Journal of Organometallic Chemistry 577 (1999) 358–360

Preliminary Communication

Photooxidation of $Rh(PPh_3)_2(CS)Cl$ induced by metal-to-ligand charge transfer excitation[☆]

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Received 5 October 1998

Abstract

The longest-wavelength absorption of $Rh^I(PPh_3)_2(CS)Cl$ at $\lambda_{max} = 452$ nm is assigned to a metal-to-ligand charge transfer (MLCT) transition which terminates at the π^* orbital of the thiocarbonyl ligand. MLCT excitation of the complex in CH_2Cl_2 initiates a photooxidation which finally leads to $Rh^{III}(PPh_3)_2(CS)Cl_3$ as a stable photoproduct with $\phi = 0.003$ at $\lambda_{irr} = 436$ nm. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Photochemistry; Charge transfer; Rhodium; Thiocarbonyl

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1. Introduction

Metal carbonyls comprise the largest and most important class of light-sensitive organometallic compounds [1–3]. Generally, carbonyl complexes undergo photochemical ligand substitutions which are induced by ligand-field (LF) excitation with long-wavelength irradiation. On the other hand, metal-to-ligand charge transfer (MLCT) transitions terminating at the π^* orbitals of CO are formally associated with the oxidation of the metal and reduction of the ligand. This redox process which is related to the water gas shift reaction [4] could be exploited for various applications. Unfortunately, ML (π^* CO) CT transitions occur only at very high energies and are thus not easily accessible. Accordingly, very little is known on the reactivity of such MLCT states [5].

Thiocarbonyl complexes [6] share some basic features with carbonyl complexes, but may be quite different with regard to their spectral and photochemical properties. Since π-bonding in CS is much weaker than in CO the π^* orbitals of CS are located at much lower energies [7,8]. It follows that MLCT transitions to the CS ligand occur also at comparably low energies [9–11]. Indeed, the longest-wavelength absorption of $W(CO)_5CS$ is apparently of the MLCT ($W \rightarrow \pi^*$ CS) type [9,10]. Unfortunately, this MLCT state seems to be quite unreactive. $W(CO)_5CS$ undergoes only a photosubstitution with low efficiency. This photolysis may originate from a LF state which is situated above the MLCT state.

However, it is now well known that a variety of metal complexes are characterized by reactive MLCT states [12]. Thiocarbonyl complexes are not expected to be an exception. We explored this possibility and selected the complex $Rh(PPh_3)_2(CS)Cl$ [13,14] for the present study. This choice was guided by the following considerations. This compound is easily prepared and quite stable. Generally, Rh(I) complexes with π accepting ligands show longest-wavelength MLCT absorptions in their electronic spectra [15]. Moreover, MLCT

[☆] Dedicated to Professor Helmut Werner, on the occasion of his 65th birthday.

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PII: S0022-328X(98)01079-1

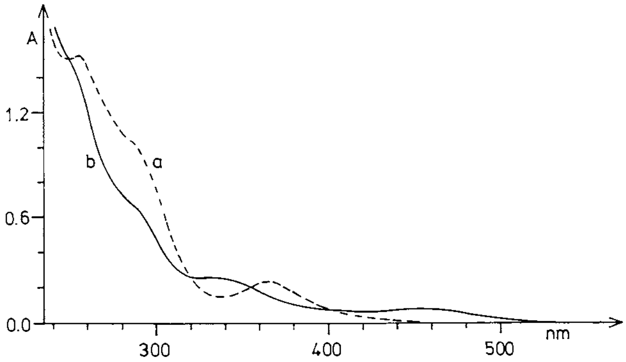

Fig. 1. Electronic absorption spectra of 8.06×10^{-5} M $Rh^{I}(PPh_3)_2(CO)Cl$ (a, ---) and 5.65×10^{-5} M $Rh^{I}(PPh_3)_2(CS)Cl$ (b, —) in CH_2Cl_2 under argon at r.t, 1 cm cell.

excitation may yield Rh(III) as a stable photooxidation product. Finally, it should be useful to compare the behavior of $Rh(PPh_3)_2(CS)Cl$ with $Rh(PPh_3)_2(CO)Cl$. The spectral [16,17] and photochemical [18–20] properties of the latter complex are well known.

2. Results

The electronic spectrum of $Rh(PPh_3)_2(CS)Cl$ in CH_2Cl_2 (Fig. 1) shows absorptions at $\lambda_{max} = 452$ ($\varepsilon = 1300$ M^{-1} cm^{-1}), 338 (4500), 290 (11300) and 253 nm (sh, 25600). The spectrum is only slightly dependent on the solvent. In CH_3CN some band maxima are shifted by a few nanometers. The absorptions of $Rh(PPh_3)_2(CO)Cl$ [16,17] in CH_2Cl_2 (Fig. 1) appear at $\lambda_{max} = 364$ (2800), 290 (12200) and 256 nm (18600). Both complexes are not emissive at room temperature (r.t.) or 77 K.

Solutions of $Rh(PPh_3)_2(CS)Cl$ in CH_2Cl_2 are light sensitive. The photolysis is accompanied by spectral changes (Fig. 2) which can be duplicated by the thermal reaction of $Rh(PPh_3)_2(CS)Cl$ with Cl_2 [13]. The product of this oxidative addition is $Rh(PPh_3)_2(CS)Cl_3$. The photolysis is monitored by measuring the decrease of the optical density at 253 nm taking into account the residual absorption of $Rh(PPh_3)_2(CS)Cl_3$ at this wavelength ($\varepsilon = 8300$). $Rh(PPh_3)_2(CS)Cl$ disappears with $\phi = 0.003$ at $\lambda_{irr} = 436$ nm.

In CH_3CN solutions $Rh(PPh_3)_2(CS)Cl$ is hardly light sensitive if oxygen is excluded. However, in the presence of O_2 a photolysis takes place. The concomitant spectral changes are similar but not identical to those which are observed during the photolysis in CH_2Cl_2.

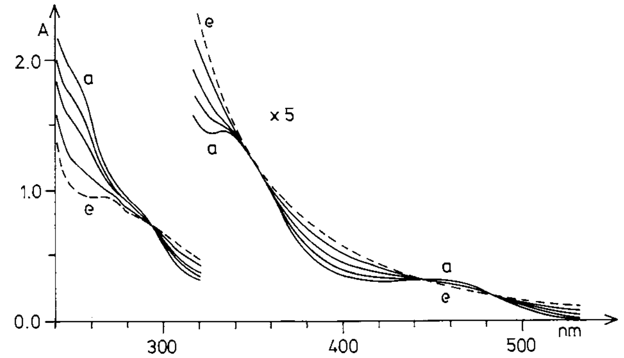

Fig. 2. Spectral changes during the photolysis of 7.11×10^{-5} M $Rh^{I}(PPh_3)_2(CS)Cl$ in CH_2Cl_2 under argon at r.t. after 0 (a), 15 (b), 30 (c), 60 (d) and 120 (e) min irradiation time with $\lambda_{irr} = 366$ nm (Xe/Hg 977 B-1 lamp), 1 cm cell.

3. Discussion

In analogy to various other Rh(I) complexes [15–17] with π-accepting ligands the longest-wavelength absorption of $Rh(PPh_3)_2(CO)Cl$ at $\lambda_{max} = 364$ nm has been assigned to a MLCT transition which terminates at the phosphine ligand [16,17]. The complex $Rh(PPh_3)_2(CS)Cl$ displays its lowest-energy band at distinctly longer wavelength ($\lambda_{max} = 452$ nm) (Fig. 1). This absorption is then logically assigned to the MLCT transition from Rh(I) to the π* orbital of the thiocarbonyl ligand. This assignment is supported by related observations on $M(CO)_5CS$ (M = Cr [11] and W [9,10]) and $Re^{I}(CO)_4(S_2COEt)$ [21].

$Rh(PPh_3)_2(CO)Cl$ is well known to undergo a photoejection of CO [18–20]. It seems likely that this photodecarbonylation originates from a LF state in agreement with the general behavior of metal carbonyls [1–3]. Although LF bands are not apparent in the spectrum of $Rh(PPh_3)_2(CO)Cl$ they may be present at relatively long wavelength but obscured by the more intense MLCT absorption at 364 nm. Reactive LF states can thus be populated from the MLCT state which is initially reached by light absorption.

The ML (π* CS) CT state of $Rh(PPh_3)_2(CS)Cl$ is located at rather low energies and apparently well separated from higher LF states. The photoreactivity of the complex is obviously initiated by MLCT excitation. In CH_2Cl_2 a photoredox reaction takes place. It can be described by the following equation:

$$Rh^{I}(PPh_3)_2(CS)Cl + 2CH_2Cl_2 \rightarrow Rh^{III}(PPh_3)_2(CS)Cl_3 + 2 \cdot CHCl_2$$

Product formation may proceed in two steps. A primary electron transfer from the MLCT excited complex to solvent leads to the generation of Rh(II) which is subsequently oxidized by a second CH_2Cl_2 molecule in a thermal process. One or two-electron photooxidations of metal complexes by the solvent, in particular chlorinated alkanes, are frequently induced by MLCT excitation [12,22]. As an alternative, in non-oxidizing solvents such as CH_3CN molecular oxygen may serve as an oxidant. In this case the photoproduct of

$Rh(PPh_3)_2(CS)Cl$ was not identified but the spectral similarity with $Rh^{III}(PPh_3)_2(CS)Cl_3$ suggests that a related Rh(III) complex such as $[Rh(PPh_3)_2(CS)(CH_3CN)_2Cl]^{2+}$ is generated.

In conclusion, it is shown that the lowest-energy ML (π^* CS) CT state of $Rh(PPh_3)_2(CS)Cl$ initiates a photoredox reaction which leads to the formation of $Rh^{III}(PPh_3)_2(CS)Cl_3$ and oxidized solvent (CH_2Cl_2). It is also feasible that other suitable substrates react with the MLCT excited complex by intercepting the reduced CS ligand.

Acknowledgements

Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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