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Synthesis of Mono-, Di-, and Trinuclear Rhodium Diphosphine Complexes Containing Light-Harvesting Fluorene Backbones

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Supporting Information

ABSTRACT: Syntheses and structural determination of rhodium complexes ligated by diphosphines containing light-harvesting fluorene backbones are presented. In these rhodium complexes, the rhodium center is surrounded by a light-absorbing diphosphine unit. The presence of Rh– Rh bonding interactions is suggested by density functional theory studies.

tilization of light energy is a promising subject that can potentially lead to the discovery of new reactions and materials fueled by clean and inexhaustible solar energy. In order to achieve this, catalysts containing various photosensitizers and reaction centers have been developed. However, their reactions are limited to (1) the use of organic radicals generated by the photoredox processes of photosensitizers, 1 (2) CO₂ reduction and H₂ formation in the presence of a sacrificial electron donor, and (3) H₂O splitting in association with artificial photosynthesis.² These reactions, especially reactions (2) and (3), are difficult to perform, and many studies have been undertaken to improve the efficiency of the catalysts. For the synthesis of suitable molecular catalysts, linkers connecting the chromophore and reaction center are important in determining the photophysical properties and photocatalytic activity. In most cases, the reaction centers and chromophores are connected by nonconjugated linkers to maintain the physical properties of each component. Conversely, we have been working on photocatalysts that consist of a chromophore and a reaction center connected by a conjugated linker.³ The electronic perturbation of the chromophore resulting from photoexcitation is transferred efficiently to the reaction site through the conjugated bridging ligand. We recently found that metal complexes containing a photosensitizing ligand can also act as photocatalysts.⁴ In order to expand the range of the photocatalyst structures, we proposed the synthesis of multinuclear photocatalysts containing a reaction site surrounded by photosensitizers.

Diphosphine ligands containing fluorene backbones, L^{R} (R = Ph, Cy), were synthesized using a procedure similar to that for the synthesis of 9*H*-fluorenyldiphenylphosphine (eq 1).⁵ The



addition of L^{R} to $[Rh(nbd)_{2}]BF_{4}$ (nbd = 2,5-norbornadiene) promptly yielded a mononuclear rhodium complex $\mathbf{1}^{R}$ [R = Ph, Cy; Scheme 1(i)]; however, purification resulted in a low isolated yield for 1^{Cy} because of its high solubility in CH₂Cl₂. For the

Scheme 1. Syntheses of Mono-, Di-, and Trinuclear Rhodium Complexes



syntheses of di- and trinuclear complexes, mononuclear precursor 1^{Ph} was used because of its higher stability. The addition of 2 equiv of the ligand to the dinuclear chloro-bridged dimer $[Rh(cod)Cl]_2$ gave dinuclear rhodium complex 2^{Ph} [Scheme 1(ii)]. Complex 1^{Ph} was converted to the corresponding bis(acetone) complex by stirring in acetone under H_2 (atmospheric pressure) via dissociation of norbornane through hydrogenation. The in situ addition of a slight excess of chloroform gave a trinuclear rhodium complex with triply bridged chloride ligands (3^{Ph}) [Scheme 1(iii)]. When the above reaction was followed by ³¹P NMR, formation of the acetone complex $(\delta_p = 12.6 \text{ in acetone-} d_6)$ was observed along with a decrease of 1^{Ph} , and after the addition of chloroform, formation of 3^{Ph} was observed $(\delta_p = 6.5 \text{ in acetone-} d_6; \text{ Figure S1})$. The reaction probably proceeded through chloride abstraction from chloroform;⁶ however, a dichloromethyl-containing byproduct could not be confirmed.

The corresponding trinuclear complexes did not form under the same conditions when other ligands such as 1,1-bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe) were used. When 1 equiv of dppm was added, a rhodium complex ligated with two bis(phosphine) ligands was formed preferentially. When dppe was used, a similar

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Figure 1. Molecular structures of (a) L^{Ph} , (b) 1^{Ph} (cationic part), (c) 1^{Cy} (cationic part), (d) 2^{Ph} , and (e) 3^{Ph} (cationic part) with 30% probability ellipsoids. Anions are omitted for clarity.

bis(acetone) complex was formed; however, the addition of an excess amount of chloroform did not yield the corresponding trinuclear complex, and gradual decomposition gave several unidentified species (Scheme S1). These results clearly indicate the advantage of the fluorene backbone in synthesizing the trinuclear structure. Although we do not know the exact reason for the difference in the reactivity, it is clear that the steric effect of the fluorenyl backbone in 1^{Ph} is larger than the dppm counterpart (Figure S2). Thus, we propose that the steric effect kinetically retards ligand exchange between the nbd and L^{Ph} ligands.

When chloroform was used as a solvent in the synthesis of 3^{Ph} , a bis(chloroform) complex formed after the hydrogenation reaction.⁷ The complex promptly precipitated from the reaction mixture; thus, only a small amount of 3^{Ph} was formed. When the precipitate was redissolved in acetone, it gave the trinuclear complex 3^{Ph} in quantitative yield via reaction with 2 equiv of the dissociated CHCl₃ ligand (Scheme S2 and Figure S3). When dinuclear complex, 3^{Ph} was formed in low yield [40%; Scheme 1(iv)]. The mono-, di-, and trinuclear complexs have been characterized via NMR spectroscopy and electrospray ionization mass spectroscopy (ESI-MS), and their molecular structures were determined by single-crystal X-ray diffraction studies.

The perspective views of L^{Ph} , 1^{Ph} , 1^{Cy} , 2^{Ph} , and 3^{Ph} are presented in Figure 1, and selected bond lengths and angles are collected in Table S1.⁸ The P–C–P angle of the ligand (116°) decreases in complexes 1^{Ph} , 2^{Ph} , and 3^{Ph} (88–91°). Bite angles to the rhodium center for the complexes range from 72 to 74°, which is very similar to those of the other rhodium complexes with the dppm ligand.⁹ These results indicate that substituting the dppm methylene with a fluorene unit does not greatly affect chelation to the rhodium center.

The Rh–Cl bond lengths (Å) and Cl–Rh–Cl angles (deg) of the Rh₃Cl₂ structure are quite similar to the values reported by Heller's group.¹⁰ The average value of the three Rh–Rh distances is 3.19 Å, which is similar to that of 2^{Ph} (3.13 Å) but slightly longer than the values reported for the Rh–Rh single bond.^{11,12} In this complex, the fluorene plane is parallel to the Rh₃ plane, and the six phenyl groups on the phosphine atoms are aligned so that the reaction site of the Rh₃ cores is not closed for the substrate (Figure S4).

The UV–vis absorption and emission ($\lambda_{ex} = 265$ nm) spectra are shown in Figure 2, and data are collected in Table 1. For the



Figure 2. UV–vis absorption (left) and emission (right; $\lambda_{ex} = 265$ nm) spectra measured in CH₂Cl₂ at room temperature.

absorption spectra of the di- and trinuclear complexes 2^{Ph} and 3^{Ph} , respectively, the intensity was normalized to 1/2 and 1/3, respectively, to compare the contribution of each metal fragment. It should be emphasized that the multinuclear complexes possess wider and broader absorption compared to the corresponding mononuclear counterpart. This result suggests that the assembly of the mononuclear unit gives rise to its light-absorbing ability. Ligand L^{Ph} showed a broad absorption band in the 250–300 nm range, and the vibrational structure of the fluorene $\pi - \pi^*$ band was absent, indicating electronic conjugation between the

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Table 1. Photophysical Properties^a

ligand or complex	absorption $\lambda_{\rm max}/{\rm nm}~(\epsilon/10^4{ m M}^{-1}{ m cm}^{-1})$	emission $\lambda_{\rm max}/{ m nm}$
fluorene	265 (1.97), 290 (0.65), 301 (0.88)	310
L^{Ph}	259 (1.88), 276 (1.41)	327
1 ^{Ph}	294 (0.30)	Ь
$2^{\rm Ph}$	С	Ь
3 ^{Ph}	292 (1.29), 353 (0.40)	349, 361
^{<i>a</i>} Measured in CH	I_2Cl_2 at room temperature. $\lambda_{ex} = 265$	nm for emission

spectra. ε values are normalized per rhodium atom for complexes 1^{Ph} , 2^{Ph} , and 3^{Ph} , respectively. ^bNo emission. ^cNo characteristic peak.

fluorene and phenyl rings via a phosphorus atom. This was also supported by the absorption spectra of the rhodium complex 1^{Ph}, which showed only a broad and gradually attenuating band from the UV region to 400 nm, suggesting the presence of electronic interaction between the fluorene unit and a rhodium unit via phosphorus atoms. The spectrum of the dinuclear complex 2^{Ph} was very similar to that of 1^{Ph} , with an ε value nearly twice that of 1^{Ph}, although each value was calibrated for a single rhodium atom. The spectrum of the trinuclear complex 3^{Ph} contains a unique band at ca. 350 nm and higher absorption in the lower-energy region compared to that of the other complexes. This may be due to the electronic interaction between two or three rhodium atoms via bridging chloride atoms or electronic metal-metal interaction (vide infra). L^{Ph} displays relatively intense emission compared to the rhodium complexes. Upon excitation of the fluorene unit, the mono-, di-, and trinuclear complexes showed quenched emission; however, 3^{Ph} showed emission in the lower-energy region. One possible explanation for the quenching is energy transfer taking place from the surrounding fluorene moiety to the central rhodium atom.

Density functional theory (DFT) calculations were conducted to determine the origin of the photochemical properties of the trinuclear rhodium complex 3^{Ph} using the *Gaussian 09* program package.¹³ Frontier molecular orbitals of the optimized structure in the *C*₃-symmetry constraint are shown in Figure 3.

The highest occupied molecular orbital (HOMO) and HOMO-1 were degenerate, and these orbitals including



Figure 3. Energy diagram of the orbitals of 3^{Ph}.

HOMO-2 (MO 460) possessed Rh d_{Z^2} orbital character, indicating the presence of direct electronic interaction between the rhodium centers, as was suggested from the electronic absorption studies.¹⁴ Additionally, orbitals HOMO-3, -4, and -5 (MO 459, 458, and 457) possessed d_{yz} or d_{yz} character (Figure S17). The lowest unoccupied molecular orbital (LUMO) clearly possessed Rh-Cl antibonding orbital character. The LUMO+1 and LUMO+2 were nearly degenerate and possessed conjugated orbital character among the rhodium, phosphorus, and fluorenyl ligands. LUMO+3, LUMO+4, and LUMO+5 (MO 466, 467, and 468) possessed π^* -orbital character in the fluorenyl ring (Figure S17). Photoirradiation of the complex 3^{Ph} caused gradual decomposition and gave an unidentified product with a broad signal around 6.5 to 8.5 ppm in ¹H NMR. Transitions from occupied orbitals to LUMO probably took place, resulting in Rh-halogen bond cleavage and decomposition of the trinuclear complex to mono- or dinuclear complexes. These results show the potential photoreactivity of our rhodium catalysts with organic substrates such as alkenes, alkynes, and carbonyl compounds.

In conclusion, we have synthesized novel rhodium complexes ligated by diphosphine containing a fluorene backbone, which acts as a light-harvesting moiety as well as a wall-like structure. The structures of the rhodium complexes have been determined by single-crystal X-ray diffraction studies. From photophysical analyses, di- and trinuclear rhodium complexes showed strong electronic conjugation with multiple metals, bridging ligands, phosphines, and fluorene moieties, and these tendencies were supported by the DFT study.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02423.

Experimental procedures, NMR data, crystal data and structure refinement, orbital diagrams, and *xyz* coordinates of the optimized structures $(3^{Ph} \text{ and } 2^{Ph})$ (PDF) X-ray crystallographic data in CIF format (ZIP)

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Notes

The authors declare no competing financial interest.

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(13) Geometry optimization in the *Gaussian 09* program packages: Lanl2DZ for the rhodium atom, 6-31G+ for the phosphorus and chlorine atoms, and 3-21G for the other carbon and hydrogen atoms.

(14) A DFT calculation of 2^{Ph} in C_s -symmetry constraint similar to that of 3^{Ph} was conducted (Figure S18 and Table S4). The HOMO-1 of 2^{Ph} also possessed bonding character by the Rh d_z^2 orbital similar to that of 3^{Ph} . Clear differences were observed in the LUMO and the orbitals close to LUMO, which did not have any involvement of the bridging chlorine character.