Photophysics and Photoredox Catalysis of a Homoleptic Re^{I} Tris(diisocyanide) Complex

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Photophysics and Photoredox Catalysis of a Homoleptic Re(I) Tris(diisocyanide) Complex

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Supporting Information Placeholder

ABSTRACT: Herein is communicated a homoleptic Re(I) complex bearing three chelating diisocyanide ligands, and its photophysical properties. The complex emits weakly from a high energy ^{3}MLCT excited state with an 8 ns lifetime in de-aerated CH_3CN at 22 °C, and is shown to act as an efficient photoredox catalyst comparable to $[Ir(ppy)_3]$ (ppy = 2-phenylpyridine) in representative test reactions.

Photoredox catalysis is rapidly emerging as a useful method for C-C bond formations.[1-2] d^6 precious-metal complexes are the prototypical photoredox catalysts and have played a pivotal role in the development of photoredox catalysis as a field.[3-4] Despite growing interest in organic and earth-abundant metal complex photoredox catalysts,[5-8] d^6 precious-metal complexes remain the first choice for many photoredox transformations – with $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and $[Ir(ppy)_3]$ (ppy = 2-phenylpyridine) among the most popular.[1-3, 9] This largely stems from their ease of synthesis, favourable photophysical properties, tunability, and robustness.

Interestingly, despite significant attention having been paid to the photoluminescent properties of $[Re(CO)_3(\alpha$-diimine)(X)]$ complexes (X = Cl$^-$, Br$^-$, CN$^-$, SCN$^-$, py)[10-16] and their performance in the catalytic photoreduction of CO_2,[15, 17-24] Re(I) complexes have been essentially unused as catalysts in organic photoredox transformations.

d^6 metal complexes typically exhibit photoluminescent metal-to-ligand charge-transfer (MLCT) excited states.[3] The energies of these excited states are easily tunable through the choice of metal and ligand design. A key feature of such complexes is that in their emissive ^{3}MLCT excited states they are both better oxidants and reductants than in their electronic ground states. The magnitude by which the oxidation potential of a complex is altered between ground and excited state may be estimated using the Rehm-Weller equation:[25]

$$E_{1/2}(C^+/C^*) \approx E_{1/2}(C^+/C^o) - E_{oo}$$

Where $E_{1/2}(C^+/C^o)$ and $E_{1/2}(C^+/C^*)$ are the ground- and excited-state state oxidation potentials, respectively, and E_{oo} the energy of the electronic origin for the excited state (the difference in energy between the oth vibrational levels of the ground and excited states). With the goal of increasing the reducing power of a catalyst, and therefore increasing its substrate scope, the pertinent design principles are to combine an easily oxidized metal (to decrease $E_{1/2}(C^+/C^o)$) with difficult to reduce ligands (to increase E_{oo} for the MLCT excited state). Using $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_3]$ as examples, the metal-centred (Ru^{II} and Ir^{III}, respectively) ground-state oxidation potentials of these complexes are 1.29 and 0.77 V vs SCE, respectively, and the ligand-based (bpy vs ppy, respectively) reductions -1.33 and -2.19 V vs SCE, yielding E_{oo} values of 2.10 and 2.50 eV, respectively.[6] Inserting these values into the Rehm-Weller equation, it is unsurprising that $[Ir(ppy)_3]$ is the more powerful photoreductant with $E_{1/2}(C^+/C^*)$ of -1.73 V vs SCE, compared to -0.81 V vs SCE for $[Ru(bpy)_3]^{2+}$.

Our recent investigations into photoluminescent earth-abundant zero-valent d^6 metal complexes have identified chelating diisocyanides as promising ligands for the development of strongly photoreducing complexes.[26-28] These ligands are more difficult to reduce than bpy or ppy, and their strong σ-donor character makes metal-based oxidations more facile. In combination with their strong π-accepting character, these attributes also increase the energy of deactivating ligand-field states relative to desirable MLCT states. Furthermore, the strong-field character of isocyanides is akin to that of carbonyls,[29-30] stabilizing the low-valent Re(I).[31-32] Prior studies of Re(I) complexes with monodentate isocyanide ligands demonstrated that this compound class has very promising photophysical properties,[33-35] but analogues with chelating ligands seem to be unknown so far.

We have therefore prepared a homoleptic Re(I) tris(diisocyanide) complex, $[Re(L^1)_3]PF_6$ (Scheme 1), with the goal of developing a strong photoreductant, anticipating that the chelating nature of the ligand would increase robustness compared to Re(I) complexes with monodentate arylisocyanide ligands.[27] The relevant photophysical properties of the complex are presented, in combination with the photoredox catalytic performance for two representative test reactions.

The Re(I) complexation of L^1 was achieved through adaptation of the method of Wang *et al.*[36] for the synthesis of $[Re(^{Me}bpy)_3]PF_6$ from $[ReCl_4(THF)_2]$ to afford $[Re(L^1)_3]PF_6$ in 76% yield (Scheme 1). L^1 and $[ReCl_4(THF)_2]$ were prepared according to literature procedures.[26, 37]

Electronic absorption and emission spectra of $[Re(L^1)_3]PF_6$ in CH_3CN are presented in Figure 1, and in THF, CH_2Cl_2 and

CH₃CN in Figure S1. Both absorption and emission profiles exhibit only minor differences across this solvent range.

Scheme 1. Synthesis of [Re(L¹)₃]PF₆
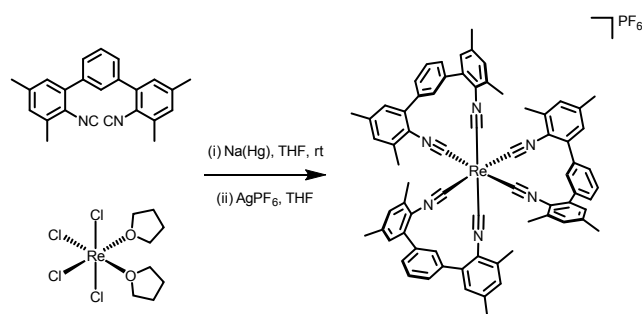
(i) L¹, Na(Hg), THF, rt, 15 h; (ii) AgPF₆, NH₄PF₆, THF, 76%.

The electronic absorption spectrum of $[Re(L^1)_3]PF_6$ in CH₃CN (blue trace) exhibits a maximum at 318 nm (ε = 34,000 M^{-1} cm^{-1}) not present in the ligand spectrum (dotted black trace), which tails past 400 nm and is assigned as MLCT in nature. Upon photoexcitation into this MLCT absorption feature (λ_{ex} = 350 nm) in de-aerated CH₃CN at 22 °C, photoluminescence is observed at ~480 nm (red trace in Fig. 1) with a quantum yield of 0.6% and lifetime of 8 ns (inset in Fig. 1). Photoluminescence is quenched in the presence of oxygen, and is therefore characterized as ^{3}MLCT in nature. From the intersection of the absorption and photoluminescence spectra, a ^{3}MLCT excited state energy of 2.96 eV is estimated.

The low quantum yield and short excited-state lifetime may be explained by thermal population of ligand-field excited states. These states are typically not readily accessible in $[Re(CO)_3(\alpha\text{-diimine})(X)]$ complexes;[10-16, 38] however, our complex has a higher energy ^{3}MLCT state than $[Re(CO)_3(\alpha\text{-diimine})(X)]$ complexes,[16, 39] and the isocyanide ligands destabilize ligand-field states to a lesser degree than carbonyls, resulting in thermally accessible ligand-field states. A previously studied homoleptic Re^I hexakis(arylisocyanide) complex with monodentate ligands was non-emissive at room temperature due to thermal occupation of ligand-field states.[40] Thus, the chelating ligand leads to markedly improved photophysical properties.

Electrochemical studies performed on $[ReCl(CO)_3(N\text{-}N)]$ complexes typically exhibit an irreversible Re^{II}/Re^I oxidation near the solvent limit,[41] and for the $[Re(2,6\text{-dimethylphenylisocyanide})_6]^+$ complex a potential of 1.08 V vs. SSCE was reported.[40] $[Re(L^1)_3]PF_6$ exhibits such an oxidation at 1.36 V vs SCE in CH₃CN (Figure S3). In combination with the excited-state energy (see above), an estimated $E_{1/2}(C^+/C^*)$ of -1.60 V vs SCE can be obtained. $[Re(L^1)_3]PF_6$ is photostable in de-aerated CH₃CN, with its electronic absorption spectrum in deaerated CH₃CN remaining unchanged after irradiation at 405 nm (1 W) for 24 h (Figure S2). This is an important finding in view of the known photolability of the $[Re(2,6\text{-dimethylphenylisocyanide})_6]^+$ complex, which undergoes efficient ligand exchange in presence of halide anions.[42]

Many organic photoredox catalysts have excited-state lifetimes that are similarly short as that of $[Re(L^1)_3]PF_6$,[5, 43] and it therefore seemed reasonable to perform photoredox catalysis

experiments with this complex, particularly in view of its comparatively high reducing power and photostability.
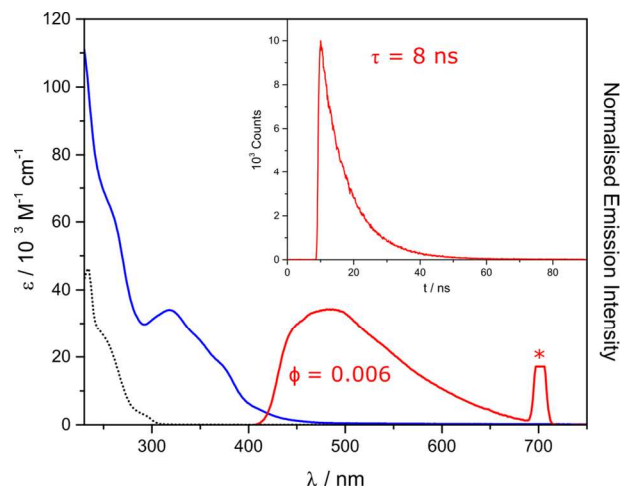

Figure 1. Electronic absorption (blue trace) and emission (red trace, λ_{ex} = 350 nm) spectra of $[Re(L^1)_3]PF_6$, recorded in de-aerated CH₃CN at 22 °C. Inset: Photoluminescence decay of $[Re(L^1)_3]PF_6$ recorded in de-aerated CH₃CN (λ_{ex} = 405 nm). *Stray excitation light. Black dotted trace represents ligand UV-Vis spectrum in CH₃CN.

Our initial approach was to try and match the excited-state oxidation potential of the complex with the reduction potential of a known substrate of interest. To this end, we chose the dimerization of benzyl bromide (E^o_{red} = -1.3 V vs SCE)[1] as a test reaction (Table 1).[44] Reactions were performed in flame-sealed NMR tubes containing the substrate (0.1 M), catalyst (1 mol %) and *N,N*-diisopropylethylamine (DIPEA, 4 mol eq.) as a sacrificial electron donor in de-aerated CD₂Cl₂. Over the course of 20 h under 405 nm (1 W) irradiation at room temperature, $[Re(L^1)_3]PF_6$ completely converted the substrate, with 81% dimerizing to afford dibenzyl and 19% presumably abstracting an H-atom from trace water present in the solvent to afford toluene. Catalyst-based photoluminescence was still observable after consumption of the substrate with no obvious loss of intensity, indicating that the catalyst is stable over long reaction times. As a control experiment, $[Ru(bpy)_3](PF_6)_2$ ($E_{1/2}(C^+/C^*)$ = -0.72 V vs SCE) converted only 49% of the substrate under 455 nm irradiation for the same duration at room temperature, yielding dibenzyl and toluene in 45% and 4% yields, respectively. The different excitation source was used to better coincide with the absorption maximum of the $[Ru(bpy)_3](PF_6)_2$ MLCT absorption band. No reaction occurred in the absence of either catalyst or light.

Encouraged by the catalytic performance of $[Re(L^1)_3]PF_6$ in this test reaction, we chose to explore the scope of the complex for more challenging catalytic photoreductive transformations. Given an $E_{1/2}(C^+/C^*)$ of -1.60 V vs SCE for $[Re(L^1)_3]PF_6$, the reduction of iodobenzene ($E^o_{red} \approx$ -1.6 V vs SCE in DMSO)[45] to benzene was chosen as a demanding transformation (Table 2). Reactions were once again performed in flame-sealed NMR tubes with de-aerated solvent, using conditions modified from Nguyen *et al.* for $[Ir(ppy)_3]$ (Table 2).[46]

Table 1. Benzyl bromide dimerization.
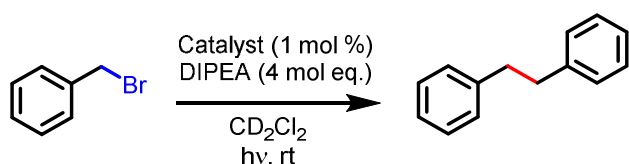
Catalyst	Irradia-tion Wave-length / nm	Benzyl Bromide Consump-tion / %	Diben-zyl For-mation / %	Toluene For-mation / %
$[Re(L^1)_3]PF_6$	405	100	81	19
$[Ru(bpy)_3](PF_6)_2$	455	49	45	4

Conditions: 20 h continuous irradiation in vacuum flame-sealed NMR tubes. Conversions obtained from ^1H NMR integrals. See the Supporting Information for details.

Over the course of 20 h under 405 nm irradiation at room temperature, both $[Re(L^1)_3]PF_6$ and $[Ir(ppy)_3]$ catalyzed the reaction to completion. No reaction occurred in the absence of either catalyst or light. Next we attempted the even more demanding reduction of bromobenzene ($E^o_{red} \approx$ -2.1 V vs SCE in DMSO)[45] to benzene. Under exactly the same conditions as for the reduction of iodobenzene to benzene, $[Re(L^1)_3]PF_6$ catalyzed the reaction to 22%, and $[Ir(ppy)_3]$ to 18%. These values are within experimental error, indicating that despite the short excited-state lifetime, $[Re(L^1)_3]PF_6$ operates at a similar catalytic efficiency to $[Ir(ppy)_3]$.

Table 2. Reduction of halobenzenes.
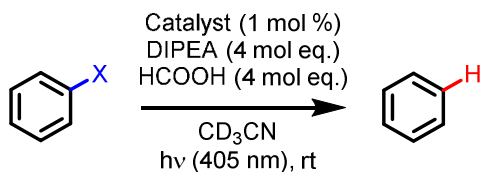
Catalyst	X	Conversion / %
$[Re(L^1)_3]PF_6$	I	100
$[Ir(ppy)_3]$	I	100 [a]
$[Re(L^1)_3]PF_6$	Br	22
$[Ir(ppy)_3]$	Br	18

Conditions: 20 h continuous irradiation in vacuum flame-sealed NMR tubes. Conversions obtained from ^1H NMR integrals. [a] Obtained from Nguyen *et al.* [46] See the Supporting Information for details.

In conclusion, we have herein communicated a new homoleptic Re^I tris(diisocyanide) complex with a high energy ^{3}MLCT excited state that can be exploited for photoredox catalysis. The low photoluminescence quantum yield and the comparatively short excited state lifetime presumably arise from thermal population of ligand field excited states.[40] Previously investigated Re^I complexes with monodentate arylisocyanide ligands were not emissive in solution at room temperature and seemed to undergo more rapid photo-decomposition,[40, 42] hence chelating isocyanide ligands lead to much improved photophysical properties and greater chemical robustness, in analogy to what we recently found for Cr^o and Mo^o complexes.[26-28] The Re^I tris(diisocyanide) complex catalyses representative photoredox transformations with similar efficiencies to the popular $[Ir(ppy)_3]$ catalyst.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, variable solvent UV-Vis and emission spectra, UV-Vis photostability experiment, cyclic voltammetry and photoredox catalysis NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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A homoleptic Re^I complex bearing chelating diisocyanide ligands and exhibiting a weakly photoluminescent high-energy ^{3}MLCT excited state is studied and exploited for photoredox catalysis.