

Excited state properties of $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ with NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and quinone = 1,4-naphthoquinone

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Abstract

The carbene complex $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ with NHC = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene and quinone = 1,4-naphthoquinone shows two long-wavelength absorptions at 312 and 399 nm which are assigned to (NHC→quinone) LLCT and ($\text{Pd}^0 \rightarrow \text{quinone}$) MLCT transitions. The MLCT state is not reactive, but emissive ($\lambda_{\text{max}} = 564 \text{ nm}$ at 77 K). At r.t., the complex undergoes a photoredox decomposition which is initiated by the LLCT state.

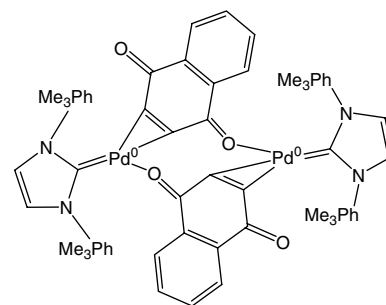
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1. Introduction

N-heterocyclic carbenes (NHCs) have attracted much attention in recent years [1–4]. These compounds exist as stable species and function as ligands in coordination chemistry. A variety of such complexes has been prepared, characterized and applied in organometallic catalysis. Surprisingly, very little is known about the photochemistry and photophysics of transition metal complexes with NHC ligands [5]. Since the light-sensitivity of these compounds may interfere with their role in stoichiometric or catalytic reactions a deeper insight in their excited state behavior is of considerable importance. Of course, this subject is also rather interesting in its own right. Our present study is an extension of a previous investigation of $\text{Ni}^0(\text{NHC})(\text{CO})_2$ and $\text{Ti}^{\text{IV}}(\text{NHC})_2\text{Cl}_4$ [5]. The new observations show that additional ligands which are introduced in NHC complexes may modify or even completely change the excited state properties of such complexes. While this is not unexpected such studies are necessary to understand

the reactivity of NHC complexes in general. Our present investigation of $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ [6] with NHC = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene and quinone = 1,4-naphthoquinone is facilitated by the reasonable thermal stability of this compound under ambient conditions.



2. Experimental

1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene(1,4-naphthoquinone) palladium(0) dimer (ABCR GmbH&Co)

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and 1,4-dihydroxynaphthalene (Acros Organics) were commercially available and used without further purification. All solvents used for spectroscopic measurements were of spectrograde quality (“Uvasol”) from Merck and saturated with argon.

The light source used for irradiation was an Osram HBO 200 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using Schott PIL/IL interference filters or a Schoeffel GM/1 high-intensity monochromator (band width 18 nm) with additional Schott cutoff filters to avoid short-wavelength and second order irradiation. In all cases the light beam was focused on a stirrable photolysis cell by a quartz lens. The photolyses were carried out in acetonitrile under argon in 1 cm spectrophotometer cells at room temperature under argon. Progress of the photolyses was monitored by UV–Vis 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 by ferrioxalate actinometry and equipped with an RkP-345 detector.

Absorption spectra were measured with a Varian Cary 50 or a Uvikon 860 spectrophotometer. Emission and excitation spectra were recorded on a Hitachi 850 fluorescence spectrometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

3. Results

The electronic spectrum of $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ in CH_3CN (Fig. 1) shows absorptions at $\lambda_{\text{max}} = 399$ ($\epsilon = 10800 \text{ M}^{-1} \text{ cm}^{-1}$), 312 (sh, 18500), 281 (sh, 32300), 245 (sh, 89600) and 206 (sh, 156500) nm. At 77 K in an ethanol glass the complex displays a weak, but distinct

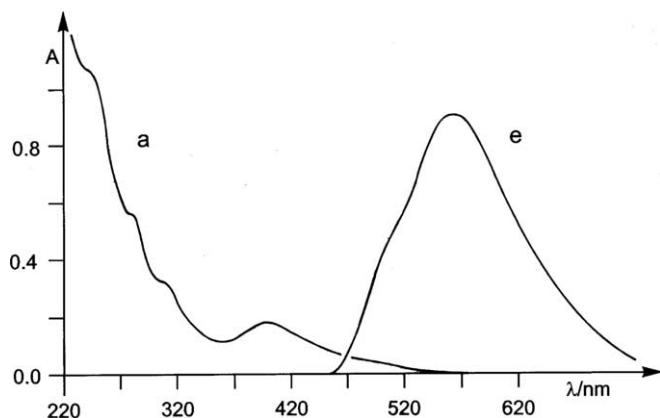


Fig. 1. Electronic absorption (a) and emission (e) spectrum of $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ under argon. Absorption: $1.57 \times 10^{-5} \text{ M}$ in CH_3CN at r.t. 1-cm cell. Emission: $2.25 \times 10^{-5} \text{ M}$ in EtOH at 77 K, $\lambda_{\text{exc}} = 380 \text{ nm}$, intensity in arbitrary units.

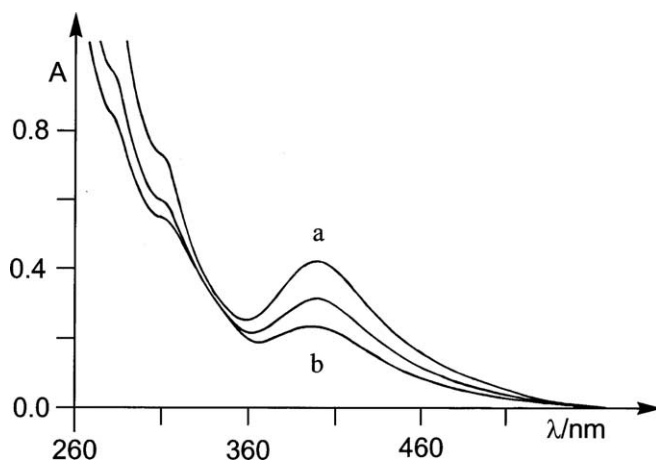


Fig. 2. Spectral changes during the photolysis of $3.93 \times 10^{-5} [\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ in CH_3CN under argon at room temperature after 0 (a), 20 and 80 s (b) irradiation times with $\lambda_{\text{irr}} = 405 \text{ nm}$ (Hanovia Xe/Hg 977 B-1 lamp), 1-cm cell.

yellow photoluminescence (Fig. 1) at $\lambda_{\text{max}} = 564 \text{ nm}$. The excitation spectrum roughly matches the absorption spectrum. At r.t. $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ is not emissive, but light sensitive. The photolysis in wet CH_3CN leads to a bleaching (Fig. 2) and at later stages to the appearance of palladium black. The colloidal metal causes an apparent absorption by light scattering which extends over the entire spectrum and increases towards shorter wavelength [7]. Naphthohydroquinone (or 1,4-dihydroxynaphthalene) was formed as a further photoproduct. It was identified by its characteristic fluorescence ($\lambda_{\text{max}} = 405 \text{ nm}$) which increased its intensity with the duration of the irradiation. The progress of the photolysis was monitored by measuring the decrease of the optical density at 399 nm taking into account the residual absorption of the photolysis products. The complex $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ disappeared with $\phi = 0.12$ at $\lambda_{\text{irr}} = 313 \text{ nm}$ and $\phi = 0.02$ at $\lambda_{\text{max}} = 436 \text{ nm}$.

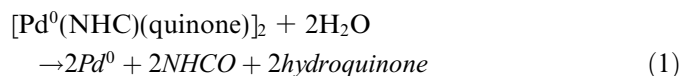
4. Discussion

The dimeric compound $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ consists of two monomeric $\text{Pd}(0)$ complex fragments which contain a carbene ligand and two quinones [6]. They provide the bridges for the dimeric structure. To a first approximation, the electronic features can be explained by the properties of the mononuclear components. $\text{Pd}(0)$ has a closed shell (d^{10}) and LF states are thus not available. Owing to this reducing character, $\text{Pd}(0)$ can function as CT donor. Carbenes of the NHC type are strong σ donors and accordingly also CT donors of considerable strength [5]. Simultaneously, they are weak π and CT acceptors [5]. Quinones are strong oxidants and powerful CT acceptors [8].

From these considerations, it follows that $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ should be characterized by two low-energy electronic transitions: $\text{Pd}(0)$ to quinone MLCT (metal-to-ligand charge transfer) and NHC to quinone LLCT (ligand-to-ligand charge transfer). In agreement with the

spectral and photochemical properties of the complex, we suggest that the longest-wavelength absorption at $\lambda_{\max} = 399$ nm (Fig. 1) is of the MLCT type while the next band at 312 nm (sh) belongs to the LLCT transition. Both absorptions are relatively intense and the corresponding transitions are thus spin-allowed. At 500 nm (Fig. 1) a weak inflection can be recognized which probably belongs to a spin-forbidden (singlet–triplet) MLCT transition. Generally, MLCT states are frequently luminescent [9] and only occasionally reactive [10,11]. We assume that the emission of $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ at 77 K originates from the lowest-energy MLCT triplet. In agreement with this suggestion, there is some overlap of the emission with the long-wavelength tail of the absorption which was assigned to the spin-forbidden MLCT transition.

At r.t. the phosphorescence of $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ is absent while the compound is photoreactive. The photochemical observations are consistent with the following simple equation:



The quinone undergoes a two-electron reduction and protonation to hydroquinone. Since Pd(0) does not donate these electrons they should be provided by NHC. A variety of oxidation products are conceivable, but within the scope of the present study we did not pursue any further analysis. As a very simple possibility the carbene delivers two electrons to the quinone and undergoes an oxidation and subsequent addition of oxide from water. As a result, a cyc-

lic ketone NHCO might be generated but further fragmentations could take place. Irrespective of this detail the photolysis is initiated by CT from NHC to the quinone. The photoreactivity can thus be attributed to the lowest-energy LLCT state. In agreement with this conclusion the photochemical quantum yield is higher upon irradiation of the LLCT band ($\phi = 0.12$ at $\lambda_{\text{irr}} = 313$ nm) compared to that for the MLCT excitation ($\phi = 0.02$ at $\lambda_{\text{irr}} = 436$ nm). The residual photosensitivity which is observed on MLCT excitation can be explained, at least partially, by a thermally activated population of the reactive LLCT state. As a further consequence the phosphorescence of $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ is quenched at r.t.

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