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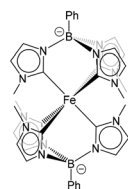
Shining light on the ferrous analogue: excited state dynamics of an Fe(II) hexa-carbene scorpionate complex†

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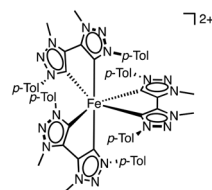
A ferrous complex bearing tris(carbene)borate ligands with imidazol-2-ylidene donors has been characterized by experimental and computational methods. Despite the pronounced destabilization of metal centered states by the exceptionally σ -donating ligand, the high-energy $^3\text{MLCT}$ state of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ is rapidly deactivated by the barrierless conversion to the ^3MC state.

In recent years, complexes of Earth-abundant transition metals have garnered increasingly more attention as light harvesters for both photovoltaic as well as photocatalytic applications.^{1,2} One very successful approach to overcome the rapid deactivation of charge transfer (CT) states in iron complexes has been the introduction of strongly σ -donating N-heterocyclic carbene (NHC) ligands.^{3–5} The most notable progress was made with hexa-NHC ligand sets in ferric complexes, namely $[\text{Fe}(\text{III})(\text{phtmeimb})]^+$ (phtmeimb = tris(3-methylimidazolin-2-ylidene)(phenyl)borate)⁶ and its derivatives⁷ as well as $[\text{Fe}(\text{III})(\text{btz})_3]^{3+}$ (btz = 3,3'-dimethyl-1,1'-bis(*p*-tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene))⁸ that benefit from particularly strong destabilization of metal centered (MC) states. As a result, deactivation of their doublet ligand-to-metal CT ($^2\text{LMCT}$) state *via* MC states is exceptionally disfavored, and with $^2\text{LMCT}$ lifetimes of 100 ps ($[\text{Fe}(\text{III})(\text{btz})_3]^{3+}$) and 2 ns ($[\text{Fe}(\text{III})(\text{phtmeimb})]^+$) the Fe(III) hexa-NHC complexes exhibit room temperature photoluminescence and engage in bimolecular excited state electron transfer (EET) which has resulted in first photocatalytic applications.^{9–14} Moreover, for $[\text{Fe}(\text{III})(\text{btz})_3]^{3+}$ we have previously shown that the same NHC ligand set results in sizeable ES lifetimes not only for the Fe(III)- but also the Fe(II)-complex.^{8,15} The $^3\text{MLCT}$ state with a lifetime of 528 ps has recently been used as a photo-reductant in a two photon-exci-

tation mechanism for a photoredox reaction, where both the Fe(III)- $^2\text{LMCT}$ and the Fe(II)- $^3\text{MLCT}$ partake in bimolecular EET reactions.¹¹ Generally, the ferrous complexes can be expected to offer attractive complementary properties such as more reducing excited states for applications in *e.g.*, photoredox catalysis or higher cage escape yields due to the spin forbidden recombination of triplet radical pairs.^{16,17} However, ferrous tetra-NHC complexes with complementary pyridyl^{18–25} or cyclo-metalating ligands^{26,27} feature $^3\text{MLCT}$ or ^3MC ESs with lifetimes on the order of 10 ps which preclude efficient bimolecular reactions. Hence, hexa-NHC complex $[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$ with its 528 ps ES life time and demonstrated EET reactivity stands out among all Fe(II)-NHC complexes. We were therefore intrigued whether also the ferrous analogue of hexa-NHC complex $[\text{Fe}(\text{III})(\text{phtmeimb})]^+$ could benefit from the superior ligand field splitting by the even more electron donating phtmeimb[−] ligand. The correspondingly high-energy MC states might ideally prevent rapid $^3\text{MLCT} \rightarrow \text{MC}$ deactivation or could possibly be photoactive themselves.²⁸ However, the facile oxidation of the $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ ground state prevents its isolation which has hitherto hindered investigations into its excited state dynamics. Here, we report on the *in situ* characterization of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ by transient absorption spectroscopy that revealed excited state deactivation on the ps time scale, and on computational results that rationalize the origins of its short $^3\text{MLCT}$ lifetime.



$[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ (Ph = phenyl)



$[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$ (p-Tol = *p*-tolyl)

As shown previously, electrochemical one-electron reduction of $[\text{Fe}(\text{III})(\text{phtmeimb})]^+$ (−1.16 V vs. Fc in acetonitrile) yields an EPR silent product attributed to the Fe(II) complex $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$.⁶ Here we show that the same

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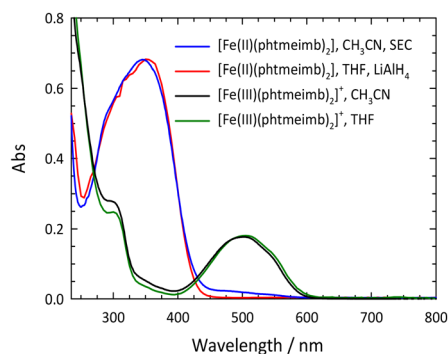


Fig. 1 Electronic absorption spectra of $[\text{Fe}(\text{III})(\text{phtmeimb})_2]^+$ and $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ obtained by spectroelectrochemistry (SEC) in acetonitrile (0.6 mM, $l = 0.1$ cm) or reduction by LiAlH_4 in THF solution. (Spectra in THF scaled at the maxima of the LMCT and MLCT bands, respectively.)

product can be obtained by chemical reduction of $[\text{Fe}(\text{III})(\text{phtmeimb})_2]^+$ by LiAlH_4 (Fig. 1) and the *in situ* reduced complex could be characterized by NMR (ESI).

The ^1H NMR spectrum exhibited well-resolved signals as would be expected for a diamagnetic compound (Fig. S1†) and peak assignments were made possible by 2D NMR spectroscopy (COSY, HMQC, HMBC, see ESI†). In the ^{13}C NMR spectrum (Fig. S2†), a strong downfield shift (216.9 ppm) of the carbene-carbon signal is observed. This value exceeds previously reported values for a *tetra*-carbene $\text{Fe}(\text{II})$ complex (201.2 ppm)³ but also for a *hexa*-carbene complex $[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$ (206.7 ppm)¹⁵ and can be attributed to the particularly strong electron donation of the six imidazol-2-ylidene donors and the double negative charge of the two phtmeimb^- ligands. Correspondingly large ligand-field splitting in the title complex is in accordance with computational results for the ^3MC energies of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ and $[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$ (see below).

The lowest energy absorption band of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ falls into the UV range ($\lambda_{\text{max}} = 348$ nm, $\epsilon_{\text{max}} = 10\,850\text{ M}^{-1}\text{ cm}^{-1}$). Consistent with electrochemical data ($E_{1/2}(\text{Fe}^{\text{III/II}}) = -1.16$ V, $E_{1/2}(\text{L}/\text{L}^{\cdot-}) < -3$ V), this band can be tentatively attributed to an MLCT transition. Support for this assignment was obtained from computational results for the ground state electronic structure. The QC calculations were performed at the B3LYP+D2/6-311G*(B,C,H,N),^{29–32} SDD(Fe)³³ level of theory using the Gaussian 16 Revision A.03 software³⁴ (see ESI† for details). The resulting molecular orbitals for the singlet ground state (^1GS) of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ are shown in Fig. 2 and an orbital energy diagram is found in Fig. S13.† The highest occupied molecular orbitals (HOMO through HOMO–2) are predominantly iron t_{2g} -based. Occupied MOs at lower energies (HOMO–3 through HOMO–12) are phtmeimb^- -based orbitals, with HOMO–3 through HOMO–9 predominantly localized on carbene moieties and HOMO–10 through HOMO–12 localized on aryl groups. The lowest unoccupied molecular orbitals (LUMO–LUMO+3) are aryl-based π^* orbitals delocalized over both phtmeimb^- ligands. Carbene π^* orbitals are observed from LUMO+5 to LUMO+7. With the first three

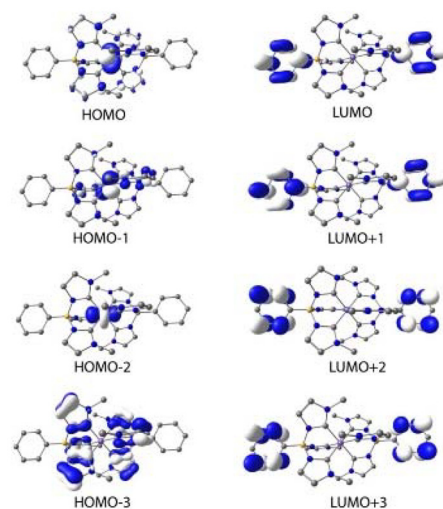


Fig. 2 Calculated molecular orbitals (HOMO–3 to LUMO+3) of the singlet ground state of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ using B3LYP+D2/6-311G*, SDD(Fe) in acetonitrile. Contour isovalue of $0.04\text{ e } \text{\AA}^{-3}$.

HOMOs being metal t_{2g} -based and the LUMOs (LUMO to LUMO+7) being ligand π^* -orbitals, the computational results support the notion that the lowest energy transitions would in fact be MLCT.

The excited state dynamics of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$, obtained by *in situ* LiAlH_4 reduction of the $\text{Fe}(\text{III})$ congener, upon MLCT excitation was studied by femtosecond transient absorption (TA) spectroscopy. Spectra at selected delay times and kinetic traces at selected wavelengths are shown in Fig. 3.

The initial TA spectra are composed of a ground state bleach (GSB) signal spanning from 320 nm to around 400 nm, and broad excited state absorption (ESA) above 400 nm, peaking at around 430 nm. Both features decay to a large extent within the first ten ps, along with a blue shift of the ESA signal to around 405 nm. The TA data is accurately described by three exponential terms for which a global fit returned lifetimes of 4.0 ps and 7.1 ps for the dominating components. The third term (>800 ps) was included to account for some very minor, essentially non-decaying features probably related to the limited photostability of the complex (Fig. S6†). Kinetic traces at selected wavelengths together with the fit results are shown in Fig. 3, middle. Corresponding evolution associated spectra (EAS, Fig. 3, bottom) apply to a simple sequential decay model (see Fig. S9† for decay and species associated spectra for other decay models). Complementary TA measurements performed on $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ obtained by electrochemical *in situ* reduction in MeCN solution yielded very similar results in terms of spectra and lifetime (Fig. S10†). The agreement corroborates the notion that the observed excited state deactivation is intrinsic to the complex and the lifetime not restricted by reactions with solvent, excess reductant or products of the latter. Since intersystem crossing from the initially populated $^1\text{MLCT}$ state can be expected to occur within the time resolution of the experiment,³⁵ EAS-1 might be



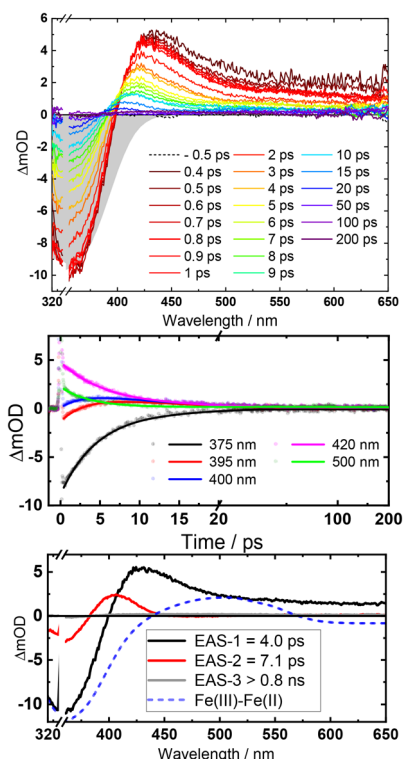


Fig. 3 Top: fs-TA spectra of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ at selected delay times after 350 nm excitation (gray-shaded area indicates the inverted ground-state absorption). Middle: kinetic traces at the indicated wavelengths (dots) and fit results (solid lines). Bottom: evolution associated spectra (EAS).

tentatively assigned to the $^3\text{MLCT}$ state that returns to the GS *via* a similarly short-lived MC state described by EAS-2 ($^3\text{MLCT} \rightarrow ^3\text{MC} \rightarrow ^1\text{GS}$). Computational results (see below) confirm the notion of efficient $^3\text{MLCT}$ deactivation *via* the ^3MC state while additional formation of ^3MC states directly from a short-lived MLCT precursor, as previously reported for complexes with py_2NHC_4 ligand sets,^{21–23} cannot be excluded from our TA data (ESI). The broad absorption of EAS-1 resembles spectra recently assigned to $^3\text{MLCT}$ states of $\text{Fe}(\text{II})(\text{py})_2(\text{NHC})_4$ complexes^{18,19} based on support from vibrational coherence spectroscopy²³ and fluorescence up-conversion studies.²⁴ On the other hand, it has been recognized that pronounced visible absorption can as well emerge from LMCT excitation of ^3MC states^{18–20} and our MLCT assignment of EAS-1 cannot be supported by spectroelectrochemistry³⁶ as the ligand based reduction of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ is electrochemically inaccessible.[‡] Some support for the above assignments might be provided by reports on $(\text{py})_2(\text{NHC})_4$ complexes where ^3MC states have been associated with narrower, blue-shifted absorption more similar to EAS-2.^{18,19} We note however that EAS-2 could as well be in line with a hot GS invoked in previous studies of $(\text{py})_2(\text{NHC})_4$ complexes.^{21,22} It can hence not be excluded that the $^3\text{MLCT}$ state decays on a sub-ps time scale and that it is instead the ^3MC state of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ that accounts for EAS-1. While definite assignments will require additional

experimental and computational work, it can be safely concluded that the $^3\text{MLCT}$ state of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ is considerably shorter-lived than for $[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$. Despite the superior σ -donating ability of the phtmeimb[−] ligand, destabilization of MC states is apparently insufficient relative to the rather high-energy $^3\text{MLCT}$ state of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$. This notion was corroborated by computational results. Potential energy curves of GS, $^3\text{MLCT}$, ^3MC and ^5MC excited states (Tables S1, S2 and Fig. S15†) show that the ^3MC state of $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ is lower in energy than its ^5MC state across all conformations. This result is consistent with a strong ligand field and indicates that deactivation of the $^3\text{MLCT}$ state is likely to occur *via* internal conversion to the ^3MC state. Fig. 4 compares potential energy surface diagrams for $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ and $[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$. The computational results confirm the expectation of significantly higher ^3MC energy for the phtmeimb[−] complex. However, due to its much more energetic $^3\text{MLCT}$ state, the driving force (ΔE) for $^3\text{MLCT} \rightarrow ^3\text{MC}$ internal conversion (IC) is rather exceeding the value for $[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$ (Table 1). Together with the lower reorganization energy (λ), IC is predicted to be barrierless ($\Delta E_{\text{act}} = 0$) in case of $[\text{Fe}(\text{II})$

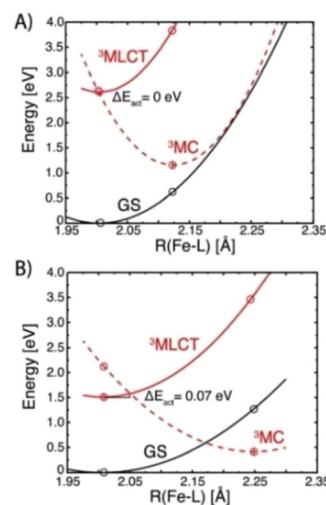


Fig. 4 Extrapolated diabatic harmonic singlet and triplet potential energy surfaces for $[\text{Fe}(\text{II})(\text{phtmeimb})_2]$ (A) and $[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$ (B) along an effective one-dimensional average Fe–C reaction coordinate calculated at B3LYP+D2/6-311G*(C,H,O,N), SDD (Stuttgart/Dresden pseudopotentials and basis set) level of theory in acetonitrile. The energies of the ^3MC and $^3\text{MLCT}$ states were obtained from TD-DFT (time-dependent density functional theory) calculations using ^1GS (singlet ground state) as the reference.

Table 1 Parameters for $^3\text{MLCT} \rightarrow ^3\text{MC}$ internal conversion calculated at B3LYP+D2/6-311G*(C,H,O,N), SDD(Fe) level of theory in acetonitrile using the polarizable continuum model (PCM)

	ΔE (eV)	λ (eV)	ΔE_{act} (eV)
$[\text{Fe}(\text{II})(\text{phtmeimb})_2]$	−1.45	1.35	0.00
$[\text{Fe}(\text{II})(\text{btz})_3]^{2+}$	−1.09	1.89	0.07



(phtmeimb)₂] for which the calculations (ESI) also result in a larger electronic coupling constant relative to [Fe(II)(btz)₃]²⁺.

In summary, our results indicate that the superior σ -donating ability of the phtmeimb[−] ligand results in extraordinary destabilization of MC states not only in the previously studied ferric complexes but also in a ferrous analogue investigated in this study. At the same time, the ligand is particularly difficult to reduce and thus the ³MLCT state of [Fe(II)(phtmeimb)₂] is also unusually high in energy compared to other Fe(II)NHC complexes. Its short ³MLCT life time can hence be attributed to rapid conversion to the ³MC state. With a close match between driving force and reorganization energy, the ³MLCT → ³MC transition is essentially barrierless and further benefits from strong electronic coupling between these states. Regarding the on-going quest for Fe(II)-NHCs with practically useful ES lifetimes, tuning of these parameters²⁵ will be essential. The directed design of ligands remains however a formidable challenge and computational studies might be an essential asset to further progress.

Data availability

Experimental details and additional experimental and computational data can be found in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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† Comparison of EAS-1 with the differential spectrum for the metal centered oxidation suggests that absorption of the reduced ligand should be expected below 450 nm and above 550 nm.



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