Inorganica Chimica Acta, *183* (1991) 131-132

Inorganica
Chimica Acta
LETTER

Dependence of reduction site on nature of ligand in Pt(II) square planar complexes

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(Received April 11, 1991)

We have performed electrochemical and spectroelectrochemical studies in the UV–Vis–near-IR regions on the square planar Pt(II) complexes, $[Pt(bpy)(Ph)_2]$ (**I**), $[Pt(Me_2\text{-}bpy)(Ph)_2]$ (**II**) and $[Pt(bpym)(Ph)_2]$ (**III**) (bpy, 2,2′-bipyridine; Ph, phenyl; Me_2-bpy, 4,4′-dimethyl-2,2′-bipyridine; bpym, 2,2′-bipyrimidine), in dichloromethane solution, with tetra-n-butyl ammonium tetrafluoroborate ($TBABF_4$) supporting electrolyte. In these complexes, the first reduction is a chemically and electrochemically reversible one electron process, and is in the range expected for the reduction of a coordinated bipyridyl or bipyrimidyl attached to a divalent metal. A second reduction was observed at potentials around 600 mV more cathodic, consistent with this reduction also being ligand-based, but was chemically irreversible under our conditions in all compounds studied; thus we have no definite evidence regarding the site of this second reduction. The observed peak potentials for reduction are presented in Table 1.

The parent complexes all show two MLCT transitions in the regions between 310 and 460 nm, assignable as metal–ligand charge transfers [1] to the lowest and second lowest unoccupied ligand orbitals. These bands disappear when the complexes are reduced. The absorption spectra of the singly reduced complexes show the characteristic intraligand $\pi(6) \rightarrow \pi(7)$, $\pi(7) \rightarrow \pi(10)$ and $\pi(7) \rightarrow \pi(8,9)$ transitions [2] of coordinated reduced ligands [3]. The electronic spectra of the parent and reduced species are shown in Fig. 1 and the results for the latter collected in Table 2.

TABLE 1. Reduction potentials of Pt(II) complexes[a]

Compounds	$E_{red}^{(0/-)}$	$E_{red}^{(-/2-)}$
I	−1.646 (0.064)[b]	−2.257 (irr)[c]
II	−1.753 (0.065)	−2.348 (irr)
III	−1.516 (0.061)	−2.127 (irr)

[a] Data from cyclic voltammetry, potentials in V vs. ferrocene/ferrocenium$^+$ in $TBABF_4$–CH_2Cl_2 at 25 °C. [b] $E_{pa}-E_{pc}$ (V). [c] Denotes (chemically) irreversible redox processes with peak potentials given (scan rate 200 mV s^{-1}).

Comparing the first reduction of **I** with that [4] of the isoelectronic charged species $[Pt(bpy)(py)_2]^{2+}$ (**IV**), we would expect a shift to more cathodic potentials of around 350 mV, simply because of the difference in charge, all other things being equal. However, we note that the spectra of $\mathbf{I}^-$, $\mathbf{II}^-$ and $\mathbf{III}^-$ all clearly show the characteristic π–π^* and π^*–π^* bands of the singly reduced ligands, features absent in $\mathbf{IV}^-$ but present in $\mathbf{IV}^{2-}$ [4]; for these reasons we relate the first reduction of compounds **I–III** to the second reduction of **IV**.

We infer that the two classes of complex differ in the nature of the orbital to which an electron is added on reduction. The platinum aryls show ligand-based reductions, while the first reductions of the closely related pyridine and doubly charged bipyridyl complexes occur at the metal. We ascribe these differences to the difference between the ligand field

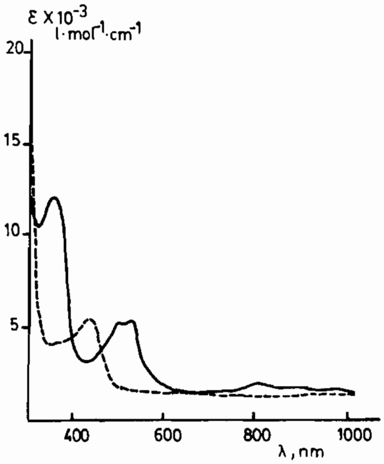

Fig. 1. Absorption spectra of $[Pt(bpy)(Ph)_2]^{0/-}$ in CH_2Cl_2 at 25 °C (V vs. ferrocene/ferrocenium$^+$): – · –, parent; ——, reduced species at −1.675 V.

TABLE 2. Main absorption bands of singly reduced complexes in $TBABF_4$–CH_2Cl_2 solution at 25 °C ($\tilde{U}/10^3$ cm^{-1})($10^{-3}\epsilon/M^{-1}$ cm^{-1})

Compounds	$\pi(6) \rightarrow \pi(7)$	$\pi(7) \rightarrow \pi(10)$	$\pi(7) \rightarrow \pi(8,9)$
I	367(27.3)(14.8)	520(19.2)(5.8)	965(10.4)(2.4)
II	355(28.2)(16.7)	509(19.6)(6.1)	913(11.0)(2.7)
III	369(27.1)(17.5)	495(20.2)(7.7)	821(12.2)(3.2)

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0020-1693/91/$3.50

strengths in **I**, **II** and **III** on the one hand, and **IV** and related complexes [4] on the other. In the former, the strong field of the aryl ligands raises metal d(σ^*) above the π^* orbital of the bipyridyl-type ligand; in the latter, the opposite ordering is found.

Our results strongly suggest that four-coordinate, mononuclear organo–Pt(I) species are unlikely to be important reaction intermediates; however, Pt(I) with less strong field ligands need not necessarily be excluded from consideration.

Acknowledgements

We acknowledge support from the University of North Texas Faculty Research Fund and from the Robert A. Welch Foundation. We also thank Dr G. Brent Young, of Imperial College, London, for gifts of samples.

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