Highly selective photo-catalytic dimerization of α-methylstyrene by a novel palladium complex with photosensitizing ruthenium(II) polypyridyl moiety†

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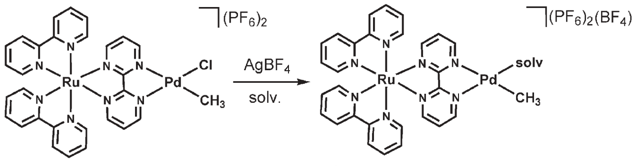
Received (in Cambridge, UK) 10th June 2005, Accepted 6th September 2005
First published as an Advance Article on the web 4th October 2005
DOI: 10.1039/b508013d

A novel dinuclear complex containing the photo-sensitizing Ru unit and a Pd center is effective toward selective catalytic dimerization of α-methylstyrene leading to 2,4-diphenyl-4-methyl-1-pentene under visible-light irradiated conditions.

The challenge to highly efficient conversion of abundant solar energy into chemical energy has received much attention in recent years.[1] In the natural photosynthetic processes, two types of photochemical molecular devices play key roles for the conversion: (1) an antenna device to collect solar light and (2) a reaction center where the excitation energy is used to perform the charge-separation process converting the electronic energy into redox chemical energy. Thus far, Ru(II) polypyridyl complexes have been widely used as a building block for redox-active, luminescent supramolecules because of their attractive photophysical properties such as absorption of visible light and long excited-state lifetime.[2] However, studies of the polynuclear Ru(II) polypyridyl complexes combined with a catalytic system are limited.[3] One of the reasons may be ascribed to the properties of the second metal fragment introduced as a reaction center, which should possess a certain stability against photo-decomposition as well as a high reactivity toward outer substrates to construct an effective catalytic system for utilizing solar energy. Based on the strategies, we designed a dinuclear system, $(bpy)_2Ru(BL)Pd(R)(L)$ (bpy = 2,2′-bipyridyl, BL = bridging ligand, R = alkyl), in expectation of an excited energy transfer from the Ru center to the Pd center, from which a highly reactive species is easily generated by dissociation of a weakly bound solvent ligand (L). In this communication, we report selective photo-catalytic dimerization of α-methylstyrene to yield 2,4-diphenyl-4-methyl-1-pentene by novel dinuclear Ru···Pd complexes, $[(bpy)_2Ru(bpm)PdMe(solv)](PF_6)_2(BF_4)$ (bpm = 2,2′-bipyrimidine, solv = Me_2CO (**1**), CH_3CN (**2**)), under visible-light irradiated condition.

Polypyridyl ruthenium complexes containing the solvated Pd center, $[(bpy)_2Ru(bpm)Pd(Me)(Me_2CO)](PF_6)_2(BF_4)$ (**1**) and $[(bpy)_2Ru(bpm)Pd(Me)(CH_3CN)](PF_6)_2(BF_4)$ (**2**), were prepared in quantitative yields by Cl^- abstraction from $[(bpy)_2Ru(bpm)Pd(Me)Cl](PF_6)_2$[4] with $AgBF_4$ in acetone and acetonitrile, respectively (eqn (1)).



1: solv = $(CH_3)_2CO$, 91 %
2: solv = CH_3CN, 91 %

(1)

Complexes **1** and **2** were unambiguously identified on the basis of their ^1H and ^{13}C NMR spectra as well as ESI-MS spectral data. The NMR signals for the methyl group of **1** appeared at δ_H 1.30 (s, 3H) and δ_C 5.2. The methyl signals for the coordinated acetone (δ_H 2.23, δ_C 32.0) significantly broadened at low temperature suggesting a fast dissociation process. The solid-state structure of **2** (Fig. 1), as determined by X-ray crystallography, is consistent with the solution structure.[5] Structural features of **2** are comparable to those of $[(bpy)_2Ru(dpp)PdCl_2](PF_6)_2$ (dpp = 2,3-bis(2-pyridyl)-pyrazine) reported by Yam[3] and related mononuclear complexes.[6] The Pd center was slightly distorted from a normal square planar geometry with the N–Pd–N bite angle (N(6)–Pd(1)–N(8)) of 79.9(3)°, showing a subtle strain brought about by linking with $[(bpy)_2Ru(bpm)]^{2+}$.

Complexes **1** and **2** are photochemically stable in CH_3NO_2 solution, and no deterioration was observed after irradiation for over 50 h.

The absorption spectrum of **2** shown in Fig. 2 is apparently a superposition of those of the related mononuclear complexes, $[(bpy)_2Ru(bpm)](PF_6)_2$ and $[(bpy)PdMe(MeCN)](BF_4)$. Complex **2**

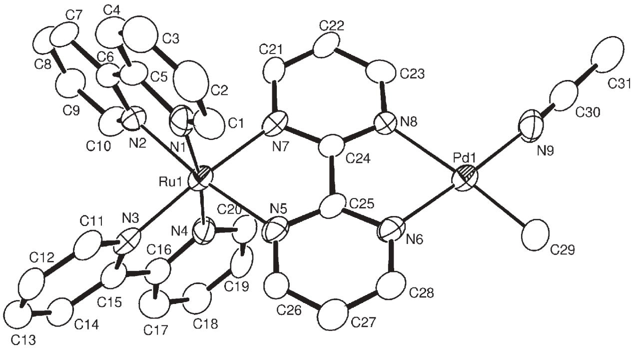


Fig. 1 Molecular structure of the cationic part of $[(bpy)_2Ru(bpm)\text{-}Pd(Me)(MeCN)]^{3+}$ (**2**), drawn with thermal ellipsoids at the 30% probability level.

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† Electronic supplementary information (ESI) available: Experimental section. See http://dx.doi.org/10.1039/b508013d

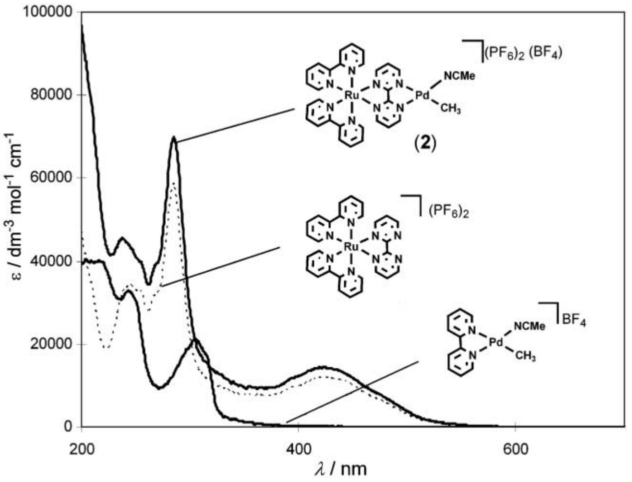
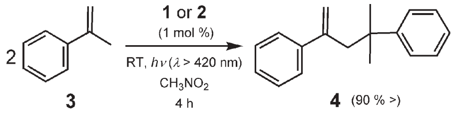


Fig. 2 Absorption spectra of **2**, [(bpy)$_2$Ru(bpm)](PF$_6$)$_2$ and [(bpy)PdMe(MeCN)]BF$_4$ in deaerated CH$_3$CN solution.

exhibited a low-energy absorption band at 420 nm (λ_{max} = 424 nm) due to the incorporation of Ru(II) polypyridyl moiety. Thus, Ru(II) polypyridyl moiety should act as a visible light-harvesting unit to collect light energy to the Pd center. If the Ru(II) and the Pd center are properly channeled in this system, excitation of the Ru unit would result in population of the excited state Pd center which may promote insertion/dissociation processes in the intermolecular reactions. Based on this scenario, photochemical reactions by dinuclear complexes **1** and **2** were investigated.

During the reactivity study toward various unsaturated hydrocarbons, complexes **1** and **2** were found to be catalytically active toward dimerization of terminal olefins such as styrene, 1-hexene, methyl acrylate and α-methylstyrene (**3**).[7] Above all, α-methylstyrene was most suitable for the mechanistic study (*vide infra*) and thus further details of the reaction were investigated as follows. A nitromethane solution of α-methylstyrene **3** containing a catalytic amount of **1** (1 mol%) was irradiated by visible light (150 W Xe lamp, $\lambda > 420$ nm) at room temperature under an Ar atmosphere.[8] Under these conditions, α-methylstyrene (**3**) was selectively dimerized to give a head-to-tail dimer, 4-methyl-2,4-diphenyl-1-pentene (**4**), over 90% yield together with small amounts of trimers (*ca.* 3%)[9] (eqn (2)). The dimer **4** was characterized by comparison with a commercially available authentic sample. Reactions in acetone and acetonitrile were sluggish compared with those in nitromethane, presumably because the reaction was suppressed by solvent coordination.

 (2)

The reaction was monitored by GC and the time–product distribution curves are shown in Fig. 3(a) and (b). Within 4 h of irradiation, 100 equivalents of **3** was completely consumed to give the dimer **4** for over 90% yield (Fig. 3(a)). Repetitive addition of the monomer **3** (100 equiv.) up to three times also resulted in the complete consumption of **3** to give **4**. Within 30 h, the reaction did not proceed in the dark nor in the absence of the catalyst. In order to verify the effect of light, the lamp was switched off at an appropriate time intervals, and the reaction did not proceed during the "dark" periods (Fig. 3(b)).

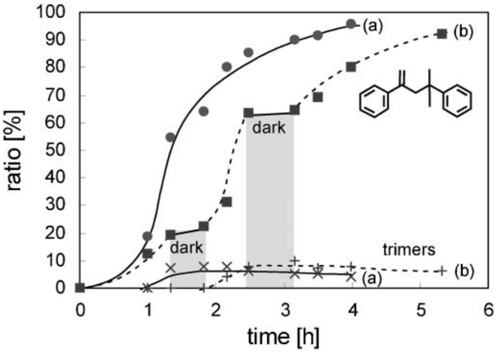
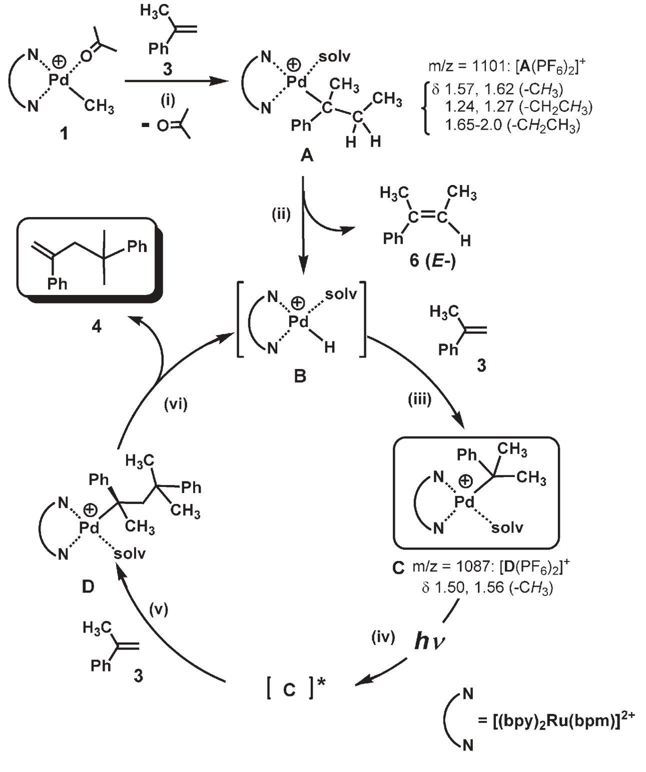


Fig. 3 Time–product distribution curves for the reaction of **1** with α-methylstyrene **3**: (a) without switching off and (b) light was switched off during the "dark" periods.

A dinuclear structure with the light-harvesting Ru(II) unit and the Pd center in close proximity was essential for the catalysis. Not only complexes **1** and **2** but also an intermediate **C** (*vide infra*) were effective for the dimerization, while analogues for the mononuclear components of **1**, [(bpy)$_3$Ru](PF$_6$)$_2$ and [(bpy)PdMe(Me$_2$CO)]BF$_4$ (**5**), or a 1:1 mixture of them were totally ineffective. Thus far, any precedent work of selective dimerization of **3** to give **4** mediated by transition metal catalysts has not been reported.[10]

A plausible reaction mechanism for the catalytic dimerization is outlined in Scheme 1. The reaction sequence consists of two processes, *i.e.* the initial step to form the hydride intermediate **B** and the catalytic cycle.

The first process involves insertion of **3** into the Pd–CH$_3$ bond in **1** to form **A** (step (i)) and subsequent β-elimination gives 2-phenyl-2-butene (**6**) and **B** (step (ii)). In the second process, successive insertion of **3** into **B** (step (iii)) and **C/C*** (steps (iv)–(v))



Scheme 1

gives **D**, which undergoes β–H elimination to yield **4** and **B** (step (vi)).

A series of control experiments has been done to establish the proposed reaction mechanism. Addition of 5 equivalents of **3** to **1** caused immediate formation of an equimolar mixture of **A** and (*E*)-**6**.[11] Further irradiation caused a gradual conversion of **A** into **C** preceding the formation of **4**. Both intermediates **A** and **C** were characterized by ^{1}H, ^{13}C NMR (for **C**) and ESI-MS spectroscopy.[12,13] Complex **C** was stable enough to be isolated by treating **1** with an excess amount of **3** for 1 h. Its intermediacy was confirmed by the addition of **3** to an isolated sample of **C**, which resulted in the catalytic formation of **4** under the same irradiated condition. Notably, steps (i), (ii) and (iii) could be undergone without light to give **C**,[14] although the rate of formation from **A** was substantially smaller comparing to that under the irradiated condition.[15] Judging from these results, photo-excitation of **C** seems to be essential for the second insertion step which leads to the progress of the catalytic cycle.

This work demonstrates that novel dinuclear Ru···Pd complexes containing a photo-sensitizing Ru(II) unit and a reactive Pd center catalyze selective dimerization of α-methylstyrene **3** to give **4** under visible-light irradiation. On the basis of the mechanistic study, generation of the photoexcitated species [**C**]* by visible-light by which the second insertion step can proceed is most likely the key step in the catalytic cycle. Further studies to elucidate the effect of light as well as applications to various substrates are now in progress.

We are grateful to the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government and the Japan Society for Promotion of Science and Technology (Grant-in-Aid for Young Scientists (B): No. 16750046) for financial support of this research.

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5 X-Ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-Kα radiation at −60 °C. *Crystal data* for **2**·$3CH_3CN$: $C_{37}H_{37}B_2F_{14}N_{12}$-PPdRu, $M = 1175.85$, triclinic, space group $P\bar{1}$, $a = 12.147(11)$, $b = 12.263(11)$, $c = 16.624(16)$ Å, $\alpha = 88.05(4)$, $\beta = 71.97(4)$, $\gamma = 89.15(4)^\circ$, $V = 2353(4)$ Å^3, $Z = 2$, $D_c = 1.691$ g cm^{-3}, $\mu = 8.75$ cm^{-1}, $R1$ ($wR2$) = 0.076 (0.180) for the 9577 unique data with $I > 2\sigma(I)$ and 593 parameters. In the solid state, counter anions of complex **2** was composed of one PF_6 and two BF_4 anions which was different from that of the solution (two PF_6 and one BF_4) CCDC 275767. See http://dx.doi.org/10.1039/b508013d for crystallographic data in CIF or other electronic format.

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7 Reaction of **1** with styrene and 1-hexene gave the corresponding head-to-tail dimers (a mixture of *cis*- and *trans*-RCH=CHCRCH$_3$, R = Ph, ^{n}Bu), however, that with methyl acrylate gave a head-to-head dimers (a mixture of Δ^2- and Δ^3-dimethyldihydromuconate). When the formation rate of the dimers were compared under the same reaction condition, that of styrene, 1-hexene and methyl acrylate was much smaller than that of α-methylstyrene (α-methylstyrene > 1-hexene, methyl acrylate > styrene).

8 *Typical reaction procedures*: To a CD_3NO_2 solution (0.37 mL) of **1** (11.3 mg, 1.00 μmol, 1 mol%) was added α-methylstyrene **3** (130 μL, 1.00 mmol, substr./cat. = 100) and adamantane (10.0 mg, an internal standard). The solution was divided into two 5 mm i.d. glass tubes; one for the irradiation and the other for the dark reaction which was covered with aluminium foil. The two samples were placed at a distance of 10 cm from an Xe lamp (150 W, with a L42 cut-off filter ($\lambda > 420$ nm)). The reaction was followed by ^{1}H NMR and/or GC after appropriate time intervals.

9 Formation of the trimers was indicated by the GC-MS peak at *m*/*z* 354 ($C_{27}H_{30}$).

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11 *Spectral data* for **6**: ^{1}H NMR (200 MHz, CD_3NO_2, RT): δ 1.79 (dq, $J = 6.84$, 0.98 Hz, 3H, –CH$_3$), 2.02 (m, 3H, –CH$_3$), 5.91 (qq, $J = 6.84$, 1.38 Hz, 1H, =C(Me)H). Ph protons were not fully characterized because they overlap with other aromatic protons. *m*/*z* (GCMS) 132 (M, 59%), 117 (M − 5, 100). **6** was characterized according to the reported spectroscopic data in the following references: E. Vedejs, J. Cabaj and M. J. Peterson, *J. Org. Chem.*, 1993, **58**, 6509; P. Fristrup, D. Tanner and P.-O. Norrby, *Chirality*, 2003, **15**, 360.

12 *Spectral data* for **A**: Two sets of the two methyl signals (δ_H 1.57, 1.62 for –C*H*$_3$, δ_H 1.24, 1.27 for –CH$_2$C*H*$_3$) were attributed to the two diastereomers of **A** with the chiral carbon atom attached to Pd. ^{1}H NMR (200 MHz, CD_3NO_2, RT): δ 1.20 (t, $J = 7.4$ Hz, 3H, PdCCH$_2$C*H*$_3$), 1.27 (t, $J = 7.4$ Hz, 3H, PdCCH$_2$C*H*$_3$), 1.57 (s, 3H, PdC*Me*), 1.62 (s, 3H, PdC*Me*), 1.8–2.0 (m, 2H, PdCC*H*$_2$CH$_3$), 7.5–9.2 (m, 27H, Ph). ESI-MS spectrum: *m*/*z* 1101: $\{(Pd\text{CMeEtPh})(PF_6)_2\}^+$, 1043: $\{(Pd\text{CMeEtPh})(PF_6)(BF_4)\}^+$, 985: $\{(Pd\text{CMeEtPh})(BF_4)_2\}^+$. $Pd = \{(bpy)_2{}^{102}Ru(bpm)^{106}Pd\}$.

13 *Spectral data* for **C**: The two signals for the diastereotopic methyl groups were located at δ_H 1.50 and 1.56. Additional ^{1}H, ^{13}C NMR, and ESI-MS spectral data are given as Electronic supplementary information.

14 Although the formation of **C** was observed under the dark condition, the dimer **4** did not form over a prolonged reaction time.

15 When the formation rate of **C** from **A** was compared between the irradiated and dark conditions, the rate under irradiation was nearly as twice as fast compared to that under the dark condition.