling of 12.2 G is much diminished when compared with that of $[cis\text{-}PtCl_2(bpy)]^{\bullet-}$ (58 G) or $[cis\text{-}PtCl_2(bpym)]^{\bullet-}$ (46 G).[6a,b,7a] The ratio between 12.2 G and the isotropic hyperfine constant[22] of 12 278.4 G for ^{195}Pt is thus unusually[23a] small at 10^{-3}. The typically[23b] smaller ^{105}Pd isotope coupling (22.2%, $I = {}^5/_2$) is thus not resolved. Another EPR parameter

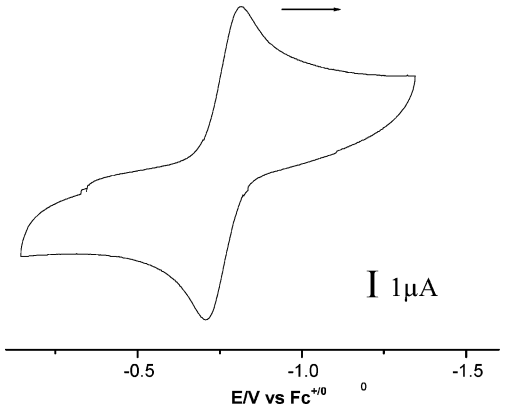

Figure 3. Cyclic voltammogram of $PdCl_2$(big) at −30 °C in CH_2Cl_2/0.1 M Bu_4NPF_6 (100 mV/s scan rate, potentials vs $[Fe(C_5H_5)_2]^{+/0}$).

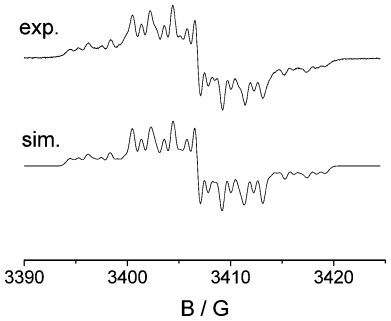

Figure 4. EPR spectrum of electrochemically generated $[PtCl_2(big)]^{\bullet-}$ at 298 K in CH_2Cl_2/0.1 M Bu_4NPF_6 (top) with simulation (bottom): $a(^{195}Pt) = 12.2$ G, $a(^{14}N, 2N) = 2.18$ G, $a(^{14}N, 2N) = 0.79$ G.

reflecting the contribution from a heavy metal with a high spin−orbit coupling constant[22] such as Pt is the *g* anisotropy $\Delta g = g_1 - g_3$ from frozen solution spectra. From $g_1 = 2.024$, $g_2 = 2.003$, and $g_3 = 2.000$, the resulting $\Delta g = 0.024$ compares with the significantly higher $\Delta g = 0.103$ for $[cis\text{-}PtCl_2(bpy)]^{\bullet-}$ and a similar number for $[cis\text{-}PtCl_2(bpym)]^{\bullet-}$ (0.96).[6a,b,7a]

The small effects of $PtCl_2$ coordination on $big^{\bullet-}$ are reproduced by the DFT calculations of the singly occupied molecular orbital (SOMO) and of the spin densities (Figure 5).

Like in the previously reported[24] compound $[PtR_2(dppz)]^{\bullet-}$, R = mesityl, dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine, the small orbital overlap at the metal−ligand interface is caused by the predominant charge and spin localization at a remote, noncoordinating site of the radical ligand. In the present case, the reduction affects mainly the α-diketo group[15] with a small but detectable and possibly coordination-enhanced spin contribution from metal-binding N1/N3 (2.18 G) and, to a lesser extent, from N2/N4 (0.79 G) and C2/C7 (Figure 5). Accordingly, the observed ^{14}N hyperfine splitting (Figure 4) is attributed to these centers.

On reduction of *cis*-$PtCl_2$(big) in CH_2Cl_2, the CO stretching band at 1680 cm^{-1} vanishes; its probable reappearance at lower energies could not be detected, possibly due to

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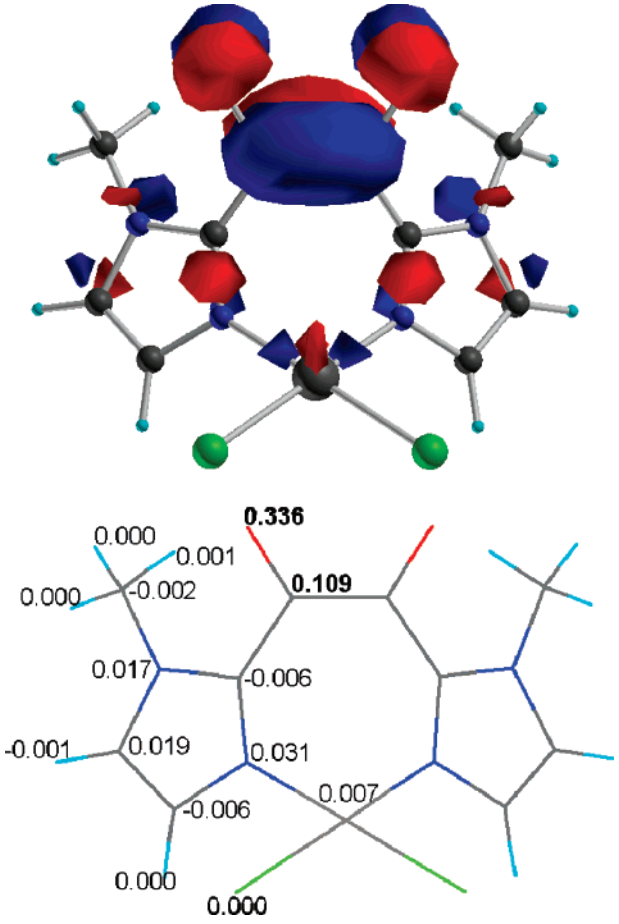

Figure 5. SOMO representation (top) and DFT calculated spin densities (bottom) of $[PtCl_2(big)]^{\bullet-}$.

overlapping of the band of the poorly soluble compound with a strong solvent absorption.

The UV−vis spectrum of $[PtCl_2(big)]$ in CH_2Cl_2 exhibits a band with an absorption maximum at 318 nm, not far from the band of the free big ligand (297 nm in CH_3CN[10]). However, the complex spectrum obviously implies the existence of two transitions (Figure 6), tentatively ascribed to the intraligand band overlapping with a metal-to-ligand charge transfer band. Excitation at 310 nm in CH_2Cl_2 at room temperature produces luminescence with a 365 nm emission maximum, which would correspond to an intraligand-based excited state involving an approximately planar π system instead of the twisted free ligand.[9,15]

In the course of the spectroelectrochemical reduction to $[PtCl_2(big)]^{\bullet-}$, the 318 nm band diminishes and slightly shifts to 322 nm. Simultaneously, a new band at 471 nm appears, which can be assigned to ligand-to-metal charge transfer into the unoccupied metal orbital ($d_{x^2-y^2}$) arising after the reduction of the big ligand. In comparison, the reversibly reducible free big exhibits only a weak broad absorption band system in the visible region.

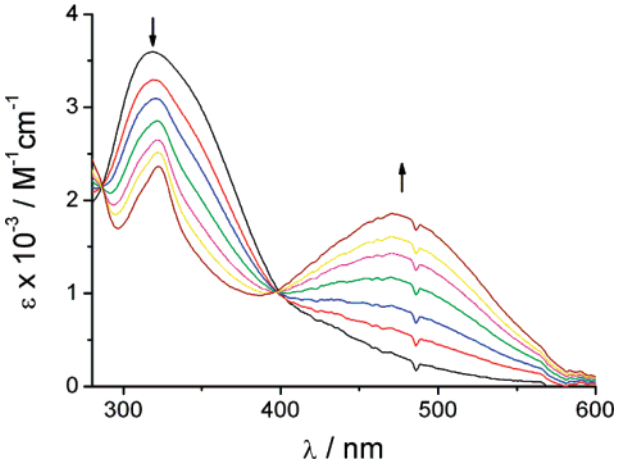

Figure 6. UV−vis spectroelectrochemical reduction of $[PtCl_2(big)]^{0\rightarrow-}$ in CH_2Cl_2/0.1 M Bu_4NPF_6.

The spectroelectrochemical behavior of $[PdCl_2(big)]$ is similar to that of the Pt analogue, involving a decrease of the band at 319 nm and growing absorption at 450 nm. However, the emerging band in the visible is weak, and an additional intense band is formed at 285 nm. Furthermore, the spectral isosbestic points are lost at the end of the electrolysis and reoxidation does not lead to the original spectrum of $[PdCl_2(big)]$. The coupled reaction thus indicated can be partially suppressed when the optically transparent thin-layer electrode (OTTLE) experiment is performed with an excess of Et_4NCl; in this case, a higher and better developed band of the primary reduction product $[PdCl_2(big)]^{\bullet-}$ at 448 nm can be observed. Hence, it can be concluded that the reduced palladium complex $[PdCl_2(big)]^{\bullet-}$ is unstable on the longer time scale ($\geq$1 min) of the OTTLE experiment, undergoing chloride dissocation and possibly subsequent dimerization or other irreversible change.

Concluding, we could show how the MCl_2 groups, M = Pd, Pt, can coordinate not only conventional oligo-imidazole ligands but also their one-electron reduced forms, the radical anions. There is a current interest in the electron-transfer activation of metal-based anticancer drugs.[25] The additional potential of big to bind *two* metal ions in various ways[10,15] represents a further challenge for studies in this area.

Acknowledgment. Support from the Land Baden-Württemberg, the DFG, the FCI, and from COST (D36 action, OC140 grant from the Ministry of Education of the Czech Republic) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for $PtCl_2(big)$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC070185B

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