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Review

Homogeneous catalysis of platinum(II) complexes in photochemical hydrogen production from water

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Contents

Abstract

This review concentrates on the Pt(II)-catalyzed reduction of water into molecular hydrogen, with emphasis given to the works undertaken thus far by the authors' group. The homogeneous catalysis of (i) dinuclear platinum(II) complexes, (ii) mononuclear platinum(II) complexes, (iii) platinum(II) complexes having electron-acceptor groups, and (iv) platinum(II) complexes having photosensitizing groups is described. The dependences of the H_2-evolving activity on the metal–metal interaction, the Pt(II) d_{z^2} orbital energy, the steric factor, and the electron-acceptor ability are discussed. Moreover, the first active model of a photo-hydrogen-evolving molecular device made up of a tris(2,2′-bipyridine)ruthenium(II) derivative and a homogeneous platinum(II) catalyst is discussed.

Keywords: Water splitting; Photochemical hydrogen production; Platinum; Ruthenium; Methylviologen; Molecular devices

1. Introduction

Tris(2,2′-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$, bpy = 2,2′-bipyridine) and its derivatives have attracted considerable attention for many years due to their potential application as photosensitizers in water splitting reactions [1–4]. The fundamental concepts on the application of such photosensitizers have been well demonstrated until the early 1980s [5–8]. The studies showed that the photochemical hydrogen production is effectively promoted by visible-light irradiation of an aqueous solution containing three key components in the presence of a sacrificial electron donor, such as EDTA (ethylenediaminetetra–acetic acid disodium salt) and TEOA (triethanolamine), where the three components correspond to $[Ru(bpy)_3]^{2+}$, methylviologen (*N*,*N*′-dimethyl-4,4′-bipyridinium, abbreviated as MV^{2+}), and an H_2-evolving catalyst such as colloidal platinum (Fig. 1).

Although a sharp decrease was given in the number of papers in this field after the early 1980s, it has now again

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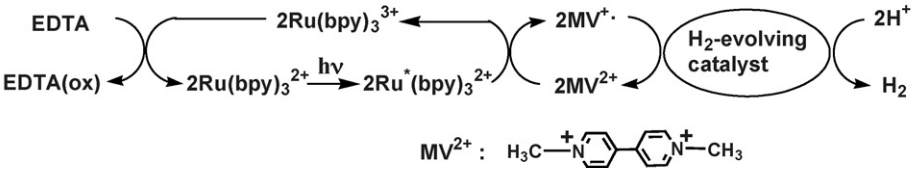


Fig. 1. A photochemical model system for the H_2-evolving half cell, which consists of $[Ru(bpy)_3]^{2+}$ as a photosensitizer, MV^{2+} (methylviologen) as an electron relay, and either colloidal platinum or a platinum(II) catalyst as an H_2-evolving catalyst. The overall reaction can be understood as a visible-light-induced reduction of water into molecular hydrogen using EDTA as a sacrifacial electron donor.

become one of the hottest areas because of the remaining environmental problems and the world's energy needs [9]. Recently, Bernhard et al. reported on the photochemical hydrogen production from a TEOA/PS/$[Co(bpy)_3]^{2+}$ system in which $[Ir(phenylpyridinato)_2(bpy)]^+$ and its derivatives were employed as photosensitizers (PS) [9a]. In this system, $[Co(bpy)_3]^{2+}$ serves as an electron relay and its decomposed species, such as $[Co(bpy)_2]^+$ [8e], plays a role of an H_2-evolving catalyst. Eisenberg et al. also reported on the photochemical hydrogen production from a TEOA/PS/MV^{2+}/Pt(colloid) system in which $[Pt(II)(4'\text{-}p\text{-tolyl-terpy})(arylacetylide)]^+$ (terpy = 2,2′:6′,6″-terpyridine) was used as a PS instead of $[Ru(bpy)_3]^{2+}$ [9b]. These studies mainly focus on the use and/or development of new photosensitizers. Moreover, the photochemical hydrogen production promoted by dirhodium(I) and diiridium(I) complexes, $[M(I)_2(\mu\text{-bridge})_3X_2]$ (M = Rh and Ir; bridge = bis[difluorophosphino]methylamine and other bidentate diphosphazane ligands; X = halogen ion), have been extensively studied thus far by Nocera's group, in which HX addition to the photochemically generated $M(0)_2$ species takes place to give the $M(II)_2H_2X_2$ species (dihydride–dihalide species), which photoeliminates H_2 with concomitant regeneration of the original $M(I)_2X_2$ species [9c,d].

On the other hand, the author's group has been focusing on the H_2-evolving activities of the platinum(II) complexes as given in the title of this review. As an alternative approach to catalyze the reduction of water into molecular hydrogen, we first realized that the amidate-bridged *cis*-diammineplatinum(II) dimers $[Pt(II)_2(NH_3)_4(\mu\text{-amidato})_2]^{2+}$ (amidate = acetamidate, 2-fluoroacetamidate, α-pyrrolidinonate, α-pyridonate, etc.), serve as effective H_2-evolving catalysts in the three-component system given in Fig. 1 [10]. Within this review, the results of our on-going studies, in the last decade, on the homogeneous catalysis of mononuclear and dinuclear Pt(II) complexes in the photochemical reduction of water into molecular hydrogen will be described, in which several important factors affecting the catalytic activities of the Pt(II) complexes will be discussed in detail. In the final stage of this review, our success in the development of a photo-hydrogen-evolving molecular device driving the visible-light-induced reduction of water into molecular hydrogen using EDTA as a sacrifacial electron donor will be discussed, together with some related studies carried out by other groups.

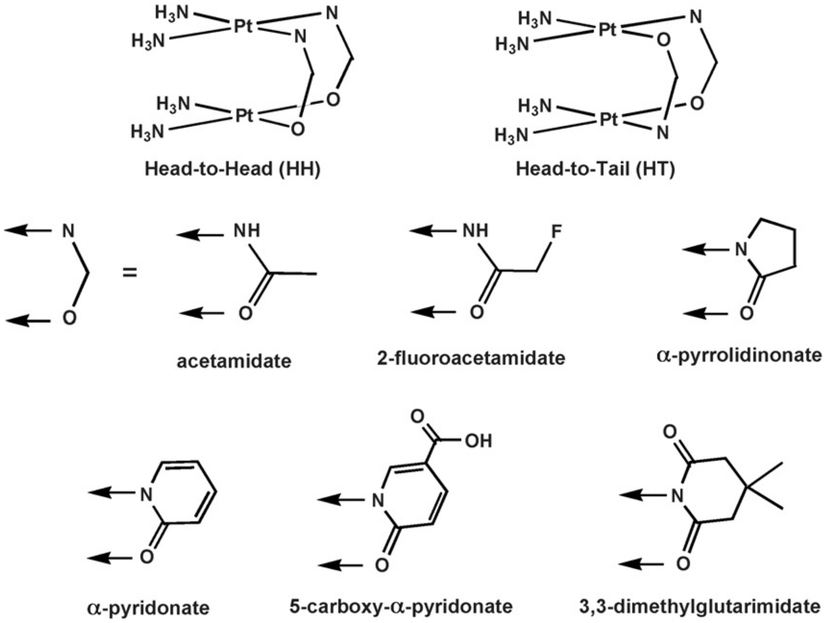
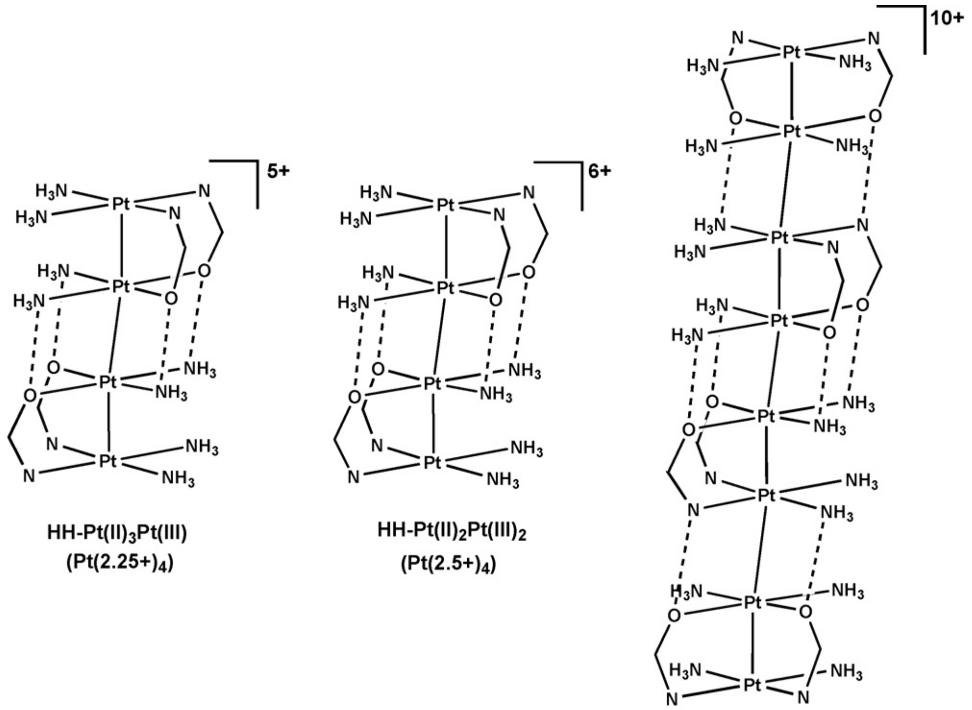


Fig. 2. Two stereo isomers, HH and HT, for the amidate-bridged *cis*-diammineplatinum dimers, together with some examples of bridging amidate ligands.



HH-Pt(II)$_3$Pt(III)
(Pt(2.25+)$_4$)

HH-Pt(II)$_2$Pt(III)$_2$
(Pt(2.5+)$_4$)

HH-Pt(II)$_6$Pt(III)$_2$
(Pt(2.25+)$_8$)

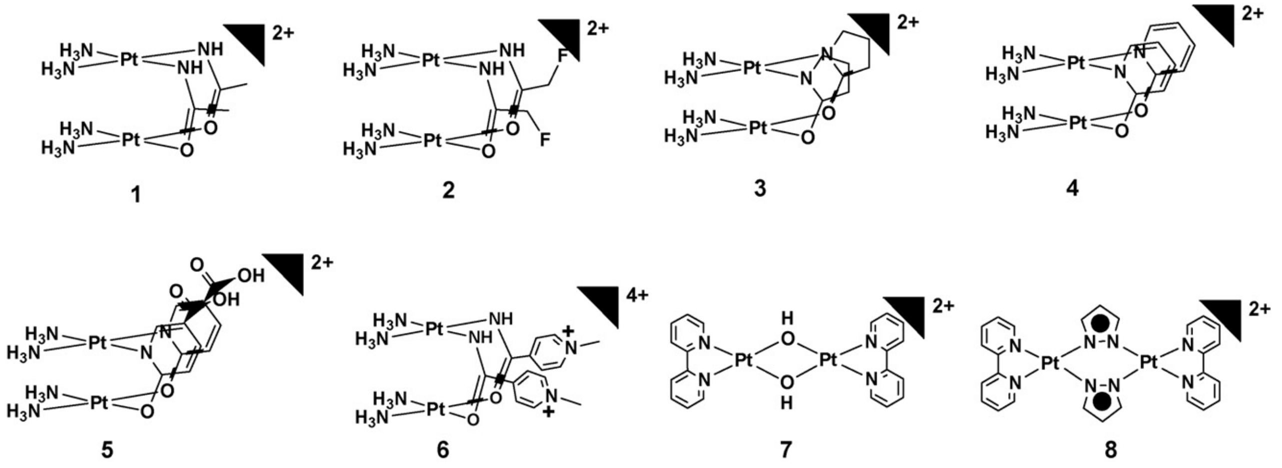
Fig. 3. Structures of HH-Pt(II)$_3$Pt(III) (dark blue compound), HH-Pt(II)$_2$Pt(III)$_2$ (dark red compound) and HH-Pt(II)$_6$Pt(III)$_2$ (reddish purple compound), where the abbreviated N-O is used to express each bridging amidate ligand. Dashed lines denote hydrogen bonds achieved between the ammines and the oxygen atoms of amidates, or those achieved between the N-H(amidate) groups and the oxygen atoms of amidates.

2. H_2-evolving activities of platinum(II) complexes

2.1. *Amidate-bridged platinum(II) dimers: structure–activity relationship*

2.1.1. *Redox disproportionation of mixed-valence tetranuclear and octanuclear platinum–blue related complexes*

The amidate-bridged *cis*-diammineplatinum(II) dimers with a general formula of $[Pt(II)_2(NH_3)_4(\mu\text{-amidato})_2]^{2+}$ (see Figs. 2–4) were reported to afford the so-called mixed-valence tetranuclear and octanuclear platinum–blue complexes upon the partial oxidation at the metal centers, $[Pt_2(NH_3)_4(\mu\text{-amidato})_2]_n^{z+}$ ($n = 2$ or 4; charge z depends on the average Pt oxidation state, such as $n, z = 2, 5$ for Pt(II)$_3$Pt(III), $n, z = 2, 6$ for Pt(II)$_2$Pt(III)$_2$, and $n, z = 4, 10$ for Pt(II)$_6$Pt(III)$_2$, etc.) [11–14]. Note that these compounds were characterized as Robin-Day Class III-A mixed-valence systems [12b]. For these compounds, the Pt(II) and Pt(III) peaks in the Pt 4f region of XPS, i.e. $4f_{7/2}$ and $4f_{5/2}$ peaks, are respectively averaged into a single compo-



1 **2** **3** **4** **5** **6** **7** **8**

Fig. 4. Structures of the Pt(II)$_2$ dimers with a variety of bridging ligands, where only the structures of HH isomers are shown for **1**–**6**.

nent within the time scale of XPS (10^{-17} s) [12a]. Therefore, the expressions with non-integral values, $\mathrm{Pt(2.25+)_4}$, $\mathrm{Pt(2.5+)_4}$, and $\mathrm{Pt(2.25+)_8}$, have been often used to describe their oxidation levels. In this review, the formal oxidation states rather than the non-integral ones will be used to describe their oxidation states together with their abbreviations.

In the 1970s and 1980s, the platinum–blue related compounds were not only investigated because of interests in the antitumor activity of the starting material, *cis*-$\mathrm{PtCl_2(NH_3)_2}$, but also due to interests in their unusual dark blue colors. All of these amidate-bridged $\mathrm{Pt(II)_2}$ dimers afford two stereo isomers, HH and HT isomers (Fig. 2), where the HH and HT isomers, respectively correspond to the head-to-head and head-to-tail isomer. In other words, this isomerism arises from the asymmetric character of the amidate ligand. The HH/HT isomerism largely affects the dimerization and tetramerization properties of the dimers, primarily due to the steric factors, as discussed below. The tetranuclear and octanuclear platinum complexes are given only from the stack of HH dimers [11–14]. Moreover, a dimer of HH dimers is generally given from the stack of the $\mathrm{N_2O_2}$-coordinated platinum ions in which the dimer–dimer association is generally stabilized with four hydrogen bonds formed between the ammines and the oxygen atoms of bridging amidate ligands (Fig. 3).

On the other hand, the interdimer interaction between the N(exocyclic amidate)-coordinated platinum ions (i.e., $\mathrm{N_4}$-coordinated ones) are hindered due to the steric bulks of exocyclic amidate rings. However, in the case of chain amidate ligands, such as acetamidate and 2-fluoroacetamidate, the octanuclear platinum chain structures are achieved due to the lower steric hindrances around the N(chain amidate)-coordinated platinum ions (see Fig. 3) [14]. In the earlier studies, the solution properties of these mixed-valence compounds remained unexplored. It was later ascertained that they are readily converted into the $\mathrm{Pt(II)_2}$ species in aqueous media in the presence of a sacrificial electron donor, such as EDTA, hydroquinone, etc. [10c,15]. For example, a dark red (tan) mixed-valence $\mathrm{Pt(II)_2Pt(III)_2}$ tetramer undergoes pH-dependent cleavage into the homovalence dimers, reaction (1) [10b,11a,15]. The $\mathrm{Pt(III)_2}$ dimer produced is then reduced by a sacrificial electron donor to give a solution of the $\mathrm{Pt(II)_2}$ dimer, reaction (1) [10c,15]. These behaviors were successfully characterized by UV–vis spectrophotometry and ^{1}H NMR spectroscopy. The observed pH-dependence was interpreted in terms of a hydrolysis equilibrium shown in reaction (2), since the rate law was observed to obey $k_{\mathrm{obs}} = k_1 + k_2K_{\mathrm{h}}/[\mathrm{H^+}]$ [15]. A nitrato-coordinated tetramer ($\mathrm{O_2NO{-}Pt(II)_2Pt(III)_2{-}ONO_2}$) and a chloro-coordinated tetramer ($\mathrm{Pt(II)_2Pt(III)_2{-}Cl}$) were structurally characterized by X-ray diffraction to confirm the axial ligation capability of the $\mathrm{Pt(II)_2Pt(III)_2}$ complex [11a]. The crystal structures of aqua-coordinated $\mathrm{Pt(II)_2Pt(III)_2}$ tetramers of both α-pyrrolidinonate and α-pyridonate ($\mathrm{Pt(II)_2Pt(III)_2{-}OH_2}$) have also been characterized by X-ray diffraction (unpublished results). The reaction rate for the bond dissociation at the central Pt–Pt bond supporting the tetranuclear structure is greatly accelerated by the stronger trans effect originated by the hydroxide ligand at the terminal site; the k_2 path is much faster than the k_1 path in reaction (2).

$$\begin{aligned} \mathrm{Pt(II)_2Pt(III)_2} &\longrightarrow \mathrm{Pt(II)_2} + \mathrm{Pt(III)_2} \\ &\xrightarrow{\text{Red}} 2\mathrm{Pt(II)_2} \end{aligned}$$

Red = EDTA, hydroquinone, etc.

(1)

$$\begin{tikzcd} \mathrm{Pt(II)_2Pt(III)_2\text{-}OH_2} \arrow[r, "k_1"] \arrow[d, shift left, "K_h"] & \mathrm{Pt(II)_2} + \mathrm{Pt(III)_2\text{-}OH_2} \arrow[d, shift left, "K_h'"] \\ \mathrm{Pt(II)_2Pt(III)_2\text{-}OH} \arrow[r, "k_2"] \arrow[u, shift left, "H^+"] & \mathrm{Pt(II)_2} + \mathrm{Pt(III)_2\text{-}OH} \arrow[u, shift left, "H^+"] \end{tikzcd}$$

$$\left[\; k_{obs} = \frac{k_1 + \dfrac{k_2K_h}{[\mathrm{H^+}]}}{1 + \dfrac{K_h}{[\mathrm{H^+}]}} \simeq k_1 + \frac{k_2K_h}{[\mathrm{H^+}]} \quad (K_h \ll [\mathrm{H^+}]) \;\right] \tag{2}$$

The dark blue mixed-valence $\mathrm{Pt(II)_3Pt(III)}$ tetramer was also reported to undergo a similar disproportionation reaction to give a 3:1 mixture of the $\mathrm{Pt(II)_2}$ and $\mathrm{Pt(III)_2}$ dimers via the formation of the $\mathrm{Pt(II)_2Pt(III)_2}$ tetramer, reaction (3) [10b,11a]. Thereby, the α-pyridonate-bridged $\mathrm{Pt(II)_2}$ dimer (**4** in Fig. 4) must be similarly given by dissolving the tetranuclear $\mathrm{Pt(II)_3Pt(III)}$ blue reported by Barton et al. [12a]. In addition to the $\mathrm{Pt(II)_2}$ dimers generated upon dissolution of these tetramers, the reddish purple mixed-valence $\mathrm{Pt(II)_6Pt(III)_2}$ octamer similarly gives the corresponding $\mathrm{Pt(II)_2}$ species in the presence of EDTA, as illustrated in reaction (4) [10c,14].

$$\begin{aligned} 2\mathrm{Pt(II)_3Pt(III)} &\rightleftharpoons \mathrm{Pt(II)_2Pt(III)_2} + 2\mathrm{Pt(II)_2} \\ &\rightleftharpoons 3\mathrm{Pt(II)_2} + \mathrm{Pt(III)_2} \\ &\xrightarrow{\text{EDTA}} 4\mathrm{Pt(II)_2} \end{aligned} \tag{3}$$

$$\begin{aligned} \mathrm{Pt(II)_6Pt(III)_2} &\xrightarrow{\substack{\text{extremely} \\ \text{rapid}}} \mathrm{Pt(II)_2Pt(III)_2} + 2\mathrm{Pt(II)_2} \\ &\rightleftharpoons 3\mathrm{Pt(II)_2} + \mathrm{Pt(III)_2} \\ &\xrightarrow{\text{EDTA}} 4\mathrm{Pt(II)_2} \end{aligned} \tag{4}$$

As a result, it has been ascertained that all the mixed-valence tetranuclear and octanuclear platinum blues and the related complexes are readily converted into a single redox species, i.e. the $\mathrm{Pt(II)_2}$ dimer, after dissolution of each compound into the photolysis solution involving an excess amount of EDTA (typically, 30 mM), as far as the dimer concentration is as low as those in the photolysis experiments (typically, 0.2 mM). Thus, the observed $\mathrm{H_2}$-evolving activities of these platinum–blue related complexes must reflect the activities of the corresponding $\mathrm{Pt(II)_2}$ dimers.

It is also noteworthy that some of the HH-$\mathrm{Pt(II)_2}$ dimers in Fig. 4 undergo rapid HH → HT isomerization, reaction (5), to give a mixture of two isomers. The α-pyrrolidinonate-bridged $\mathrm{Pt(II)_2}$ dimer (**3** in Fig. 4) was reported to establish the equilibrium within the time of dissolution [16]. On the other hand, the α-pyridonate-bridged $\mathrm{Pt(II)_2}$ dimer (**4**) was reported to be extremely slow in the HH → HT isomerization [17], presumably due to the lower structural flexibility of the dinuclear core [11a]. Therefore, the α-pyridonate-bridged $Pt(II)_2$ dimer (**4**) is expected to serve as an HH-$Pt(II)_2$ dimer during the catalysis. The rate of HH → HT isomerization for a 3,3-dimethylglutarimidate-bridged Pt(bpy) dimer, $[Pt_2(bpy)_2(\mu\text{-3,3-dimethylglutarimidato})_2]^{2+}$, was also reported to be quite slow at room temperature [18]. On the other hand, the acetamidate-bridged $Pt(II)_2$ dimer (**1**) shows gradual HH → HT isomerization over a half day (unpublished results).

$$\textbf{HH-Pt(II)}_2 \rightleftharpoons \textbf{HT-Pt(II)}_2 \qquad (5)$$

2.1.2. H_2-evolving activities of amidate-bridged $Pt(II)_2$ dimers: structure–activity relationship

The H_2-evolving activity of the α-pyrrolidinonate-bridged $Pt(II)_2$ dimer (**3**) was first discovered in 1986 while studying the possibility of adopting the platinum–blue related complexes as catalysts for the oxygen evolution from water. The study was evoked from the finding of Matsumoto et al. that O_2 evolves, in the dark, upon dissolution into aqueous media of the α-pyrrolidinonate-bridged compounds in the higher oxidation levels, such as $Pt(III)_2$ and $Pt(II)_2Pt(III)_2$ [11b,19]. While attempting to utilize the compounds as O_2-evolving catalysts, a trace amount of hydrogen gas was detected. Further, several homovalence and mixed-valence dimers and tetramers, $[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonate})_2]_n{}^{z+}$ ($n = 1$ or 2), were dissolved into aqueous solutions under Ar atmosphere to confirm that reduction of water into molecular hydrogen by these compounds is thermodynamically favorable [10b]. The study showed that hydrogen gas evolves upon mere dissolution of the compounds into aqueous solutions only in the absence of molecular oxygen, even though it does not take place in a quantitative fashion.

In the above context, the activities of compounds **3** and **4** as catalysts in the photochemical EDTA-reduction of water into molecular hydrogen were first evaluated using the three-component system described above in Fig. 1 [10a,b]. As shown in Fig. 5, the α-pyrrolidinonate- and the α-pyridonate-bridged $Pt(II)_2$ dimers (**3** and **4**) were found to be very efficient as H_2-evolving catalysts, even though their activities are still lower in comparison with that of the colloidal platinum, which had been well ascertained to be efficient as an H_2-evolving catalyst until the early 1980s [3–8]. An interesting feature is that the activities of **3** and **4** are considerably different from each other, which suggested that the H_2-evolving activities of the $Pt(II)_2$ dimers might be controlled by the structural change in the ligand system, by the change in the electron-donating or -withdrawing characters of the ligands, and also by the steric factors around the active centers. Importantly, it must be noted that the hydrogen evolution profiles of **3**, **4**, and the colloidal platinum well resemble with each other. In order to settle down the structure–activity relationship for the Pt(II)-catalyzed H_2 production from water, extensive efforts have been made to synthesize and structurally characterize new mononuclear and dinuclear platinum(II) complexes.

Further, it was found that the acetamidate- and 2-fluoroacetamidate-bridged $Pt(II)_2$ dimers (**1** and **2**) are similarly active as H_2-evolving catalysts [10c]. Importantly, the catalytic activities of these compounds together with the α-pyridonate and α-pyrrolidinonate compounds (**1**–**4**) are not correlated with their redox potentials corresponding to the $Pt(II)_2/Pt(III)_2$ couple, which lie in the range ca. 0.4–0.7 V: 0.42 V for **1** [10c], 0.52 V for **2** [10c], 0.53 V for **3** [20], and 0.63 V for **4** [21], where potentials are given versus SCE. These clearly indicate that a redox reaction expressed by $Pt(II)_2 + 2H^+ \rightarrow Pt(III)_2 + H_2$ is a thermodynamically unfavorable process. Nevertheless, it is important to note that the redox potential of each $Pt(II)_2/Pt(III)_2$ couple indirectly reflects the electron density at the metal center of each dimer. Importantly, the results of our studies rather suggested that the H_2-evolving activities of the $Pt(II)_2$ dimers are correlated with the Pt–Pt distances observed in X-ray crystallography (Fig. 6 and Table 1) [22]. An important consideration is that the HOMO in these amidate-bridged $Pt(II)_2$ dimers generally corresponds to the antibonding couple of the filled Pt(II) d_{z^2} orbital (the σ* orbital in Fig. 7), which must be greatly destabilized by the shortening of the Pt–Pt distance.

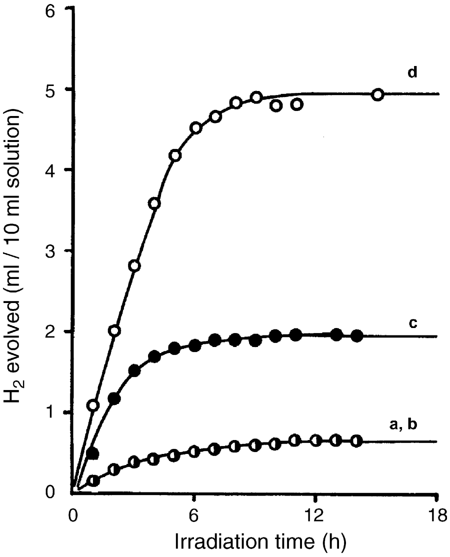


Fig. 5. Photochemical H_2 production from an aqueous acetate buffer solution (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na, pH 5.0; 10 ml) containing 30 mM EDTA, 0.04 mM $[Ru(bpy)_3]^{2+}$, and 2 mM MV^{2+} in the presence of an H_2-evolving catalyst: (a) 0.2 mM **3**, (b) 1.0 mM **3**, (c) 0.2 mM **4**, and (d) colloidal platinum reduced by citric acid (0.45 mg Pt per 10 ml). The photoirradiation was carried out using a 300 W Xe lamp. The photolysis solutions were immersed in a water bath thermostated at 20 °C (taken from Ref. [10b]).

On the other hand, the H_2-evolving activity of the 2-fluoroacetamidate dimer **2** is lower than that of the acetamidate dimer **1**, clearly due to the fact that the F atom serves as a strong electron-withdrawing group to stabilize the HOMO [10c]. The relationship between the electron-withdrawing character of the bridging amidate ligand and the bridged Pt–Pt distance will be discussed in detail in Section 2.4.

In addition to the above results, a hydroxo-bridged Pt(bpy) dimer **7** was also found to be effective as plotted in Fig. 6 [10d], where the value of Pt–Pt = 3.085(1) Å [24a] reported for *cis*-diammineplatinum(II) dimer, $[Pt_2(NH_3)_4(\mu\text{-OH})_2]^{2+}$, is adopted. More interestingly, a pyrazolate-bridged Pt(bpy) dimer **8**, which possesses a relatively long Pt–Pt distance (Pt–Pt = 3.231(1) Å [25b]), was found to be ineffective at all

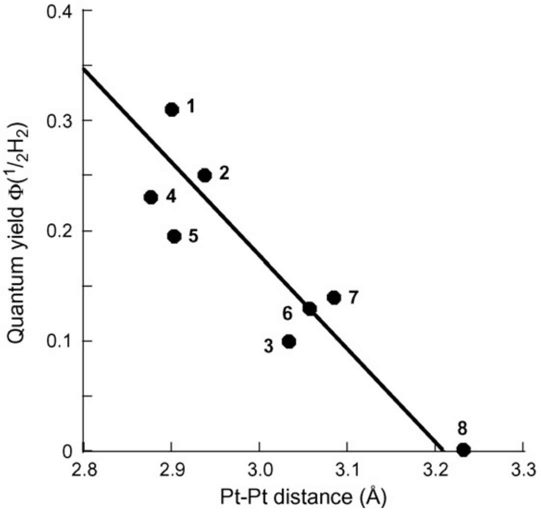


Fig. 6. Plot of the quantum yields, estimated from the initial rate of H_2 formation, as a function of the intradimer Pt–Pt distance for various Pt(II) dimers (**1**–**8**).

[10d] (see Fig. 6). These results suggested that the H_2-evolving activities of the $Pt(II)_2$ dimers are somehow correlated with the bridged Pt–Pt distances. In order to further ascertain the validity of this idea, the mononuclear platinum(II) complexes that are free of either dimerization or oligomerization in solution were examined, since such compounds allowed us to examine those having no Pt–Pt interaction. As summarized in Table 1, simple mononuclear Pt(II) complexes having amine or pyridyl type of ligands, such as $[Pt(NH_3)_4]^{2+}$ (**9**) and $[Pt(bpy)_2]^{2+}$ (**10**), exhibit much lower H_2-evolving activity under the same experimental conditions [10d]. With these considerations in mind, our prediction has been that *the dimeric compounds with a shorter Pt–Pt distance and/or a stronger Pt–Pt interaction give rise to the higher H_2-evolving activity*, in which the filled Pt(II)-d_{z^2}-based molecular orbital must be involved in the hydrogenic activation.

2.2. Mononuclear platinum(II) complexes

As discussed above, the mononuclear platinum(II) complexes were initially confirmed to exhibit much lower H_2-evolving activity, which was attributed to the relatively stabilized Pt(II) d_{z^2} orbital. In addition to the lower activities observed for **9** and **10**, some other simple complexes **11**–**13** (Fig. 8) were further confirmed to be similarly inactive as catalysts toward the hydrogen production from water (see Table 1). Nevertheless, it was later found out that some exceptions exist. An important exception is the relatively high H_2-evolving activity observed for tetrakis(thiourea)platinum(II), **14** (see Table 1) [10d]. This might be relevant to the higher polarizability of the sulfur donor atom which serves as a relatively strong donor to destabilize the filled Pt(II) d_{z^2} orbital, even though the more detailed studies must be further undertaken to rationalize the observed tendency.

Table 1

Quantum yields for the photochemical hydrogen production catalyzed by various platinum(II) complexes, together with the bridged Pt–Pt distances and the electrochemical data[a]

Catalyst (mM)	Pt–Pt dist. (Å)	$E_{1/2}(Pt_2^{II}/Pt_2^{III})$ (V vs. SCE)	$\Phi(0.5H_2)$[b]
$[Pt_2(NH_3)_4(\mu\text{-acetamidato})_2]^{2+}$ (**1**) (0.2)	2.9[c]	0.42 [10c]	0.31 [10c]
$[Pt_2(NH_3)_4(\mu\text{-2-fluoroacetamidato})_2]^{2+}$ (**2**) (0.2)	2.938(5)[d]	0.52 [10c]	0.25 [10c]
$[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2]^{2+}$ (**3**) (0.2)	3.033(2) [16]	0.53 [20]	0.10 [10c]
$[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2]^{2+}$ (**4**) (0.2)	2.8767(7) [23]	0.63 [21]	0.23 [10c]
$[Pt_2(NH_3)_4(\mu\text{-5-carboxy-}\alpha\text{-pyridonato})_2]^{2+}$ (**5**) (0.2)	2.9023(8) [35b]		0.20[c]
$[\mathbf{6}]^{4+}$ (0.2)	3.0569(8) [34a]		0.13 [22b]
$[Pt_2(bpy)_2(\mu\text{-OH})_2]^{2+}$ (**7**) (0.2)	3.085(1) [24a]		0.14 [22b]
$[Pt_2(bpy)_2(\mu\text{-pz})_2]^{2+}$ (**8**) (0.2)	3.231(1) [25b]		0.002 [22b]
$[Pt(NH_3)_4]Cl_2$ (**9**) (0.4)			0.01 [10d]
$[Pt(bpy)_2](ClO_4)_2$ (**10**) (0.4)			0.02 [10d]
$[Pt(bpy)(NH_3)_2]Cl_2\cdot 2H_2O$ (**11**) (0.1)			none [26]
cis-$[Pt(NH_3)_2(pzH)_2](NO_3)_2$ (**12**) (0.4)			none[c]
$[Pt(pzH)_4](BF_4)_2$ (**13**) (0.4)			none[c]
$[Pt(SC(NH_2)_2)_4](NO_3)_2$ (**14**) (0.4)			0.043 [10d]
cis-$PtCl_2(NH_3)_2$ (**15**) (0.1)			0.20 [26]
$PtCl_2(en)$ (**16**) (0.1)			0.24 [26]
cis-$PtCl_2(4\text{-methylpyridine})_2$ (**17**) (0.1)			0.22 [26]
$PtCl_2(bpym)$ (**18**) (0.1)			0.17 [26]
$PtCl_2(dcbpy)\cdot H_2O$ (**19**) (0.1)			0.029 [26]
$[PtCl(terpy)]Cl\cdot H_2O$ (**20**) (0.1)			0.024 [26]
$[\mathbf{24}]^{6+}$ (0.2)	3.0304(7) [34c]		0.37 [22b], 0.14[e] [22b]
$[\mathbf{25}]^{6+}$ (0.2)	3.0852(13) [34b]		0.24 [22b], 0.11[e] [22b]
$[\mathbf{26}]^{4+}$ (0.2)			0.22 [22b]
$[\mathbf{27}]^{4+}$ (0.2)			0.10 [22b]

[a] Hydrogen production from an aqueous acetate buffer solution (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na; pH 5.0, 10 ml) containing 30 mM EDTA, 0.04 mM $[Ru(bpy)_3](NO_3)_2\cdot 3H_2O$, 2 mM $[MV](NO_3)_2$, and a Pt(II)-complex catalyst, irradiated with a 350 W Xe lamp at 20 °C in Ar.

[b] The quantum yield was estimated from the initial rate of H_2 production, as previously described [10c].

[c] Unpublished results.

[d] Taken from those for the outer dimer units in the octaplatinum chain structure, for they are much longer than those in the inner two dimer units [14b,c].

[e] Values are those determined in a two-component system, in the absence of MV^{2+} under the conditions described above in footnote a.

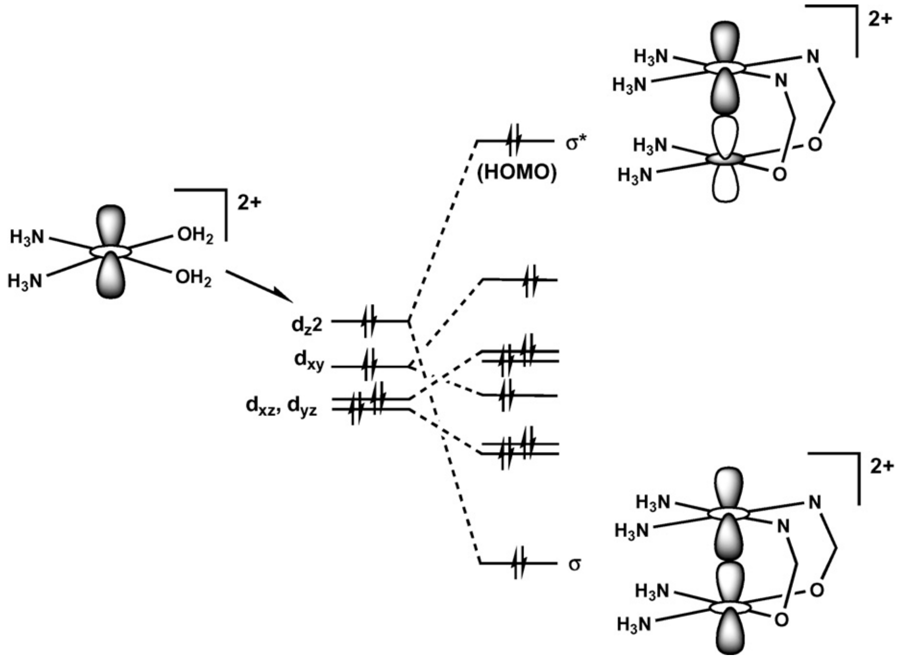


Fig. 7. Molecular orbital diagrams of *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ (left) and $[Pt(II)_2(NH_3)_4(\mu\text{-amidato})_2]^{2+}$ (right).

On the other hand, it was also ascertained that the monochloro- and dichloro-coordinated mononuclear platinum(II) complexes, such as *cis*-$PtCl_2(NH_3)_2$ (**15**), $PtCl_2(en)$ (en = ethylenediamine) (**16**), and *cis*-$PtCl_2$(4-methylpyridine)$_2$ (**17**), are, more or less, active as H_2-evolving catalysts, even though their activities are still lower in comparison with the $Pt(II)_2$ dimers having a strong Pt–Pt interaction [26]. It was suggested that the negatively charged chloride ions give rise to the higher energy level of the Pt(II) d_{z^2} orbital [26]. It seems also probable that neutralization of the Pt(II) coordination sphere by the coordination of anionic ligands improves the affinity between the Pt(II) center and a hydrogen ion.

It was also confirmed that the apparent catalytic efficiency is greatly affected by the addition of simple salts, such NaCl, NaSCN, etc. For instance, the TON (turn over number) dramatically increases when NaCl is added to the photolysis solution of $PtCl_2(dcbpy)\cdot H_2O$ (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) (**19**) [27], revealing that the solvolysis equilibrium of **19**, equilibrium (6), can be shifted to the left side under the higher Cl^-

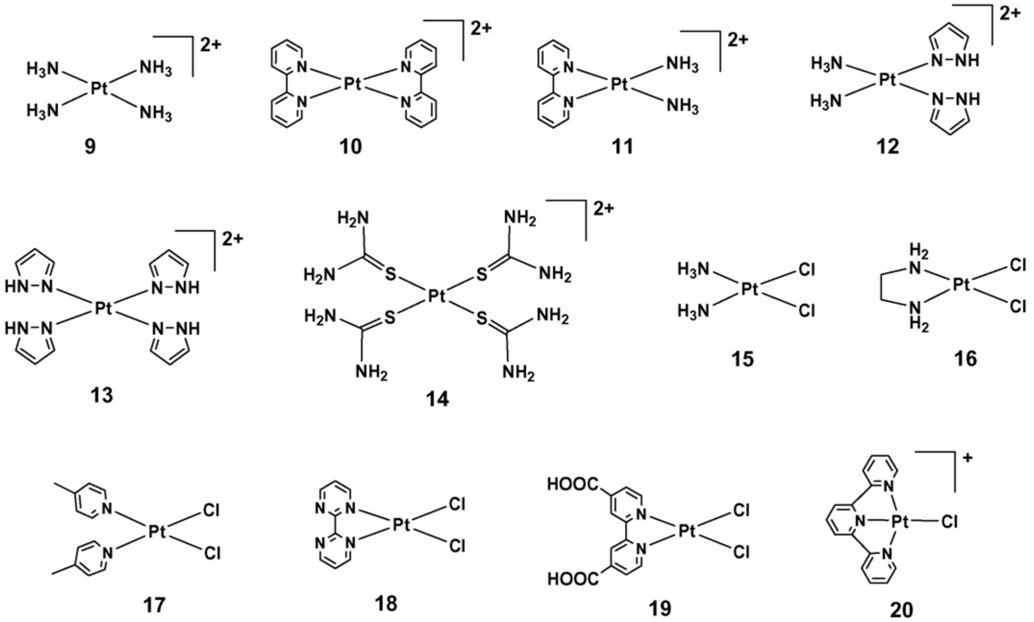
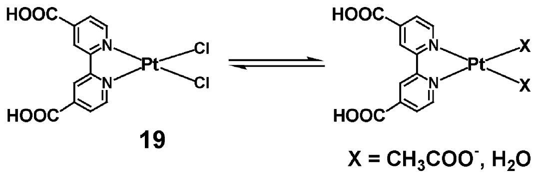


Fig. 8. Structures of mononuclear Pt(II) complexes.

concentrations to maximize the concentration of the dichloro species which is expected to have a higher H_2-evolving activity in comparison with the aqua or acetato species.



19

X = CH_3COO^-, H_2O

(6)

2.3. Some aspects on the degradation of the photosystem

Now the degradation properties of the system under the photolysis conditions given in Fig. 5 are discussed. The degradation of the photochemical system takes place due to several major reasons, as reported by other researchers [7b,c] and also by the authors' group [10c]. The most important contribution is a hydrogenation of methylviologen to give the piperidine derivatives with consumption of the hydrogen gas evolved during the photolysis, presumably catalyzed either by the colloidal platinum or by the Pt(II) complexes [7b,c,10c]. This contribution can be minimized by removing the hydrogen gas evolved within the photolysis cell by continuous bubbling of Ar (or N_2) through the solution, as carried out in our recent studies [26,28].

On the other hand, decomposition of the amidate-bridged $Pt(II)_2$ dimers gradually proceeds; ca. 30% of the $Pt(II)_2$ dimer dissolved is degraded after 2 h of photoirradiation when a closed vial system is employed [10c]. It must be emphasized here that no acceleration in the rate of H_2 formation occurs as the decomposition of the $Pt(II)_2$ dimer proceeds, indicating that a new species with a higher H_2-evolving activity is not generated upon decomposition of the complexes. The rate of decomposition of the amidate-bridged $Pt(II)_2$ dimer was also confirmed to be rather slow by using the in situ cyclic voltammetric analysis for the one-step two-electron redox wave corresponding to the $Pt(II)_2/Pt(III)_2$ couple (unpublished results). It was also suggested that the so-called 'photodecomposition' of the $Pt(II)_2$ dimer is not the major cause of decomposition, for the α-pyrrolidinonate $Pt(II)_2$ dimer does not possess any absorption band above ca. 300 nm [10b]. Importantly, it was also ascertained in our group that even the photosensitizer, $[Ru(bpy)_3]^{2+}$, decomposes as the photolysis proceeds. Under the typical photolysis conditions (350 W Xe), ca. 20% of $[Ru(bpy)_3]^{2+}$ is decomposed after 4 h of photoirradiation, which was monitored from the decrease in absorbance at 452 nm corresponding to the so-called metal-to-ligand charge-transfer (MLCT) band of $[Ru(bpy)_3]^{2+}$ (unpublished results).

Thus, the degradation must be interpreted in terms of concomitant decomposition of most of the chemical species involved in the photolysis solution. If any of the decomposition products generated in the initial stage of the reaction possesses an improved catalytic efficiency, acceleration in the H_2 formation must be observed. However, this is not the case for most of the Pt(II) complexes investigated thus far in our group. As shown in Fig. 5, the hydrogen evolution profiles of colloidal platinum together with those of the amidate-bridged $Pt(II)_2$ dimers are quite similar to each other and show no remarkable induction period.

An important example exhibiting an exceptionally long induction period in the H_2 formation curve is K_2PtCl_4, as demonstrated well in the original report of Lehn and Sauvage [5b], and also in the report of Sutin et al. [8c]. The remarkable difference between the H_2 formation curves of K_2PtCl_4 and **1** is exemplified in Fig. 9. As shown in Fig. 9, the induction period observed for K_2PtCl_4 is 30–40 min, while that of the acetamidate dimer **1** is much shorter than that of K_2PtCl_4. It also shows that the colloidal platinum generated from K_2PtCl_4 under these conditions is not so high in its activity, presumably due to the rapid aggregation leading to deposition of a large amount of black powder as the photolysis proceeds. It must be also emphasized that there is continuous increase in the rate of H_2 formation for K_2PtCl_4, which is quite different from the behavior of **1** (Fig. 9). The initial very short induction period (ca. 5 min) observed for **1** is consistent with the period required to obtain a blue photolysis solution, at the end of which the $MV^{+\bullet}$ concentration must be maximized. The induction period observed for K_2PtCl_4 in Fig. 9 is roughly consistent with that reported for the $[Ru(bpy)_3]^{2+}/[Rh(bpy)_3]^{3+}/[PtCl_4]^{2-}$ system (induction period, 20–30 min) [8c]. Lehn and Sauvage first introduced a concept that the generation of colloidal platinum from K_2PtCl_4 can be understood as a thermal reduction (*not a mere photochemical decomposition*) of $[PtCl_4]^{2-}$ because of the relatively high redox potential of the $[PtCl_4]^{2-}/Pt^0$ couple (+0.49 V versus SCE), which must be coupled with the photogenerated reducing reagent, such as Rh(I) species [5b].

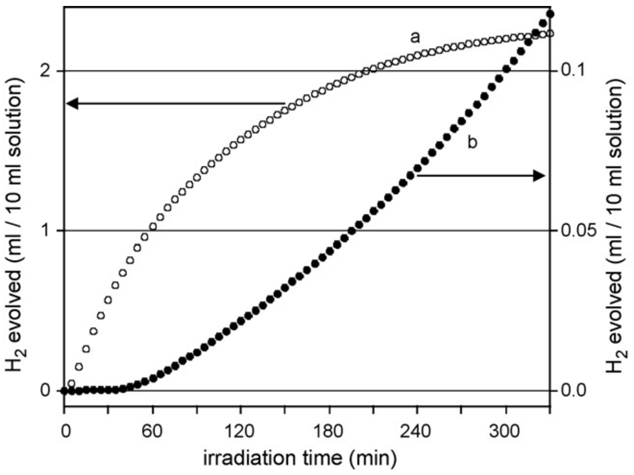


Fig. 9. Photochemical H_2 production from an aqueous acetate buffer solution (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na, pH 5.0; 10 ml) containing 30 mM EDTA, 0.04 mM $[Ru(bpy)_3](NO_3)_2·3H_2O$, and 2 mM $[MV](NO_3)_2$, in the presence of an H_2-evolving catalyst: (a) 0.2 mM **1**; (b) 0.4 mM K_2PtCl_4. The photoirradiation was carried out using a 350 W Xe lamp (Ushio UXL500D-O operated at 350 W; an ozone-free arc lamp). The photolysis solutions were immersed in a water bath thermostated at 20 °C (the automatic H_2 measurement system [26,28] was used), where a Pyrex vial itself was used to eliminate most of the ultraviolet-light irradiation.

Furthermore, it must be also noted that $[PtCl_4]^{2-}$ forms an ion pair with $[Ru(bpy)_3]^{2+}$ with the equilibrium constant being $K_{eq} = 250\,M^{-1}$ [29], leading to the effective quenching of the ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$ ($[Ru^*(bpy)_3]^{2+}$), which may be considered as another reason for the observed long induction period. It is also noteworthy that the photoirradiation (350 W Xe, 6 h) of an acetate buffer solution of K_2PtCl_4 (pH 5) does not lead to generation of colloidal platinum (unpublished results). Moreover, it was spectrophotometrically confirmed, prior to the photolysis, that the solution prepared for Fig. 9b was free of any precipitate attributable to a double salt, $[Ru(bpy)_3][PtCl_4]$.

On the other hand, our electrochemical studies have shown that the amidate-bridged $Pt(II)_2$ dimers do not exhibit any reduction wave, attributable to the Pt(II)/Pt(I) couple, down to ca. −1.3 V versus SCE (unpublished results). It is also noteworthy that the Pt(II)/Pt(I) redox couple was reported to be −0.97 V versus SCE for $[Pt(bpy)_2]^{2+}$ [30] and −0.78 V versus SCE for $[PtCl(terpy)]^+$ [31]. Considering the redox potential of the $MV^{2+}/MV^{+\bullet}$ couple (−0.51 V versus SCE [32]), the reduction of these Pt(II) species into the corresponding Pt(I) species by $MV^{+\bullet}$ is thermodynamically unfavorable. In addition, the reduction of these Pt(II) species by $[Ru^*(bpy)_3]^{2+}$ is still not strongly favored due to the fact that the redox potential of the $[Ru(bpy)_3]^{3+}/[Ru^*(bpy)_3]^{2+}$ couple (−1.08 V versus SCE [1b]) is rather close to the above-mentioned Pt(II)/Pt(I) couples. Moreover, considering the relatively high concentration of MV^{2+} under the photolysis conditions (typically, 2.0 mM), it is obvious that the quenching of $[Ru^*(bpy)_3]^{2+}$ by MV^{2+} must be the major contribution to the quenching of $[Ru^*(bpy)_3]^{2+}$.

2.4. *Effects of electron-acceptor units attached to the platinum(II) complexes*

In addition to our recent finding on the considerable enhancement in the H_2-evolving activities of the chloro-coordinated complexes (Section 2.2), it was also found that the introduction of electron-acceptor ligands to the mononuclear Pt(II) complexes leads to the effective enhancement in the H_2-evolving activity [22b,26,27,33]. Various mononuclear Pt(II) complexes having *N*-methyl-4,4′-bipyridinium units (MQ^+) were prepared [27,33] to reveal that most of them are, more or less, active as H_2-evolving catalysts, even though their activities do not exceed those of both the $Pt(II)_2$ dimers (**1**–**6**) and the dichloro-coordinated complexes (**15**–**19**) [26]. For instance, compounds **21** and **22** in Fig. 10 exhibit the lowest level of catalytic activities, which are comparable to those of **19** and **20** but are much higher than those of **9**–**13**. More interestingly, compound **23** exhibits almost no activity. This has been interpreted so far in terms of the steric factors, as described below in Section 2.5.

On the other hand, some amidate-bridged *cis*-diammineplatinum(II) dimers tethered to viologen or pyridinium moieties were prepared to examine the catalytic enhancement in the H_2-evolving activity. Examples of such complexes are **6** (Fig. 4) and **24**–**27** (Fig. 10). All of these compounds were structurally characterized by X-ray diffraction (**24** [34c], **25** [34b], and **6** [34a]; the structures of **26** and **27** will appear in our future publications). The photochemical hydrogen production catalyzed by compounds **6** and **24**–**27** are shown in Fig. 11, together with that of the acetamidate-bridged $Pt(II)_2$ dimer **1**. It was found that the H_2-evolving activity is quite sensitive to

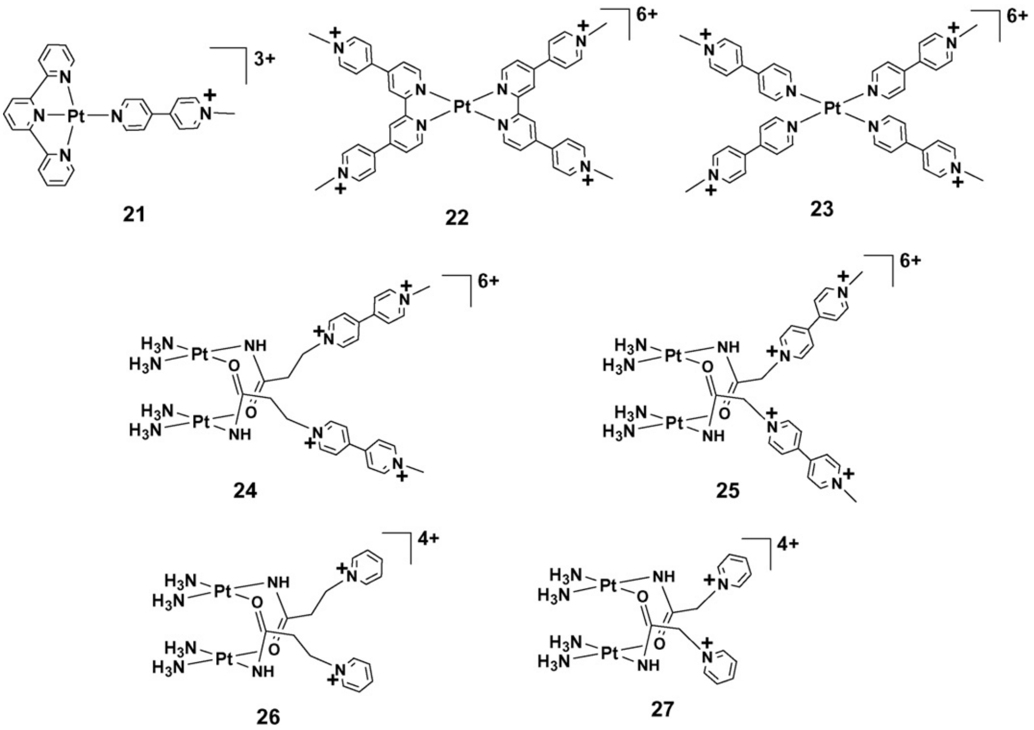


Fig. 10. Structures of mononuclear and dinuclear Pt(II) complexes having electron-acceptor units.

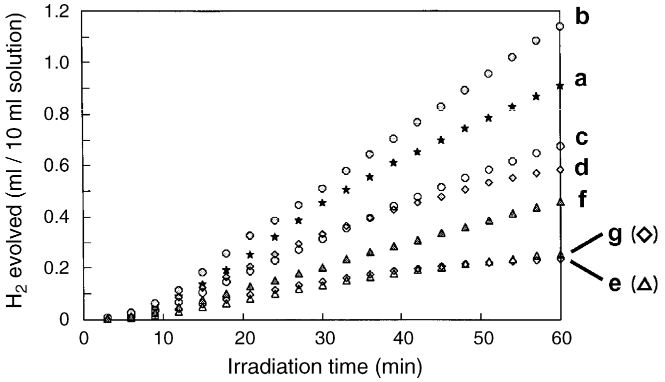
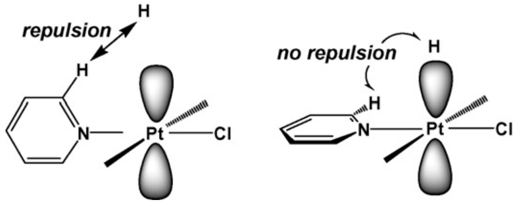


Fig. 11. Photochemical H_2 production from an aqueous acetate buffer solution (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na, pH 5.0; 10 ml) containing 30 mM EDTA, 0.04 mM $[Ru(bpy)_3](NO_3)_2 \cdot 3H_2O$ with additional components: (a) 2 mM $[MV](NO_3)_2$ and 0.2 mM **1**; (b) 2 mM $[MV](NO_3)_2$ and 0.2 mM **24**; (c) 2 mM $[MV](NO_3)_2$ and 0.2 mM **25**; (d) 2 mM $[MV](NO_3)_2$ and 0.2 mM **26**; (e) 2 mM $[MV](NO_3)_2$ and 0.2 mM **27**; (f) 0.2 mM **24**; (g) 0.2 mM **25**. The photoirradiation was carried out using a 350 W Xe lamp. The photolysis solutions were immersed in a water bath thermostated at 20 °C (the automatic H_2 measurement system [26,28] was used).

the length of the alkyl chain connecting the bridging amidate ligand and the electron-acceptor unit. The fact indicated that the introduction of a strongly electron-withdrawing pyridinium or bipyridinium unit into the amidate ligand results in marked elongation of the bridged Pt–Pt distance, leading to the lowering in the H_2-evolving activity. Such an elongation in the bridged Pt–Pt distance has been well discussed in our recent structural reports [34,35]. For instance, the bridged Pt–Pt distance in **24** (3.0304(7) Å [34c]) was reported to be shorter than that in **25** (3.0852(13) Å [34b]), since the shorter alkyl chain length permits the closer contact between the positively charged MV^{2+} derivative and the bridging amidate ligand, giving rise to the stronger electron-withdrawing effect of the ligand towards the Pt center. As shown in Fig. 11, the H_2-evolving activity of **24** (Fig. 11b) is much higher than that of **25** (Fig. 11c), which is consistent with the structure–activity relationship proposed in Fig. 6. In the same manner, the activity of **26** (Fig. 11d) is much higher than that of **27** (Fig. 11e).

Another important character found for compounds **24** and **25** is that hydrogen evolves even in the absence of MV^{2+} (see Fig. 11f and g). In the presence of MV^{2+} (Fig. 11b and c), $[Ru^{*}(bpy)_3]^{2+}$ must be efficiently quenched by MV^{2+}, since MV^{2+} is contained at a relatively high concentration (2 mM). On the other hand, the net concentration of a quencher, i.e. the dimer tethered to MV^{2+}, under the conditions in Fig. 11f and g (0.2 mM) is much lower than the standard concentration (2 mM), revealing that compounds **24** and **25** are regarded not only as an efficient H_2-evolving catalyst but also as an efficient quenching reagent. These results, for the first time, reveal that relatively efficient two-component systems ($[Ru(bpy)_3]^{2+}$ and an H_2-evolving catalyst) can be achieved by the introduction of such electron-acceptor units onto the Pt(II)-catalyst molecules. It must be also noted that the activity of **24** (Fig. 11b) is slightly higher than that of the acetamidate-bridged $Pt(II)_2$ dimer with no tethering viologen moiety **1** (Fig. 11a).

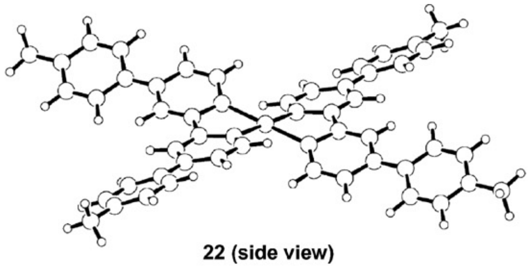


Scheme 1.

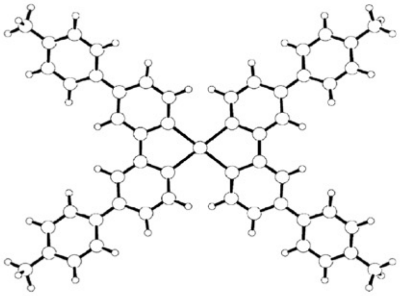
These facts together with the enhancement observed for the Pt(II)-MQ derivatives clearly indicate that the overall H_2 evolution efficiency is not only governed by the catalytic efficiency in the actual H_2-evolving process but also controlled by the electron-transfer efficiency between $[Ru^{*}(bpy)_3]^{2+}$ and the Pt(II)-catalyst molecule. It was also confirmed that **26** and **27** do not exhibit any reduction wave near the redox potential for the $MV^{2+}/MV^{+\bullet}$ couple (*vide supra*), indicating that the pyridinium units in **26** and **27** are not suitable as electron-acceptor units. Consequently, photochemical hydrogen production is not driven by the two-component system made up of $[Ru(bpy)_3]^{2+}$ and **26** (or **27**).

2.5. *Steric effects for the H_2-evolving activities of platinum(II) catalysts*

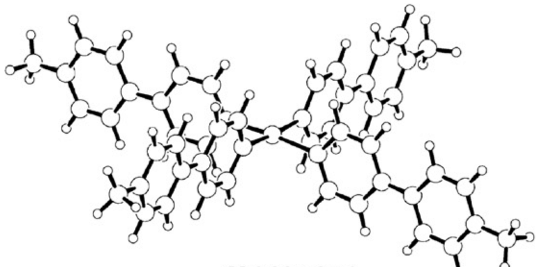
Steric factors at the axial site of the Pt(II) ion also affect the catalytic efficiency in the H_2 formation. As illustrated in Scheme 1, when a hydrogen atom attached to the coordinated pyridyl ligand is closely located near the filled Pt(II) d_{z^2} orbital, approach of a hydrogen ion towards the d_{z^2} orbital is sterically hindered due to the steric repulsion between the two H atoms (Scheme 1, left). On the other hand, the hydrogenic activation at the axial site of the Pt(II) ion is sterically allowed when the pyridyl ligand bound to the Pt(II) ion is coplanar with the Pt(II) coordination plane (see Scheme 1, right). At the moment, there are two good examples consistent with this interpretation. One is that compound **23** exhibits almost no activity, in sharp contrast with the relatively high H_2-evolving activity observed for compound **22** [27,33c]. As shown in Fig. 12, compound **23** does not have a planar geometry due to the steric contacts between the hydrogen atoms on the 2,6-positions of the four coordinated pyridyl ligands, and rather favors a conformation in which the bipyridinium planes are perpendicularly located with respect to the Pt(II) coordination plane. On the other hand, compound **22** has a planar geometry, in which a Pt–H interaction at the axial site is sterically allowed. The other example is given by a Ru(II)Pt(II) dimer **33** (see Fig. 13). When **33** is employed as an H_2-evolving catalyst in the three-component system, hydrogen production does not occur at all [26]. Nevertheless, *cis*-$PtCl_2$(4-methylpyridine)$_2$ (**17**), which is regarded as a structural analog for the Pt(II) center involved in **33**, exhibits effective H_2-evolving activity [26]. The facts indicated that the formation of a relatively rigid metallocycle in **33** affords canted geometries of the pyridyl ligands (Scheme 1, left), which is unfavorable for the hydrogenic activation at the axial site of the Pt(II) ion [26]. Such Pt–H interactions have been extensively investi-



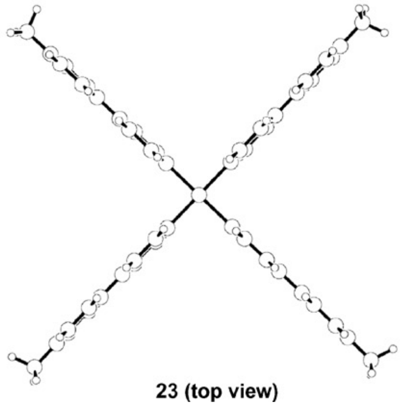
22 (side view)



22 (top view)



23 (side view)



23 (top view)

Fig. 12. Structures of mononuclear Pt(II) complexes **22** and **23**, fully optimized at the B3LYP level of DFT calculations using the LanL2DZ basis set (Gaussian 03 [36]).

gated in our group using the DFT MO calculations (unpublished results).

3. Development of photo-hydrogen-evolving molecular devices

Efforts have also been made to develop molecular devices made up of both the photosensitizing $[Ru(bpy)_3]^{2+}$ derivatives and the H_2-evolving Pt(II) catalysts. A variety of heteronuclear Ru(II)Pt(II) complexes had been prepared and evaluated until the authors realized the first effective model of a photo-hydrogen-evolving molecular device (**34** [28] in Fig. 13). In the earlier studies, relatively simple models (**28–31**) were developed and their photo-hydrogen-evolving activities were tested [22,37]. However, it was found that these compounds do not preserve the important photochemical properties required to enhance the visible-light-induced charge separation process: the strong electronic coupling between the $Ru(bpy)_3{}^{2+}$-like moiety and the heavy Pt ion promotes the quenching of the ^{3}MLCT excited state of the $Ru(bpy)_3{}^{2+}$-like moiety [26]. Thus, in the later studies, the multinuclear Ru(II)Pt(II) compounds having luminescent $Ru(bpy)_3{}^{2+}$-like moieties have been the major targets in our research [26,38]. Although luminescent compounds **32** and **33** do not exhibit any desirable photo-hydrogen-evolving activity at all, compound **34** actually drives the reduction of water by EDTA into molecular hydrogen under the visible-light illumination [28]. Importantly, a mere mixture of two precursor compounds of **34** (e.g., a combination of $[Ru(bpy)_2(5\text{-amino-1,10-phenanthroline})]^{2+}$ and **19**) does not give rise to the photochemical H_2 generation, which clearly rejects a possibility that a certain decomposed species, such as colloidal platinum, serves as a catalytically active species in the H_2 formation. In other words, this finding can be regarded as another important evidence for the Pt(II)-catalyzed H_2 production from water. In spite of the structural similarity between compounds **32–34**, only compound **34** behaves as a photo-hydrogen-evolving molecular device [26]. This was interpreted in terms of the fact that only the bridging spacer connecting the Ru(II) and Pt(II) centers in **34** has a wholly sp^2-hybridized character, in sharp contrast with the aliphatic bridging spacer moieties involved in **32** and **33** (propylene units in **32** and methylene units in **33**).

On the other hand, a trinuclear $Ru(II)_2Pt(II)$ complex **35** and a tetranuclear $Ru(II)_2Pt(II)_2$ complex **36** were successfully prepared and characterized [27]. However, they were also found to be inactive as a photo-hydrogen-evolving molecular device. It was suggested that the intramolecular energy transfer quenching among the two Ru(II) chromophores is strongly enhanced and therefore deactivation of the ^{3}MLCT excited state of the complex is rather fast in these systems. In the latter case, it was also suggested that the so-called metal–metal-to-ligand charge transfer transition at the diplatinum entity in **36** (the values of $\lambda_{max} = 475$ nm and $\varepsilon = 2110\,M^{-1}\,cm^{-1}$ were reported for the analogous $Pt(II)_2$ dimer $[Pt_2(bpy)_2(\mu\text{-pivalamidato})_2]^{2+}$ [39]) promotes the energy transfer quenching of the ^{3}MLCT excited state of the $Ru(bpy)_3{}^{2+}$-like unit [27].

Finally, some important Ru(II)Pt(II) analogs, together with other combined systems consisting of a photosensitizer and a non-platinated H_2-evolving catalyst, must be discussed as follows. In 1986, Rillema et al. reported on several Ru(II)Pt(II) complexes having a *cis*-$PtCl_2$ unit (compounds **37–39** in Fig. 14), with some attention paid to their potential use as photo-hydrogen-evolving molecular devices [40]. Yam et al. and Brewer et al. also reported on the syntheses of some related Ru(II)Pt(II) dimers, even though their studies did not focus on the photo-hydrogen-evolving activities of the complexes [41,42]. As discussed above, the ineffectiveness of **29**, which was first prepared by Yam et al. [41], was ascertained by the

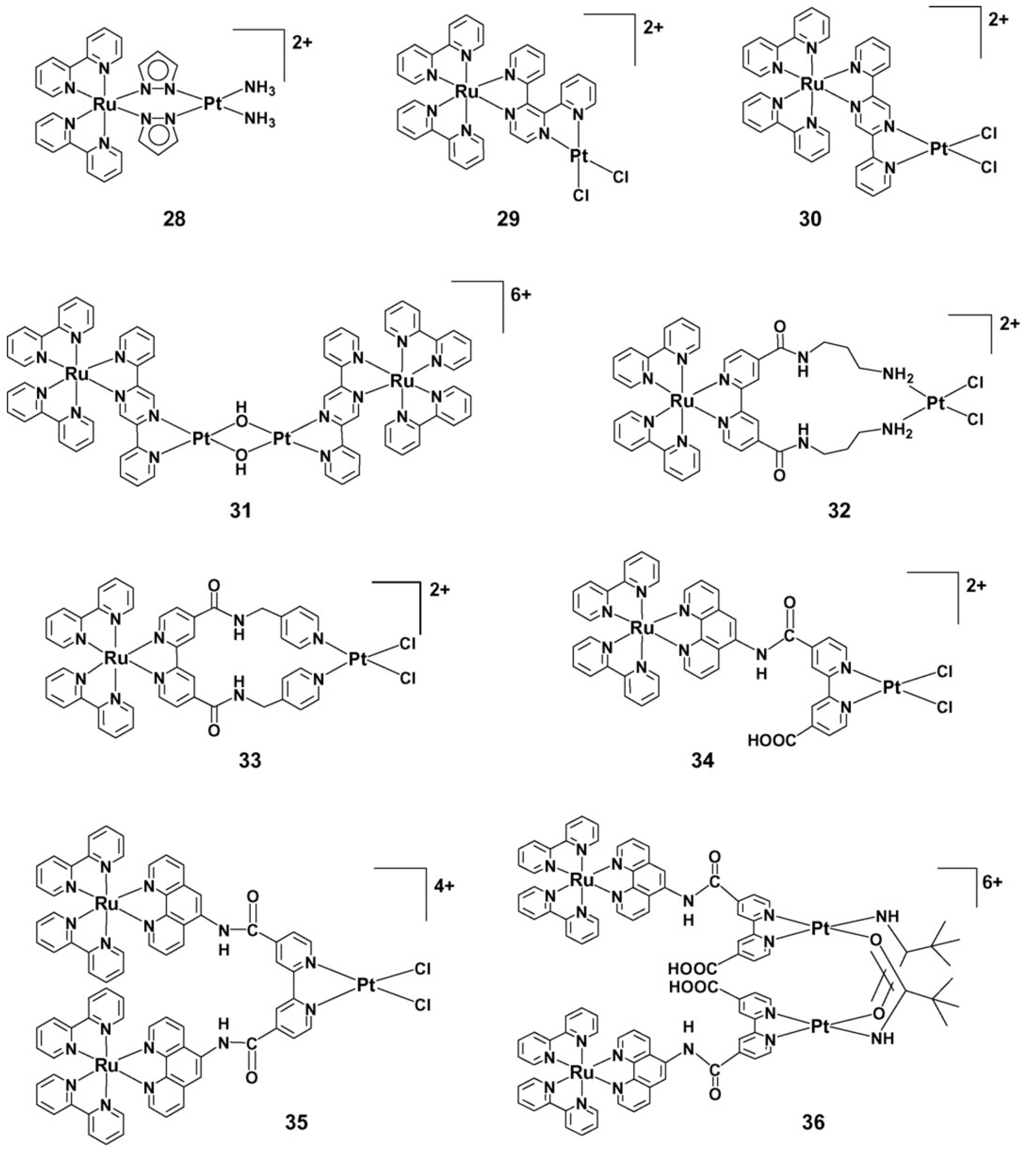


Fig. 13. Structures of multinuclear Ru(II)Pt(II) complexes.

authors [26]. On the other hand, Brewer et al. also reported on the syntheses and DNA-binding properties of $[(bpy)_2Ru(\mu\text{-bridge})PtCl_2]^{2+}$ (bridge = 2,3-bis(2-pyridyl)quinoxaline and 2,3-bis(2-pyridyl)benzoquinoxaline), even though the photo-hydrogen-evolving activities of these compounds remain unexplored.

Examples of the photosensitizers combined with non-platinated catalysts can be noted as follows. Several works report on the iron hydrogenase active sites covalently linked to a Ru(II) photosensitizer, such as a $[Ru(bpy)_3]^{2+}$ derivative and a $[Ru(terpy)_2]^{2+}$ derivative [43]. An example of such models (**40** [43b,c]) is depicted in Fig. 15. As an analog for these models, the same diiron core tethered to a porphyrin photosensitizer (**41**) was also reported [44]. However, none of these reports was successful in the photochemical hydrogen production from water.

On the other hand, Rau et al. recently reported on their success in the development of another active model of photo-hydrogen-evolving molecular device, compound **42** [45]. A remarkable difference in the activity of **34** and **42** is that **34** evolves H_2 in aqueous media at pH 5 while **42** evolves H_2 from triethylamine (an electron donor as well as a source of H^+) in acetonitrile in the absence of water. Importantly, **34** and **42** possess three common features as follows. In both systems, (i) the bridging spacer preserves the aromaticity, (ii) the charge transferred at the ^{3}MLCT excited state seems localized on the spacer unit, which can be judged by estimating the LUMO using the DFT MO calculations, and (iii) the electronic coupling between the two metal centers seems relatively weak, presumably allowing the molecule to have an excited-state life time sufficiently long to conduct the H_2-evolving process.

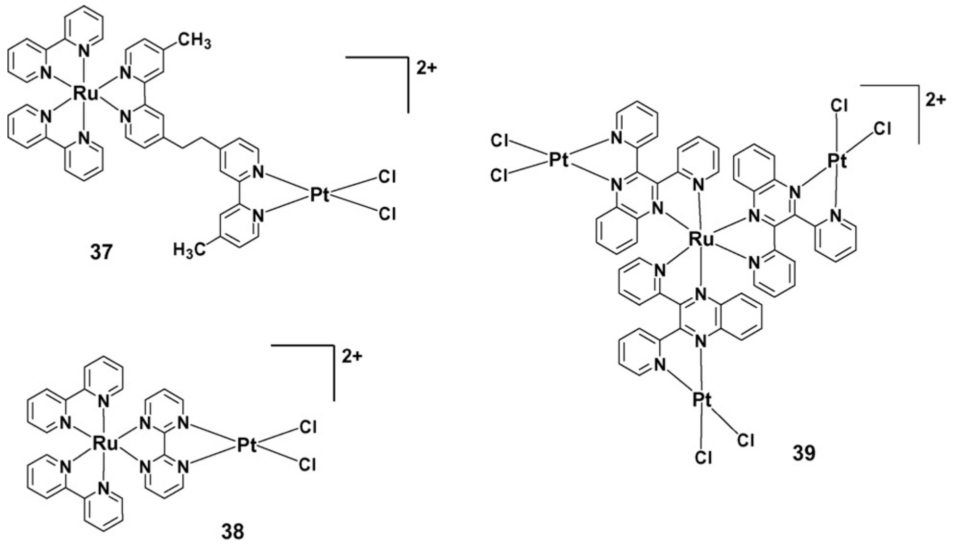


Fig. 14. Some related Ru(II)Pt(II) complexes reported by Rillema et al. [40].

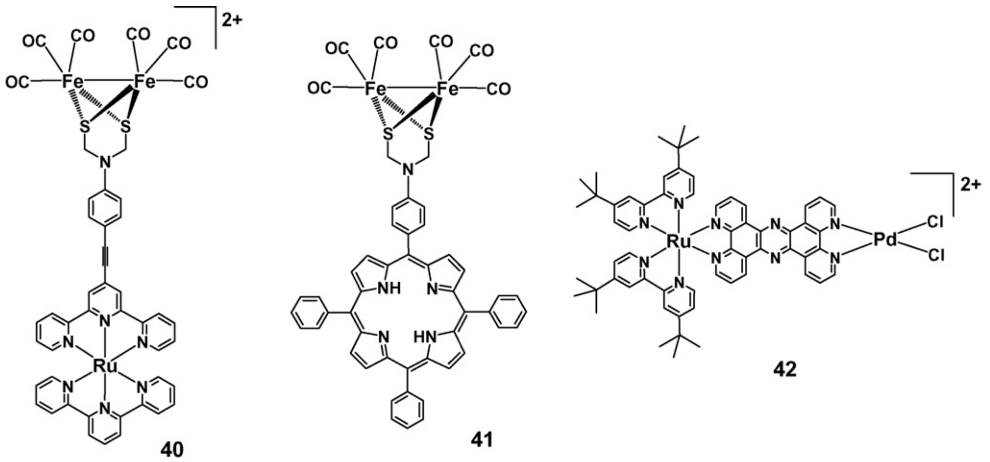


Fig. 15. Some model compounds for the photo-hydrogen-evolving molecular devices having non-platinated H_2-evolving centers [43–45].

4. Conclusions

This review describes that the results obtained in our group in the last 20 years are quite consistent with our idea that the Pt(II)-catalyzed H_2 production can be well understood as homogeneous catalysis of coordination compounds, since the catalytic efficiency is controlled by metal–metal interactions, coordination environments, steric factors, electron-acceptor capability, and photosensitizing ability. Extended studies are still in progress in our laboratory.

Acknowledgements

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