Photoreactivity of Coordinated Phenylhydrazine.  
Intraligand Excitation of ReCl(CO)3(PhNH-NH2)2
Horst Kunkely, Arnd Vogler*
Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany
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The complex of ReCl(CO)3(PhNH-NH2)2 shows an absorption band at \( \lambda_{\text{max}} = 272 \text{ nm} \) which is assigned to an IL (intraligand) transition of the coordinated phenylhydrazine. Upon IL excitation the complex undergoes a decomposition with \( \phi = 0.03 \) at \( \lambda_{\text{end}} = 280 \text{ nm} \).

1. Introduction

Hydrazine and its derivatives play an important role as ligands in coordination chemistry [1]. Hydrazine complexes may occur as intermediates in nitrogen fixation and related processes [2]. Although a variety of hydrazine complexes are known the electronic spectra and photoreactivity of such compounds have not yet been studied. Owing to its peculiar electronic structure and redox behavior hydrazine may participate in diverse electronic transitions. In accord with its ability to disproportionate (3 N\(_2\)H\(_4\) \( \rightarrow \) 4 NH\(_3\) + N\(_2\); \( \Delta H = -336.5 \) kJ) [3] it is reducing and oxidizing [4]. It follows that low-energy LMCT (ligand-to-metal charge transfer) and MLCT (metal-to-ligand charge transfer) transitions are feasible. Moreover, IL (intraligand) transitions of the coordinated hydrazine may also occur. Finally, regular LF (ligand field) transitions are, of course, affected by hydrazine ligands, too.

While complexes with N\(_2\)H\(_4\) as ligand are frequently rather unstable coordination compounds with substituted hydrazines such as PhNH-NH\(_2\) do not decompose easily. In addition, owing to the presence of the phenyl group IL absorptions of PhNH-NH\(_2\) should appear at relatively long wavelengths which facilitates the study of its spectroscopy and photochemistry. As a suitable object for the present work we decided to prepare and to investigate the complex ReCl(CO)\(_3\)(PhNH-NH\(_2\))\(_2\). Its preparation was not anticipated to be difficult. Other hydrazine complexes of Re(I) such as Re(C\(_3\)H\(_5\))(CO)\(_3\)N\(_2\)H\(_4\) [5] or Re(C\(_5\)H\(_5\))(CO)\(_5\)N\(_2\)H\(_4\) [6] have been already described.

2. Experimental

2.1. Materials

The compounds phenylhydrazine and Re(CO)\(_5\)Cl were purchased from Merck and Aldrich, respectively, and used as received. The solvents used were spectrograde.

2.2. Synthesis ReCl(CO)\(_3\)(PhNH-NH\(_2\))\(_2\)

A suspension of 0.362 g (0.001 mol) Re(CO)\(_5\)Cl in 5 ml of argon-saturated toluene was mixed with 0.2 ml (0.002 mol) of freshly distilled phenylhydrazine and heated under reflux for 5 min. The solution immediately turned pale-yellow and upon cooling to 0 °C crystals rapidly precipitated. The analytically pure product was collected by filtration, washed with cold toluene and ether, and dried under vacuum; yield 0.42 g (80.5%).

Analysis for C\(_{37}\)H\(_{28}\)ClN\(_{12}\)Re
Calcld C 34.52 H 3.09 N 10.73%.
Found C 34.53 H 3.15 N 10.69%.

2.3. Photolyses

The light source was an Osram HBO 100 W/2. Monochromatic light was obtained by means of Schott PIL/IL interference filters 280 and 333 nm. The photolyses were carried out in solutions of CH\(_2\)CN in 1 cm spectrophotometer cells at room temperature. Solutions were air-saturated since deaeration did not affect the results. Progress of the photolyses was monitored by UV-visible spectrophotometry. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined.
by a Polytec pyroelectric radiometer which was calibrated and equipped with a RkP-345 detector.

2.4. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or a Shimadzu UV-2100 absorption spectrometer.

3. Results

The complex ReCl(CO)$_3$(PhNH-NH$_2$)$_2$ is prepared by the reaction of Re(CO)$_5$Cl with PhNH-NH$_2$ in toluene. The absorption spectrum of ReCl(CO)$_3$(PhNH-NH$_2$)$_2$ (Fig. 1) displays bands at $\lambda_{\text{max}} = 332$ ($\varepsilon = 330$ $\text{mol}^{-1} \text{cm}^{-1}$), 272 (6700) and 235 nm (25500). With the exception of the weak long-wavelength band this spectrum is rather similar to that of the protonated ligand PhNH-NH$_3^+$ ($\lambda_{\text{max}} = 274$ and 228 nm). In comparison to the free ligand PhNH-NH$_2$ ($\lambda_{\text{max}} = 292$ and 244 nm) the absorption maxima of the complex are shifted to distinctly shorter wavelength. The complex is not luminescent at r. t. or 77 K.

ReCl(CO)$_3$(PhNH-NH$_2$)$_2$ is light sensitive. Upon irradiation in CH$_3$CN it undergoes photodecomposition. The accompanying spectral changes (Fig. 1) resemble those which are observed during the photolysis of the free PhNH-NH$_2$. In both cases an additional weak band appears at approximately 420 nm. This absorption is diagnostic for the formation of phenyldiimine Ph=N=NH ($\lambda_{\text{max}} = 418$ nm, $\varepsilon = 74$) [7]. The quantum yield for the photo-decomposition of the complex is wavelength dependent. The photolysis is less efficient at longer wavelength ($\phi = 0.03$ at $\lambda_{\text{irr}} = 280$ nm and $\phi = 0.002$ at $\lambda_{\text{irr}} = 331$ nm).

4. Discussion

The compound ReCl(CO)$_3$(PhNH-NH$_2$)$_2$ was prepared according to a general procedure which leads to the substitution of two carbonyl ligands of Re(CO)$_5$Cl by two hydrazines under mild conditions [8]. The resulting complex is pseudooctahedral and contains Re(I) as central metal with a d$^6$ electron configuration.

The longest-wavelength band of ReCl(CO)$_3$(PhNH-NH$_2$)$_2$ at $\lambda_{\text{max}} = 332$ nm which is relatively weak ($\varepsilon = 330$) is assigned to the lowest-energy LF transition. Other Re(I) carbonyl complexes such as Re(CO)$_5$Cl ($\lambda_{\text{max}} = 341$ nm) and [Re(CO)$_5$(NH$_2$CH$_3$)]Cl ($\lambda_{\text{max}} = 318$ nm) display LF bands at similar energies [9]. The intense bands of ReCl(CO)$_3$(PhNH-NH$_2$)$_2$ at $\lambda_{\text{max}} = 272$ nm and 235 nm closely match those of protonated phenylhydrazine. It is concluded that these bands of the complex are of the IL type. The blue shift which occurs upon coordination or protonation is apparently caused by the stabilization of the lone pair at the terminal nitrogen atom. It has been shown that the amine function which is not substituted by the phenyl group binds a proton [10] or a metal [11]. Further absorptions are not discernible in the spectrum of ReCl(CO)$_3$(PhNH-NH$_2$)$_2$. In analogy to other Re(I) carbonyl compounds [12] the complex ReCl(CO)$_3$(PhNH-NH$_2$)$_2$ is not expected to show LMCT bands in the accessible wavelength region. However, Re(I) carbonyl complexes which contain acceptor ligands such as 2,2’-bipyridyl are characterized by low-energy MLCT absorptions [12,13]. In principle such MLCT absorptions may also appear in the spectrum of ReCl(CO)$_3$(PhNH-NH$_2$)$_2$ since hydrazines are not only reducing but also oxidizing. MLCT transitions would terminate at the $\sigma^*$ (N-N) orbital which should be located at relatively low energies in accord with the oxidizing property of hydrazines [4]. A CT transition of this type has been recently identified in the absorption spectrum of Re$_2$Br$_2$(CO)$_6$(Se$_2$Ph$_2$) which provides a low-energy $\sigma^*$ (Se-Se) orbital by the acceptor ligand Se$_2$Ph$_2$ [14]. However, other absorptions in addition to LF and IL bands do not appear in the elec-
tronic spectrum of ReCl(CO)₃(PhNH-NH₂)₂. Such MLCT bands could be obscured by the IL bands. As an alternative, they may occur below 200 nm because the population of a σ* (N-N) orbital of phenylhydrazine should be associated with a large Franck-Condon factor.

Although the photochemistry of phenylhydrazine has not yet been studied in any detail organic hydrazines are well known to undergo a light-induced disproportionation: 2 RNH-R'NH → RN=NR' + RNH₂ + R'NH₂ [15]. In the case of phenylhydrazine this dismutation yields PhN=NH which is identified by its absorption at λ_max = 418 nm [7]. Phenylidimine is not stable but decomposes to benzene and nitrogen [7]. The overall reaction proceeds then according to the equation

\[ 2 \text{PhNH-NH}_2 \rightarrow \text{C}_6\text{H}_6 + \text{N}_2 + \text{Ph-NH}_2 + \text{NH}_3 \]

Since the spectral changes during the photolysis of free phenylhydrazine and ReCl(CO)₃(PhNH-NH₂)₂ are rather similar it is suggested that the IL excitation of the coordinated phenylhydrazine leads to the same photodecomposition. In this context it is quite interesting that the thermal degradation of phenylhydrazine to benzene, nitrogen, aniline and ammonia can be catalyzed by [Ru(NH₃)₅Cl]Cl [16].

In conclusion, we have shown that the photoreactivity of phenylhydrazine is preserved upon coordination to Re(I). However, in suitable cases such as [Pb(DMC)]²⁺ with DMC = trans-2,4-dinitrostilbene-4'-monoaza-18-crown-6 the photochemistry of the coordinated ligand is quite different from that in the free state [17]. Since the coordination can modify the electronic and geometric structure of a ligand its phototransformation could yield quite unexpected, but possibly useful products which might not be obtained from the free ligand. In this context it is rather surprising that the reactivity of IL excited states has not yet attracted much attention in general although such photoreactions have a great potential for applications in organic synthesis.

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