PHOTOREDOX DECOMPOSITION OF [(R₃P)₃Au-SnCl₃] INDUCED BY METAL-TO-METAL CHARGE TRANSFER EXCITATION

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The complexes [(R₃P)₃Au-SnCl₃] with R = C₆H₅ and OCH₃ display long-wavelength absorptions in the UV which are assigned to metal-to-metal (Sn → Au) charge transfer (MMCT) transitions. MMCT excitation of the complexes in solution led to a redox decomposition with the formation of metallic gold.

PHOTOREDOXZERSETZUNG VON [(R₃P)₃Au-SnCl₃], INDUZIERT DURCH MMCT-ANREGUNG

Die Komplexe [(R₃P)₃ Au-SnCl₃] mit R = C₆H₅ bzw. OCH₃ zeigen langwellige Absorptionen im UV-Bereich, die den Metal-to-Metal (Sn → Au) Charge-Transfer-Übergängen (MMCT) zugeordnet werden. Die MMCT-Anregung dieser Komplexe in Lösung führte zu einer Redoxzersetzung unter Bildung von metallischem Gold.

1. INTRODUCTION

Photoredox reactions induced by inner-sphere metal-to-metal charge transfer (MMCT) excitation have attracted considerable attention in recent years [1–3]. MMCT transitions occur in bi- or polynuclear complexes which contain reducing and oxidizing metal centers. These redox centers may interact via bridging ligands or directly in compounds with polar metal-metal bonds. The majority of observations were restricted to transition metal complexes although a few mixed-valence main group metal complexes [4] such as $Sn_2Cl_{10}^{4-}$ [5] have been also reported to show MMCT absorptions in their electronic spectra. The present study was undertaken to search for photoactive MMCT transitions between a transition and a main group metal. Suitable candidates are complexes of the type [(R₃P)₃ Au(I)-Sn(II)Cl₃] [6] which are expected to display optical low-energy MMCT transitions from the reducing Sn(II) to the oxidizing Au(I) metal center. This expectation was based on analogous observations with [Ph₃PAu(I)-Co(−I)(CO)₄] [7]. The current investigation was facilitated by our experience with the electronic spectra and photochemical properties of $SnCl_3^-$ [8] in the free and coordinated state [9, 10]. In this context it is quite intriguing that complexes such as $[Ru(SnCl_3)_6]^{4-}$ [9] or

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$[Pt(SnCl_3)_5]^{3-}$ [10] do not undergo photoredox reactions but photosubstitutions and photofragmentations of the $SnCl_3^-$ ligand.

2. EXPERIMENTAL

The compound $[(Ph_3P)_3 Au-SnCl_3]$ was prepared according to a published procedure [11]. In analogy to this method the reaction of $[(CH_3O)_3 PAuCl]$ [12] with $SnCl_2$ and $(CH_3O)_3P$ in excess yielded $\{[(CH_3O)_3P]_3 AuSnCl_3\}$ as a white solid (Anal. Calcd. for $AuC_9H_{27}Cl_3O_9P_3Sn$: C, 13.61; H, 3.43; Cl, 13.39. Found: C, 13.31; H, 3.20; Cl, 13.41). All solvents were spectrograde. Absorption spectra were measured in solution at room temperature on a Shimadzu UV-2100 absorption spectrometer. The photolysis procedures were described elsewhere.

3. RESULTS

The absorption spectrum of $\{[(CH_3O)_3P]_3AuSnCl_3\}$ in acetonitrile (Fig. 1) displays bands at $\lambda_{max} = 292$ ($\varepsilon = 580 \, M^{-1} cm^{-1}$), 274 (1100), 237 (15600), 227 (18300), 216 (17900) and 204 nm (20800).

The spectrum of $[(CH_3O)_3 PAuCl]$ was measured for comparison. It shows absorptions at $\lambda_{max} = 232$ ($\varepsilon = 1400 \, M^{-1} cm^{-1}$), 224 (1400) and 202 nm (4400).

The spectrum of $[(Ph_3P)_3 AuSnCl_3]$ consists of bands at $\lambda_{max} = 275$ ($\varepsilon = 14300 \, M^{-1} cm^{-1}$), 267 (17700) and 237 nm (sh, 42000). The photolysis of $\{[(CH_3O)_3 P]_3 AuSnCl_3\}$ in acetonitrile led to the decomposition of the complex with a concomitant formation of metallic gold which was identified by its plasmon absorption at $\lambda_{max} = 550$ nm [13]. A reliable quantum yield could not be determined since the complex was thermally not very stable in solution but decomposed to $[(CH_3O)_3 PAuCl]$ and $SnCl_2$ as inversion of its formation.

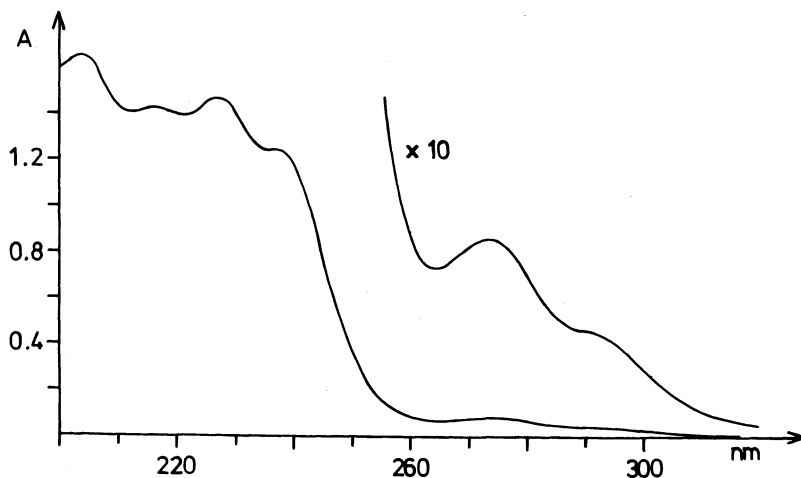**Fig. 1** Electronic absorption spectrum of 8.0×10^{-5} M $\{[(CH_3O)_3 P]_3 AuSnCl_3\}$ in acetonitrile at room temperature, 1 cm cell.

The irradiation of $[(Ph_3P)_3AuSnCl_3]$ in CH_3CN led also to the formation of gold. This photolysis was quite efficient with $\phi = 0.41$ at $\lambda_{irr} = 282$ nm.

4. DISCUSSION

While $Au[P(OCH_3)_3]_2^+$ [14] and $[(CH_3O)_3PAuCl]$ absorb only at wavelength shorter than 250 nm the complex $[(CH_3O)_3P]_3AuSnCl_3$ displays long-wavelength bands at $\lambda_{max} = 292$ and 274 nm. We assign these absorptions to $SnCl_3^-$ to Au(I) ligand-to-metal charge transfer (LMCT) transitions in analogy to other Au(I) complexes which contain strongly reducing ligands such as I^- [15, 16] and N_3^- [13]. This LMCT transition can be also described as a Sn(II) to Au(I) MMCT transition as it was observed for $[Ph_3PAu(I)-Co(-I)(CO)_4]$ [7]. In this case the longest-wavelength absorption was assigned to a $Co(-I)$ to Au(I) MMCT transition.

The absorption spectrum of $[(Ph_3P)_3AuSnCl_3]$ is dominated by the intraligand (IL) bands of triphenylphosphine which appear at $\lambda_{max} = 267$ and 274 nm [7]. The Sn(II) to Au(I) MMCT absorptions are apparently obscured by these IL bands but can be recognized by their extension to longer wavelength (shoulder at approximately 290 nm).

The photoreactivity of the complexes $[(L_3P)_3AuSnCl_3]$ can certainly be related to the presence of the low-energy Sn(II) to Au(I) MMCT absorptions. MMCT excitation generates Au(0) which finally appears as colloidal gold.

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