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Optical properties of transition metal complexes with *N*-heterocyclic carbenes as ligands. 1,3-di-*t*-Butylimidazol-2-ylidene as charge transfer donor and acceptor

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Dedicated to Professor Ernst Otto Fischer on the occasion of his 85th birthday

Abstract

The *N*-heterocyclic carbene 1,3-di-*t*-butylimidazol-2-ylidene (dbiy) can function as charge transfer (CT) donor and acceptor if it is coordinated to oxidizing and reducing metals, respectively. The complex $\text{Ti}^{\text{IV}}\text{Cl}_4(\text{dbiy})_2$ shows a ligand-to-metal CT absorption at 450 nm whereas $\text{Ni}^0(\text{CO})_2(\text{dbiy})_2$ is characterized by a metal-to-ligand charge transfer absorption at $\lambda_{\text{max}} = 365$ nm. While $\text{Ti}^{\text{IV}}\text{Cl}_4(\text{dbiy})_2$ is not luminescent, $\text{Ni}^0(\text{CO})_2(\text{dbiy})_2$ displays a room temperature emission at $\lambda_{\text{max}} = 510$ nm which is assumed to originate from the lowest-energy MLCT triplet.

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Keywords: Electronic spectra; Luminescence; Charge transfer; Carbene complexes; Nickel complexes; Titanium complexes

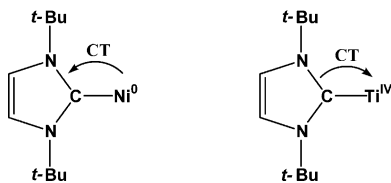
1. Introduction

N-heterocyclic carbenes (NHCs) have attracted much recent interest. They exist as stable species and function as ligands in coordination chemistry [1–3]. A variety of such complexes has been prepared, characterized and applied in organometallic catalysis. Surprisingly, very little is known about the excited state properties of transition metal complexes with NHC ligands. The photochemistry of a few NHC complexes has been reported, but in these cases the NHCs seem to act only as spectator ligands [4–7]. In contrast to these NHC complexes, the excited state properties of other carbene complexes, in particular those which have been pioneered by E.O. Fischer and his group, have been

investigated in quite some detail [8–12]. Since carbenes are generally stabilized by metals in low oxidation states, the M-carbene moiety is characterized by metal-to-ligand charge transfer (MLCT) transitions at relatively low energies [8,12]. The situation may be quite different for the M–NHC interaction. NHC ligands are only weak π -acceptor ligands [1–3]. Accordingly, (M \rightarrow NHC) MLCT transitions are expected to occur at rather high energies. Moreover, owing to their nucleophilicity NHCs coordinate also to metals in high oxidation states [1–3]. In this case NHCs should serve as charge transfer (CT) donors and low-energy ligand-to-metal charge transfer (LMCT) transitions could be observed. In order to identify (M \rightarrow NHC) MLCT and (NHC \rightarrow M) LMCT transitions with confidence a suitable choice of specific complexes is crucial. Any interferences by other electronic transitions should be avoided. For the present study we selected the complexes $\text{Ni}^0(\text{CO})_2(\text{dbiy})_2$ and $\text{Ti}^{\text{IV}}\text{Cl}_4(\text{dbiy})_2$ with dbiy = 1,3-di-*t*-butylimidazol-2-ylidene.

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This choice was guided by several considerations. Ni(0) complexes have available only low-energy MLCT transitions. Owing to the d^{10} electron configuration, dd (or ligand field, LF) transitions do not exist and metal-centered $3d \rightarrow 4s$ and $3d \rightarrow 4p$ transitions occur only at very high energies [13]. On the other hand, Ti(IV) as a d^0 -metal cannot participate in LF or MLCT transitions. It follows, that low-energy transitions of Ti(IV) complexes are generally of the LMCT type [14]. The target complexes $\text{Ni}(\text{CO})_2(\text{dbiy})_2$ and $\text{TiCl}_4(\text{dbiy})_2$ were prepared in analogy to similar complexes of the type $\text{Ni}(\text{CO})_2(\text{NHC})_2$ [15] and $\text{TiCl}_4(\text{NHC})_2$ [16].

2. Experimental

2.1. Materials

The compounds dbiy, $\text{Ni}(\text{CO})_4$ and TiCl_4 are commercially available from Strem. The complexes $\text{Ni}(\text{CO})_2(\text{dbiy})_2$ and $\text{TiCl}_4(\text{dbiy})_2$ were prepared in analogy to other compounds of the type $\text{Ni}(\text{CO})_2(\text{NHC})_2$ [15] and $\text{TiCl}_4(\text{NHC})_2$ [16]. The composition of $\text{Ni}(\text{CO})_2(\text{dbiy})_2$ was confirmed by elemental analysis: Anal. Calc. for $\text{C}_{24}\text{H}_{40}\text{N}_4\text{O}_2\text{Ni}$ (477.31): C, 60.39; H, 8.45; N, 11.74. Found: C, 60.31; H, 8.50; N, 11.66%.

For spectroscopic measurements the solvents were of spectrograde quality. They were rigorously dried and saturated with argon.

2.2. Instrumentation

Absorption spectra were measured with a Varian Cary 50 or a Kontron Uvikon 860 absorption 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.

3. Results

The electronic spectrum of dbiy in CH_3CN (Fig. 1) shows absorptions at $\lambda_{\text{max}} = 320$ nm ($\epsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}$), 264 (780) and 212 (9600). At room temperature dbiy displays a very weak emission at $\lambda_{\text{max}} = 351$ nm which is better discernible at 77 K (Fig. 1). In addition, a

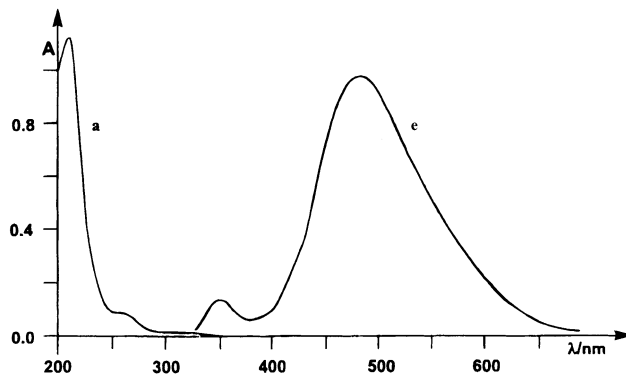


Fig. 1. Electronic absorption (a) and emission (e) spectrum of dbiy under argon. Absorption: 1.16×10^{-4} M in CH_3CN at room temperature, 1-cm cell. Emission: 3.21×10^{-4} M in EtOH at 77 K, $\lambda_{\text{exc}} = 254$ nm, intensity in arbitrary units.

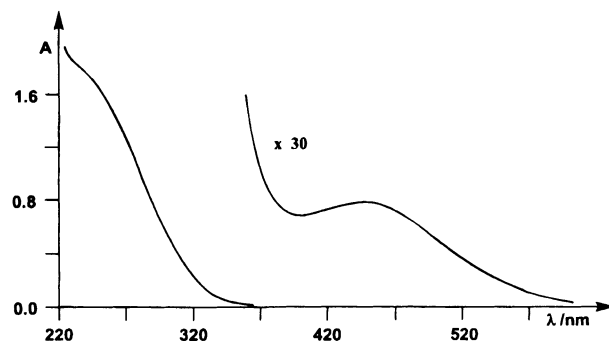


Fig. 2. Electronic absorption spectrum of 6.85×10^{-5} M $\text{TiCl}_4(\text{dbiy})_2$ in THF under argon at room temperature, 1-cm cell.

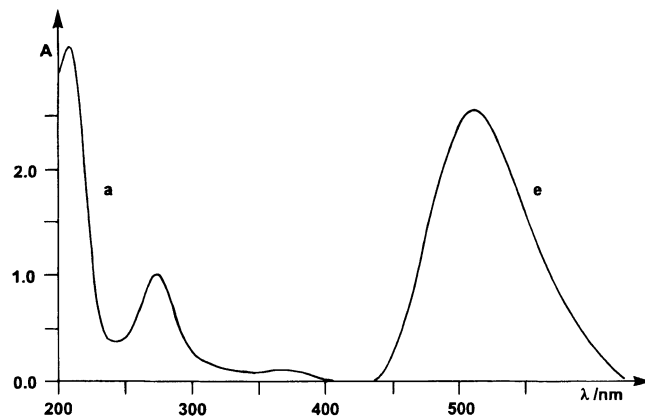


Fig. 3. Electronic absorption (a) and emission (e) spectrum of 1.19×10^{-4} M $\text{Ni}(\text{CO})_2(\text{dbiy})_2$ in CH_3CN under argon at room temperature, 1-cm cell. Emission: $\lambda_{\text{exc}} = 365$ nm, intensity in arbitrary units.

stronger luminescence appears at $\lambda_{\text{max}} = 480$ nm which is absent at room temperature

The absorption spectrum of $\text{TiCl}_4(\text{dbiy})_2$ in THF (Fig. 2) contains bands at $\lambda_{\text{max}} = 450$ nm (160) and 235 (sh, 24800). The compound is not luminescent. The complex $\text{Ni}(\text{CO})_2(\text{dbiy})_2$ in CH_3CN exhibits absorptions at $\lambda_{\text{max}} = 365$ nm (1200), 273 (8650) and 209 (27000) and a room temperature emission at $\lambda_{\text{max}} = 510$ nm (Fig. 3).

The excitation spectrum roughly matches the absorption spectrum.

4. Discussion

Generally, NHCs are characterized by singlet ground states [2,3,17–20]. The HOMO is occupied by the lone pair at the carbene carbon although filled π orbitals are close in energy. The LUMO is assumed to be a π^* orbital with a considerable contribution from the p_z orbital of the carbene carbon. Accordingly, low-energy $n\pi^*$ and $\pi\pi^*$ transitions should occur. Since $n\pi^*$ absorptions of this type are generally weak [21], the 320 nm absorption of dbiy is assigned to the spin-allowed transition from the carbon lone pair to empty π^* orbitals. The more intense bands of dbiy at 264 and 212 nm are attributed to $\pi\pi^*$ transitions. The weak emission of dbiy at 351 nm which overlaps with the 320 nm absorption and is also discernible at room temperature is assumed to be a fluorescence originating from the $n\pi^*$ state. Organic compounds with lowest-energy $n\pi^*$ states are frequently non-fluorescent or only weakly fluorescent [21]. The much stronger emission of dbiy which appears only at low temperatures is suggested to be a phosphorescence coming from the lowest-energy $n\pi^*$ triplet. Although the 0–0 transition can not be detected it is assumed to be located near 400 nm at the high-energy side of the phosphorescence band. The energy difference between the singlet ground state and the lowest-energy triplet amounts then to approximately 25000 cm^{-1} or 72 kcal. This singlet–triplet splitting of the parent NHC has been calculated to be 79 kcal [17].

Complexes of the type $\text{Ti}^{\text{IV}}\text{Cl}_4\text{L}_n$ are useful probes for the CT donor strength of L since all low-energy transitions which do not belong to TiCl_4 or L are of the LMCT type [22]. While TiCl_4 and dbiy are colourless, $\text{TiCl}_4(\text{dbiy})_2$ is yellow–brown. This colour is caused by the 450 nm absorption. It is assigned to a spin-allowed LMCT transition from the carbon lone pair to the empty d-shell of Ti(IV). In this context it is of interest that $\text{TiCl}_4(\text{PPh}_3)_n$ shows a ($\text{PPh}_3 \rightarrow \text{Ti}^{\text{IV}}$) LMCT band ($\lambda_{\text{max}} = 480\text{ nm}$) at comparable energies [23].

While carbenes have not yet been observed to function as CT donors they are well known to act as CT acceptors in transition metal complexes. Generally, carbene ligands have available an empty π^* (p) orbital at relatively low energies. In combination with a reducing metal, MLCT absorptions appear at rather long wavelengths [8,12]. However, NHCs are weak π -acceptor ligands since their carbene carbon p_z orbital is destabilized by π -interaction with the nitrogen atoms [2,3,17–20]. Accordingly, MLCT transitions are expected to occur at rather high energies. Their identification may be hampered by the presence of other electronic transitions in the same wavelength region. This interference

can be avoided if the NHC ligand is coordinated to a reducing d^{10} metal center because LMCT and LF transitions are absent. For $\text{Ni}^0(\text{CO})_2(\text{dbiy})_2$ these conditions are met. The longest-wavelength absorption at 365 nm is then assigned to a spin-allowed ($\text{Ni}^0 \rightarrow \pi^*$ dbiy) MLCT transition. The $n\pi^*$ transition of free dbiy at 320 nm should be shifted to higher energies upon coordination since the carbon lone pair must be considerably stabilized by formation of the σ -bond to the nickel atom. Unfortunately, there is only very little known about MLCT transitions of other Ni(0) carbonyl complexes. It is then difficult to evaluate the CT-donor strength of dbiy in comparison to other CT-accepting ligands. However, the complex $\text{Ni}(\text{CO})_2\text{bipy}$ (bipy = 2,2'-bipyridine) may serve as a qualitative marker. The red colour of this complex [24] is certainly caused by a ($\text{Ni}^0 \rightarrow \text{bipy}$) MLCT band in the visible part of the absorption spectrum. Of course, it is not surprising that the ($\text{Ni}^0 \rightarrow \text{dbiy}$) MLCT band ($\lambda_{\text{max}} = 365\text{ nm}$) appears at much shorter wavelength owing to the higher energy of the π^* orbitals of dbiy compared to those of bipy.

Finally, it is of interest that the MLCT state of $\text{Ni}(\text{CO})_2(\text{dbiy})_2$ is also emissive. Since this luminescence does not overlap with the spin-allowed MLCT absorption it is suggested that it originates from the MLCT triplet which is not seen in absorption. Nevertheless, it is quite intriguing that this phosphorescence appears at room temperature since nickel should not exert a strong heavy atom effect. However, $\text{Ni}(\text{PPh}_3)_2(\text{CO})_2$ shows a room temperature phosphorescence which also originates from a MLCT triplet [13]. Moreover, a variety of complexes of Cu(I) which is isoelectronic with Ni(0) are well known to emit from MLCT triplets under ambient conditions [25–27].

In conclusion, dbiy as typical NHC ligand is a strong CT donor, but only a weak CT acceptor in transition metal complexes. CT interactions of this type may lead to applications such as nonlinear optics [28].

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