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Communication

Photoreactivity of the triphenylphosphine adduct of methyl(trioxo)rhenium(VII) induced by ligand-to-metal charge transfer excitation

Horst Kunkely, Arnd Vogler *

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

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Abstract

Triphenylphosphine forms an adduct with $MeReO_3$. The yellow colour of this compound is attributed to a ($PPh_3 \rightarrow Re^{VII}$) ligand-to-metal charge transfer (LMCT) absorption at $\lambda_{max} = 380$ nm. LMCT excitation ($\lambda_{irr} = 405$ nm) leads to the reduction of Re(VII) to Re(V). This reaction has been previously observed as a thermal process (Herrmann et al., Organometallics 13 (1994) 4531). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Photochemistry; Charge transfer; Rhenium; Phosphines

1. Introduction

Organic phosphines (or phosphanes) PR_3 play an important role as ligands in coordination chemistry in general and organometallic chemistry in particular. Owing to their π-acceptor properties they are able to stabilise transition metals in low oxidation states. With regard to electronic spectroscopy and photochemistry phosphines are mainly spectator ligands although their direct involvement in intraligand (IL) [1] and metal-to-ligand charge transfer (MLCT) [2,3] excited states has been recently observed in a few cases. In this context it is quite surprising that despite their well-known reducing ability very little is known on phosphines as donor ligands for CT transitions. Jensen and Jørgensen estimated the optical electronegativity of PEt_3 (~ 2.6) on the basis of ligand-to-metal charge transfer (LMCT) assignments of absorption bands in the electronic spectra of $Co(PEt_3)_2X_2$ with X = Cl and Br [4]. However, these complexes may not be well suited for an unambiguous detection of LMCT absorptions since Co(II) is hardly oxidising. It follows that phosphine complexes of oxidising metals should be much better candidates to identify LMCT transitions and to explore their photoreactivity. In order to avoid any interference by ligand field (LF) transitions oxidising d^0 complexes would be most suitable to investigate CT spectra of complexes with phosphines as donor ligands. As an appropriate example we selected the complex $MeRe^{VII}O_3 \cdot PPh_3$ for the present study. This choice was based on the follow-

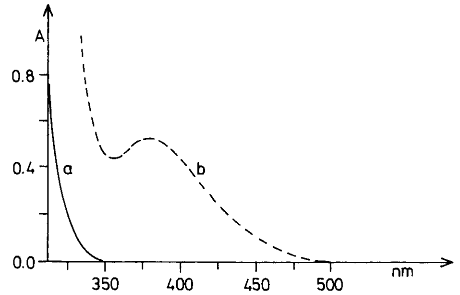

Fig. 1. Electronic absorption spectra of 1.25×10^{-2} M $MeReO_3$ and 1.25×10^{-2} M PPh_3 in CH_2Cl_2 as (a) separate solutions (—) and (b) as a mixture (- - -) under argon at 5°C, 1 cm tandem cell.

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* Corresponding author. Tel.: + 49-941-9434485; fax: + 49-941-9434488.

E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

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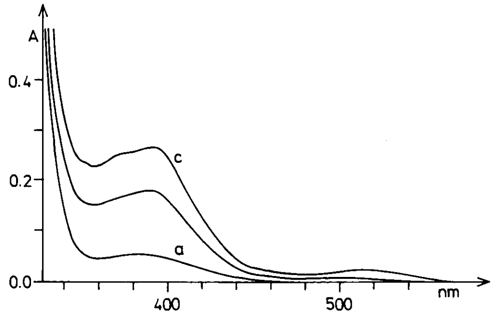

Fig. 2. Spectral changes during the thermal reaction of 5.3×10^{-4} M $MeReO_3(PPh_3)$ in CH_2Cl_2 under argon at r.t. after (a) 0, (b) 10 and (c) 40 min.

ing considerations. $MeReO_3$ is a pseudooctahedral d^0 complex that easily expands its coordination sphere by accepting further ligands [5,6]. The electronic spectra and the photochemistry of $MeReO_3$ [7–9] and several adducts $MeReO_3{\cdot}L$ [9–12] have been examined in some detail. Although $MeReO_3{\cdot}PPh_3$ is apparently not a stable compound observations on its thermal decomposition [13] were expected to facilitate the current investigation.

2. Results

When colourless solutions of $MeReO_3$ and PPh_3 in CH_2Cl_2, ether or *n*-hexane are mixed a yellow colour develops immediately. This colour is caused by an absorption at $\lambda_{max} = 380$ nm (Fig. 1). At 10^{-2} M equimolar concentrations of both components the apparent extinction coefficient at 380 nm is $\varepsilon = 85$ M^{-1} cm^{-1}. Since an increase of the PPh_3 concentration does not lead to an increase of the extinction it is assumed that the 1:1 adduct $MeReO_3{\cdot}PPh_3$ is responsible for the 380 nm absorption. If the temperature is lowered from room temperature (r.t.) to 0°C the adduct is stable for ~ 30 min. At r.t. the adduct undergoes a thermal reaction at much shorter periods. This reaction is accompanied by a colour change from yellow to red and brown [13]. The concomitant spectral variations are shown in Fig. 2. The product of this reaction is $MeRe^{V}(PPh_3)_2O_2{\cdot}MeRe^{VII}O_3$ which had been characterised previously [13]. This reaction does not only proceed thermally but also as a rather efficient photoreaction. The photolysis of the adduct $MeReO_3{\cdot}PPh_3$ in ether at 0°C with $\lambda_{irr} = 405$ nm generates the same spectral changes as those of Fig. 2. At later stages of the photolysis the pattern of the spectral variations changed indicating secondary processes. Nevertheless, a rough estimate yielded an extinction coefficient of $\varepsilon = 200$ at 510 nm for the primary photoproduct. The quantum yield of product formation was $\phi = 0.09$ at $\lambda_{irr} = 405$ nm.

3. Discussion

The yellow colour which instantly develops when solutions of $MeReO_3$ and PPh_3 are mixed is attributed to the complex $MeReO_3(PPh_3)$. Such a facile adduct formation has been observed with a variety of other ligands [5,6]. The new absorption maximum at 380 nm is then logically assigned to a LMCT transition from the reducing phosphine ligand to the oxidising d^0 metal centre. This assignment is supported by additional evidence. When PPh_3 is replaced by $P(p\text{-Cl–phenyl})_3$ the LMCT band is shifted to shorter wavelength and appears only as a shoulder near ~ 315 nm. The substitution of the phenyl rings by chlorine certainly reduces the donor strength of the phosphine and increases thus the energy of a LMCT transition. The photoreactivity of $MeReO_3(PPh_3)$ can now be attributed to a $PPh_3 \rightarrow Re^{VII}$ LMCT excited state. We suggest that the primary photochemical step consists of the reduction of $MeReO_3$ by the PPh_3 ligand:

$$MeRe^{VII}O_3(PPh_3) \xrightarrow[\lambda_{irr} = 405\text{ nm}]{\text{LMCT}} MeRe^{V}O_2 + O{=}PPh_3$$

Although the optical LMCT transition is a one-electron transfer from PPh_3 to Re(VII) the LMCT excited state should easily relax to redox products which are the result of an oxygen atom transfer from $MeReO_3$ to the phosphine ligand. Owing to the reducing properties of PPh_3 this reaction occurs also as a thermal process [13]. The primary product $MeRe^{V}O_2$ which is generated thermally or photochemically is apparently coordinatively unsaturated, but can be stabilised in the presence of an excess of $MeReO_3$ and PPh_3 [13]:

$$MeRe^{V}O_2 + 2PPh_3 + MeRe^{VII}O_3$$
$$\rightarrow MeRe^{V}(PPh_3)_2O_2{\cdot}MeRe^{VII}O_3$$

The binuclear Re^{V}/Re^{VII} mixed-valence compound is formed as final product.

In summary, the complex $MeReO_3(PPh_3)$ represents a first example which clearly demonstrates the donor ability of phosphines for optical CT. Moreover, the photoreactivity of this complex reflects the charge distribution in the $PPh_3 \rightarrow Re^{VII}$ LMCT excited state.

Acknowledgements

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