



Review

Phosphane based dyads for artificial photosynthesis

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ABSTRACT

In this mini review we present the development of phosphane bridged dyads of the past 15 years. The work mainly stems from the workgroup of Professor Peter Brüggeller.

For solar energy conversion purposes a ligand was designed to efficiently combine a photon harvesting system and a proton reduction catalyst.

The system consisting of *cis,trans,cis*-1,2,3,4-tetrakis-(diphenylphosphanyl)cyclobutane (dppcb) and two 2,2'-bipyridine, halide or acetonitrile ligated metal centers was investigated in terms of absorption, luminescence and electron transfer characteristics. Photochemical details were assigned to certain structural properties.

Excited state electron transfer from Ru^{II} to Os^{II} is shown and investigated in terms of orbital energies and transitions. Also [Os(bpy)₂.(dppcb)MCl₂](SbF₆)₂ (M = Pd, Pt) was investigated and is discussed as a model system for photocatalytic water splitting. Excited state lifetimes and quenching characteristics are compared and discussed.

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1. Introduction

Concerning the possible impact of the ongoing climate change, artificial photosynthesis is an exciting and promising field for chemists to focus on, being a feasible way to reduce carbon dioxide emissions [1].

A challenge that has occupied researchers for several decades is to create luminescent, redox-active transition metal complexes for photoinduced water splitting [2,3]. Required for this application, these complexes must consist of a light-harvesting center, that transfers an electron and hence reductive power to a reaction center through a redox-active bridge, achieving charge separation [4]. It is already known that phosphane ligands are suitable backbones, as they can influence the activity and selectivity of the catalytic center [3]. Phosphane ligands, with the chemical formula PR₃, can be classified due to their remaining lone pair as a Lewis base and can interact with metals as a σ -donor. With the application

of electron withdrawing substituents, the energy of the σ^* -orbitals can be lowered, so that they also act as π -acceptors.

Furthermore, the π -acidity of phosphane ligands has a destabilizing effect on the lowest MLCT state. In case of poorer σ -donation of phosphane ligands the excited state is destabilized in contrast to the ground state, which is stabilized as a consequence of the enhanced $d\pi(M) \rightarrow \sigma^*\pi(P)$ back bonding.

Emissive metal to ligand charge transfer excited states (MLCTs) provided new information about the stabilizing role of the ligand [5]. As a result three possible pathways were presented (1) a radiative decay pathway, which is non-sensitive to ligand variations, (2) a non-radiative transition to the ground state, specified by a rate constant which is subject to the energy gap law for radiationless transitions and (3) the rate of transition between the MLCT state and a thermally activated, metal centered d-d excited state [6].

The vast chemistry and accessibility of phosphanes has been developed over the last decades into a perfect tool for stereoelectronic modification of phosphanes, which in turn can be fine-tuned to influence (photo-)catalytic substances in the preferred manner [7–11].

Attention is directed on polyphosphane ligands, coordinated to electron rich metals capturing electron density and therefore producing electron rich coordination sites. This effect is supported by highly sterically demanding ligands.

Abbreviations: bpy, 2,2'-bipyridine; dppcb, *cis,trans,cis*-1,2,3,4-tetrakis-(diphenylphosphanyl)cyclobutane; dppen, *cis*-1,2-bis-(diphenylphosphanyl) ethene; MLCT, metal to ligand charge transfer; NMR, Nuclear Magnetic Resonance; UV/vis, ultraviolet/visible light.

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Substituents with a certain rigidity have a high impact on the photochemical reactivity, since it is well known that RuP_2N_4 moieties containing simple diphosphanes without steric influences are photochemically inert [12].

In summary the photochemical behaviour is influenced by the chemical surroundings of the metal center, intermolecular distances and general steric array, such as *cis* or *trans* conformation, which lead to distinct interactions, π -stacking, electron effects and bonds. Related systems are compared and investigated for their excited state properties, lifetime and luminescence quantum efficiencies. Detailed structural perceptions of the systems can be obtained by the original sources [12–17].

The workgroup around Peter Brüggegger focused on bridging ligands for the synthesis of (hetero-)multinuclear complexes for a photocatalytic proton reduction device. An important issue for the conversion of energy is the coupling between light absorption and electron transfer in intramolecular systems. In a related sense this mini review presents the developments on cyclobutane based phosphanes for photoinduced electron transfer.

2. Cyclobutane based ligands

Metal organic complexes containing Ru and Os, modified with a polyphosphine backbone, are reported to have photochemical behaviour that promotes the usage in photochemical water splitting systems, such as long excitement and luminescence lifetimes.

Furthermore, photoinduced ligand exchange reactions have been reported. [18] A building block, formed out of $[\text{M}(\text{bpy})_2]^{2+}$ ($\text{M} = \text{Ru}, \text{Os}$), *bpy* = bipyridine) bridged by bis(bidentate) ligands, used by several research groups for complex modification, turned out to have an excellent reactivity [19–24].

Haid et al. presented a bis(bidentate) phosphane, *cis,trans,cis*-1,2,3,4-tetrakis-(diphenylphosphano)cyclobutane (**dppcb**) (**1a**), showing excellent photochemical behavior [22]. The system, consisting of a cyclobutane-bridged backbone, was firstly synthesized by Oberhauser et al. [25] and tested for its oxidative quenching abilities.

Two diastereoisomers of the form $[\text{Ru}_2(\text{dppcb})(\text{bpy})_4]^{4+}$ occur, both being prone to a light induced ligand exchange reaction in the presence of acetonitrile. Resulting complexes represented by the structure $[\text{Ru}_2(\text{dppcb})(\text{bpy})_2(\text{MeCN})_4]^{4+}$ (**1d**) were fully characterized by NMR, mass spectrometry and X-ray diffraction methods. Before then, similar complexes were mainly substituted with carbonyl functions. In 2000 Eskelinen et al. presented photo-physical behavior of complexes of the form $[\text{Ru}(\text{L})(\text{CO})_2\text{Cl}_2]$, $\text{L} = 2,2'$ -bipyridine or 4,4'-dimethyl-2,2'-bipyridine to “provide important insights into the mechanisms of catalytic processes” [26]. Moreover, Deacon et al. conducted irradiation experiments in solution with complexes of the type $[\text{RuL}(\text{CO})_2\text{Cl}_2]$, with $\text{L} = 2,2'$ -bipyridine analogue, leading to two different types of structures, a *trans* form and an array of terminal chlorides, by Ru^{II} complex- and carbonyl alteration [27]. The synthesis and the crystallographic data of the pure diastereoisomers *meso*-($\Delta\Delta/\Delta\Delta$)- $[\text{Ru}_2-(\text{dppcb})(\text{bpy})_4](\text{PF}_6)_4$ and *rac*-($\Delta\Delta/\Delta\Delta$)- $[\text{Ru}_2(\text{dppcb})(\text{bpy})_4](\text{PF}_6)_4$ are published [22]. As a result, the photochemical reaction of the different complex forms (**1b,c**) to $[\text{Ru}_2(\text{dppcb})(\text{bpy})_2(\text{MeCN})_4](\text{PF}_6)_4$ was proven by ^{31}P NMR to proceed with a good quantum yield. Findings were compared to the established $[\text{Ru}(\text{cis-dppen})(\text{bpy})_2](\text{PF}_6)_2$ (*dppen* = 1,2-bis(diphenylphosphano)ethene) complex, introduced by Caspar et al., who investigated emissive MLCTs of a similar system. A complex series of the type *cis*- $\text{Ru}(\text{bpy})_2\text{L}_2^{2+}$ ($\text{L} = \text{pyridine}, \text{pyridazine}, 1,2\text{-phenanthroline}, 1,2\text{-bipyridine}, \text{N-methylimidazole}$ or 2-(2-aminoethyl)pyridine) was considered, to establish a theory about “the roles of different decay pathways in determining excited-state lifetimes” [5]. A steric influence of the bis(bidentate)

ligand *dppcb* was preceded in place of an electronic effect, introduced by the $[\text{Ru}(\text{bpy})_2]^{2+}$ fragment. This was proven by a study of infrared absorption of $\text{C}\equiv\text{N}$ valence deformation oscillations of complexes of the type $[\text{Pd}(\text{CN})_2(\text{L-L})]$, *L-L* is a diphosphane, and $[\text{Pd}_2(\text{CN})_4(\text{dppcb})]$, conducted by Oberhauser et al. in 2000 [28] (see Chart 1).

3. Conformational isomers

Gutmann et al. reported a light induced conformational alteration of a complex consisting of a $[\text{Ru}(\text{bpy})_2]^{2+}$ moiety ligated with a chelating phosphane and a saturated backbone (**2a,b**) [18]. The bimetallic structure of *rac*-($\Delta\Delta/\Delta\Delta$)- $[\text{Ru}_2(\text{dppcb})(\text{bpy})_4](\text{PF}_6)_4$ and *meso*-($\Delta\Delta/\Delta\Delta$)- $[\text{Ru}_2(\text{dppcb})(\text{bpy})_4](\text{PF}_6)_4$, is crucial for a long lifetime behaviour that these compounds exhibit [18]. This effect was clarified by the investigation of the monometallic complexes $[\text{Ru}(\text{dppcb})(\text{bpy})_2](\text{PF}_6)_2$ and $[\text{Ru}(\text{dppcbO}_2)(\text{bpy})_2](\text{PF}_6)_2$ (Chart 2), where *dppcbO*₂ is *cis, trans, cis*-1,2-bis(diphenylphosphanyl)-3,4-bis(diphenylphosphanyl)-cyclobutane. (**2b**) Based on the former studies about these systems, by Haid et al. in 2001 about the unexpected photochemical reactivity [22,29], investigations about photophysical features were conducted.

As previously reported in 1983 by Caspar et al, who considered the photochemical influence of MLCTs and comparable effects, the π -acidity of phosphane ligands has a destabilizing effect on the lowest MLCT state, where this phenomenon is explained more precisely in the introduction [5].

Sullivan et al. studied the electronic and redox activity of similar systems and realized the influence of phosphane ligands stabilizing Ru^{II} systems, resulting in impressive chemical stability and high reduction potential for the Ru^{III} form [30].

By inserting a saturated cyclobutane backbone Gutmann et al. reported the opportunity to optimize the yield of luminescence in mono- and bimetallic species by combining *dppcb* and $[\text{Ru}(\text{bpy})_2]^{2+}$, for the first time [18].

Temperature effects and X-ray structures were examined to comprehend delocalisation and structural rigidity. As a result, extraordinary luminescence lifetimes, 910(20) ns in CD_3CN and 794(20) ns in MeCN at 298 K could be shown. Detailed information such as lifetimes, transitions and calculated activation energies are given in [24].

In conclusion at high temperature the “electronic effects are offset by a conformational modulation” [22], restraining the available vibrational modes of the *dppcb* and *bpy* ligands [31]. Besides, the diastereoisomeric forms, characterized by NMR and X-ray crystallography, lead to unusual photophysical properties. In comparison to *rac*-($\Delta\Delta/\Delta\Delta$)- $[\text{Ru}_2(\text{dppcb})(\text{bpy})_4](\text{PF}_6)_4$ and *meso*-($\Delta\Delta/\Delta\Delta$)- $[\text{Ru}_2(\text{dppcb})(\text{bpy})_4](\text{PF}_6)_4$, showing long excited state lifetime and a pronounced emission enhancement at ambient temperature [5] the systems $[\text{Ru}(\text{dppcb})(\text{bpy})_2](\text{PF}_6)_2$ and $[\text{Ru}(\text{dppcbO}_2)(\text{bpy})_2](\text{PF}_6)_2$ show no comparable photodissociation, which enables a photochemical behaviour prediction of the complexes [18].

4. Heterometallic complexes

For the assessment of intramolecular systems, light absorption and the electron transfer properties for the homodimetallic species *meso*-($\Delta\Delta/\Delta\Delta$)- $[\text{Os}_2(\text{dppcb})(\text{bpy})_4](\text{PF}_6)_4$ (**3a**), *rac*-($\Delta\Delta/\Delta\Delta$)- $[\text{Os}_2(\text{dppcb})(\text{bpy})_4](\text{PF}_6)_4$ (**3b**) and for heterodimetallic species ($\Delta\Delta/\Delta\Delta$)- $[\text{Os}(\text{bpy})_2(\text{dppcb})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ (**3c**) and ($\Delta\Delta/\Delta\Delta$)- $[\text{Os}(\text{bpy})_2(\text{dppcb})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ (**3d**) were studied. Thereby the combination of $[\text{Ru}(\text{bpy})_2]^{2+}$ as an antenna site and $[\text{Os}(\text{bpy})_2]^{2+}$ as a trap site has been proven [32].

It is widely believed that for a metal–metal distance below 10 Å an interaction between the metal centers of heterodimetallic

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