

HYDROGEN GENERATION FROM LUMINESCENT SQUARE PLANAR PLATINUM(II) DERIVATIVES UTILIZING A SACRIFICIAL DONOR

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Abstract: Several square planar divalent platinum species have been proven to be quite interesting in regard to their ability to generate molecular hydrogen catalytically during photolysis. Previously, tolyl-terpyridine Pt(II) acetylide ($[(\text{mpt})\text{Pt}(\text{CCAr})]$) complexes using sacrificial electron donors were studied and reported by Tung and Wu in JACS in 2004. Several of the complexes were reported to produce hydrogen.¹ Castellano and Eisenberg also reported platinum complexes that generate hydrogen.²⁻⁴ The key question with regard to these reactions is to determine if colloidal platinum is present in the reaction. It was suggested that these platinum species degrade and colloidal platinum results.² This issue is crucial and must be understood. Our recent investigations of hydrogen generating platinum catalysts involve determining the fate of the complexes after photolysis in the presence of a sacrificial donor. The acetylide, L_2 , in figure 1 has been examined by ESI-MS to show degradation during photolysis yielding several platinum complexes. The solution after photolysis was also analyzed by UV-Vis and NMR. ESI-MS after photolysis revealed several platinum complexes including $[(\text{mpt})\text{PtCl}]$ which does not act as a catalyst to generate hydrogen, the starting material plus two hydrogen atoms, and the starting material plus four hydrogen atoms. Once the majority of the starting material had been converted to $[(\text{mpt})\text{PtCl}]$, hydrogen production stopped. It is believed that the acetylide is undergoing hydrogenation and then dissociates from the complex. Another complex studied as the catalyst was $[(\text{mpt})\text{PtOH}]$, L_3 , utilizing 1,4-dihydro-2,6-dimethyl-3,5-pyridine-dicarboxylate as the sacrificial donor. Hydrogen production was observed and to a much larger extent than seen with the acetylide complexes. Figure 2 shows the relative hydrogen production for the species in figure 1. The turnover number for $[(\text{mpt})\text{PtOH}]$ was 3.3 at 1690 minutes. The production of hydrogen appears to be linear with time. The $[(\text{mpt})\text{PtOH}]$ complex was especially interesting due to its relative simplicity and long lifetime of 700ns in degassed acetonitrile. The goal is to design a homogeneous system, free of colloidal platinum, that will catalytically generate hydrogen. This will require a photostable platinum species that is also effective as a catalyst for hydrogen generation.

Figure 1:

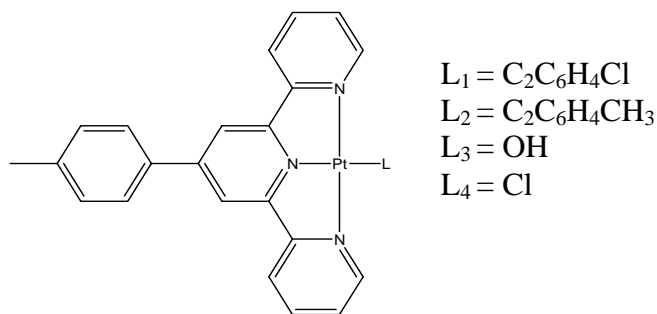
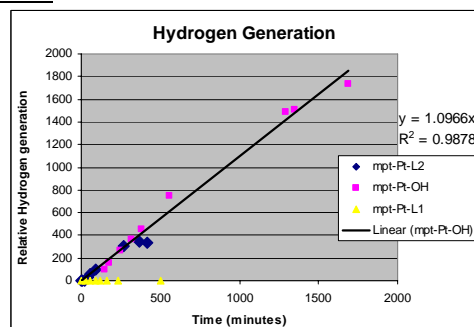


Figure 2:



References: (1) Tung & Wu, JACS, 2004. (2) Castellano & Eisenberg, JACS, 2008. (3) Eisenberg, J. Phys. Chem B, 2007. (4) Eisenberg, JACS, 2006.