

Unusual reduction products of platinum(II)azooximates

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Phenylazobenzaldoxime PhC(=NOH)NNPh(HL) reacts with K_2PtCl_4 affording the normal *trans* planar *bis* complex PtL_2 , **1**. Chemical or electrochemical $1e-1H$ reduction of **1** affords the paramagnetic complex $[\text{Pt(L)(HL)}]$, **2**, which displays reversible dimerization in solution. In the crystalline state, the complex **2** is fully dimeric. Reduction of **1** or **2** by ascorbic acid has afforded unusual species of composition PtL'_2 , **3**, where L' is the radical anion of the azoimine PhC(=NH)NNPh . The species **1**, **2** and **3** have been characterized structurally by X-ray crystallography and the electronic structure of the species have been explored both experimentally and theoretically (EHMO). The coordinated azo-oxime and azo-imine moieties are potent acceptors of electrons and the active orbital has large azo character.

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