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Photochemical Preparation of Pyrimidin-2(1*H*)-ones by Rhenium(I) Complexes with Visible Light

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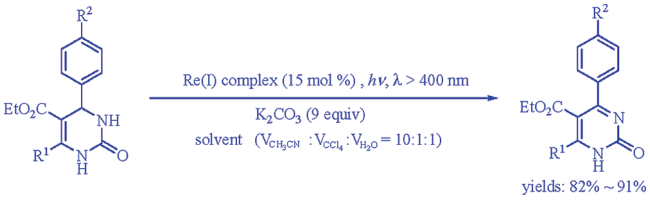
Received October 18, 2010



With visible light irradiation ($\lambda > 400$ nm) of rhenium(I) complexes (**P1**−**P4**), a photochemical conversion from 3,4-dihydropyrimidin-2(1*H*)-ones to pyrimidin-2(1*H*)-ones at room temperature has been achieved with good to excellent yields in CH_3CN-H_2O solution containing CCl_4 and K_2CO_3. Luminescence quenching study and product analysis reveal that photoinduced electron transfer between rhenium(I) complex **P** and 3,4-dihydropyrimidin-2(1*H*)-ones plays an important role in the initial event.

The construction of the functionalized pyrimidin-2(1*H*)-one moiety is of significance due to its occurrence in many biologically active and medicinally significant structures.[1] From a synthetic point of view, dehydrogenation of 3,4-dihydropyrimidin-2(1*H*)-ones (DHPMs) offers an attractive method for making pyrimidin-2(1*H*)-ones because DHPMs are easily prepared by Biginelli three-component coupling reaction.[2] However, unlike a large number of protocols available for achieving nearly quantitative transformation of Hantzsch dihydropyridine to pyridine,[3] the dehydrogenation of DHPMs is extremely difficult owing to its higher oxidation potential compared with that of dihydropyridines.[4] In general, excess corrosive and strong oxidants, such as DDQ,[5] HNO_3,[6] TBHP/$CuCl_2$,[7] CAN/$NaHCO_3$,[8] $Co(NO_3)_2$/$K_2S_2O_8$,[9] $K_2S_2O_8$/ultrasound,[10] TBHP/$PhI(OAc)_2$,[11] PCC,[12] and NO^+,[13] are required. These methods suffer from the use of toxic reagents and the safety profile, low yield of the products, and difficulty in product isolation. Developing a method that can be applied in a wide range of DHPMs with high yields under mild conditions is highly desirable. In this regard, a photochemical process holds special promise. Memarian and co-workers[14] recently found that direct irradiation of DHPMs with UV light in a $CHCl_3$ solution resulted in the formation of pyrimidin-2(1*H*)-ones with excellent yields. This is the first photochemical example for dehydrogenation of DHPMs. In this reaction, UV light was used to directly excite DHPMs, and the resultant pyrimidin-2(1*H*)-ones also display absorption in this region that may cause secondary photochemical reactions.

In the present work, we report a photochemical protocol for facile preparation of pyrimidin-2(1*H*)-ones with visible light. Herein, rhenium(I) complex was selected as a photosensitizer in view of its visible light absorption, long excited-state lifetime, strong excited-state redox potential, and thermal and photochemical stability.[15,16] Although this kind of complex has been exploited for CO_2 reduction,[16] there are few reports on the use of rhenium(I) tricarbonyl diimine complexes in organic synthesis. As compared with well developed ruthenium(II)[17] or platinum(II)[3d,18,19] complexes, the excited rhenium(I) complexes possess more powerful redox potential. This unique feature prompted us to initiate a study on the dehydrogenation of DHPMs by rhenium(I) complexes under visible light irradiation, where DHPMs and pyrimidin-2(1*H*)-ones do not absorb, thereby avoiding production of undesired products. As will be discussed later, upon irradiation with visible light ($\lambda > 400$ nm), a catalytic

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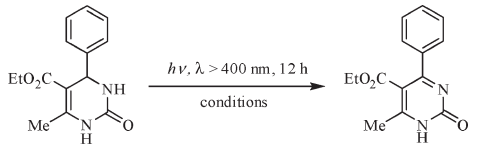
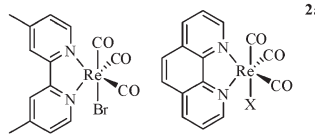
Published on Web 02/01/2011 DOI: 10.1021/jo102062u

TABLE 1. Optimization of Photochemical Dehydrogenation Conditions



1a **2a**



P1 **P2**: X = Br, **P3**: X = Cl, **P4**: X = CH_3CN

entry	conditions[a]	yield (%)[b]
1	**P1** (15 mol %), CCl_4 5 mL	33
2	*no catalyst*, CCl_4 5 mL	0
3	*no light*, **P1** (15 mol %), CCl_4 5 mL[c]	0
4	**P2** (15 mol %), CCl_4 5 mL	61
5	**P3** (15 mol %), CCl_4 5 mL	23
6	**P4** (15 mol %), CCl_4 5 mL	37
7	**P2** (15 mol %), $CHCl_3$ 5 mL	0
8	**P2** (15 mol %), CH_3NO_2 5 mL	15
9	**P2** (15 mol %), CCl_4 5 mL, K_2CO_3 (9 equiv), H_2O, 5 mL	**82**

[a]The concentration of **1a** is 2×10^{-3} M. [b]Isolated yield after purification by chromatography on SiO_2. [c]Stirred at room temperature for 12 h.

amount of rhenium(I) complex **P1**−**P4** is capable of producing pyrimidin-2(1*H*)-ones with good to excellent yields.

The photochemical reaction was carried out in degassed solution at room temperature. Typically, 50 mL of a saturated CH_3CN solution of DHPM substrate and rhenium(I) complex **P** in a Pyrex reactor was irradiated by a 500-W high-pressure Hanovia mercury lamp. A glass filter was used to cut off light below 400 nm, thereby guaranteeing that only rhenium(I) complex **P** was irradiated, while DHPMs and pyrimidin-2(1*H*)-ones are transparent (Figure S1 in Supporting Information). To our delight, pyrimidin-2(1*H*)-one **2a** was produced in a yield of 33% by 15 mol % Re(I)(bipy)-$(CO)_3Br$ **P1** when CCl_4 was present (Table 1, entry 1), whereas irradiation of **1a** in the absence of Re(I) complex with visible light at $\lambda > 400$ nm led to no product formation (Table 1, entry 2). Moreover, no conversion could be observed when the reaction was carried out in the dark (Table 1, entry 3). The results suggest that both light and rhenium(I) complex are essential for the dehydrogenation and that rhenium(I) complex remarkably accelerates the photochemical transformation.

With the initial success, several rhenium(I) tricarbonyl diimine complexes (**P1**−**P4**) were screened, and rhenium(I) complex **P2** was found to be the most efficient for the reaction (Table 1, entries 4−6). As tabulated in Table 1, irradiating a solution of CH_3CN and CCl_4 containing **1a** and **P2** for 12 h resulted in the formation of **2a** in a yield of 61%. However, no reaction took place at all when $CHCl_3$ was used to replace CCl_4 (Table 1, entry 7), and the use of CH_3NO_2 as oxidant only afforded **2a** in 15% yield (Table 1, entry 8). Evidently, CCl_4 is a crucial terminal oxidant in the reaction. It was worth noting that after irradiation the solution became acidic and chloroform was detected by GC in addition to **2a**. Considering that acidic hydrogen chloride may inhibit the production of pyrimidin-2(1*H*)-one **2a**, aqueous solution of K_2CO_3 was added to consume the acid generated during the reaction. As expected, the isolated yield of **2a** was improved from 61% to 82% with the addition of aqueous K_2CO_3 (9 equiv) to the dehydrogenation system (Table 1, entry 9).

A survey of a series of substituted DHPMs demonstrated that the DHPMs bearing alkyl and aryl substituents could be successfully transformed to their corresponding pyrimidin-2(1*H*)-ones in good to excellent yields under the optimized conditions, i.e., 1.0 mmol of DHPM substrate, 0.15 mmol of Re(I)(Phen)$(CO)_3Br$ (**P2**), and 9.0 mmol of K_2CO_3 in a solution of CH_3CN, CCl_4 and H_2O (V/V: 10:1:1) under visible light irradiation ($\lambda > 400$ nm). It was reported that a methyl group located at C-6 of DHPMs is sensitive to harsh dehydrogenation conditions.[9] Undesired byproduct such as nitrolic acids, dealkylated pyrimidin-2(1*H*)-ones, and pyrimidin-2,4(1*H*,3*H*)-diones were often obtained when HNO_3,[6] CAN,[8] or $Co(NO_3)_2/K_2S_2O_8$[9] were used as strong oxidants. In our case, however, no any dealkylation product could be detected under the reaction conditions (Table 2, entries 1−5). Substrates with a phenyl group at the C-6 position afforded the desired dehydrogenated products in much higher yields (Table 2, entries 6−8). Furthermore, with the visible light irradiation the *S*-alkylated DHPMs **3** could be successfully converted to their corresponding 2-methylthio-pyrimidines **4** in excellent yields (Scheme 1).

Since the solution became acidic, with accompanying formation of chloroform upon irradiation, we tentatively proposed an electron transfer mechanism for the photocatalytic dehydrogenation reaction shown in Scheme 2. When irradiated with visible light, the ^{3}MLCT excited state of rhenium(I) complex **P** is reductively quenched by DHPMs **1** to give reduced rhenium(I) complex $\mathbf{P}^{-\bullet}$ and the radical cation of DHPMs $\mathbf{1}^{+\bullet}$, which was well evidenced by the luminescence quenching experiment (Supporting Information). Rhenium(I) complex **P** exhibits broad absorption bands between 250 and 450 nm with ε on the order of 10^3 dm^3 mol^{-1} cm^{-1} (Figure S1 in Supporting Information). With reference to previous spectroscopic work on rhenium(I) complexes,[15] the absorption bands at 380−450 nm are ascribed to the $d\pi(Re) \rightarrow \pi^*(N-N)$ MLCT state. Excitation of the characteristic absorption of rhenium(I) complex **P** at 400 nm resulted in

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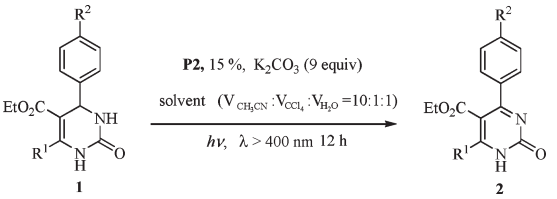
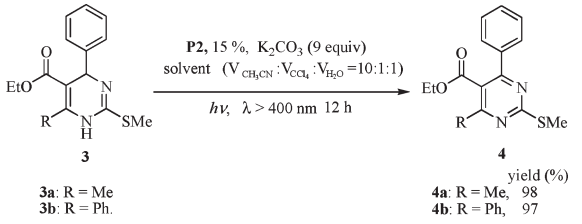
TABLE 2. Photochemical Preparation of Pyrimidin-2(1*H*)-ones[a]



entry	R^1	R^2	substrate	product	yield (%[b]
1	Me	H	**1a**	**2a**	82
2	Me	Me	**1b**	**2b**	88
3	Me	OMe	**1c**	**2c**	91
4	Me	Cl	**1d**	**2d**	86
5	Me	Br	**1e**	**2e**	84
6	Ph	H	**1f**	**2f**	84
7	Ph	Me	**1g**	**2g**	91
8	Ph	Cl	**1h**	**2h**	90

[a]Reactions conducted using substrate (1.0 mmol), Re(I)(Phen)$(CO)_3$-Br (0.15 mmol), K_2CO_3 (9.0 mmol), H_2O (5 mL), and CCl_4 (5 mL) in degassed CH_3CN (50 mL) under irradiation by a 500-W high-pressure mercury lamp. A glass filter was used to cut off light below 400 nm. [b]Isolated yield after purification by chromatography on SiO_2

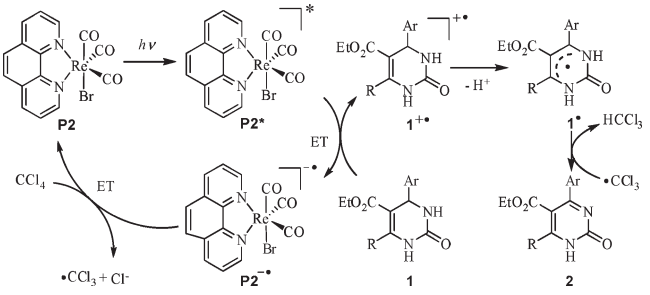
SCHEME 1. Photochemical Dehydrogenation of 2-Methylthio pyrimidines



a maximal luminescence at 600 nm (Figure S2 in Supporting Information). Progressive addition of DHPMs **1** into the solution of rhenium(I) complex **P** quenched the luminescence, but in sharp contrast, the similar quenching behavior was absent when CCl_4 was introduced (Figure S3 in Supporting Information). These results suggest no significant electronic interaction between rhenium(I) complex **P** and CCl_4 in the excited state, but indeed between rhenium(I) complex **P** and DHPMs **1**. The reductive quenching of rhenium(I) complex **P** by DHPMs **1** was further strengthened by the fact that after irradiation Re(I)(Phen)$(CO)_3$Br was partly transformed to Re(I)(Phen)$(CO)_3$Cl, implying the generation of one-electron-reduced species rhenium(I) complex $\mathbf{P}^{-\bullet}$.[16e] The reduced rhenium(I) complex $\mathbf{P}^{-\bullet}$ is in turn reacted with CCl_4 to regenerate rhenium(I) complex **P** and to produce $CCl_3^\bullet$ radical and chloride anion. Then the fast deprotonation of DHPMs $\mathbf{1}^{+\bullet}$ radical cation leads to the formation of DHPMs $\mathbf{1}^\bullet$ radical. Finally, the hydrogen abstraction by $CCl_3^\bullet$ radical completes the reaction giving rise to chloroform and pyrimidin-2(1*H*)-ones **2**. As suggested by one of the reviewers, it is also possible that chloroform is produced by reduction of $CCl_3^\bullet$ radical and subsequent protonation: $CCl_3^\bullet + e \rightarrow CCl_3^-$; $CCl_3^- + H^+ \rightarrow HCCl_3$.

To summarize, we described a photochemical approach to access pyrimidin-2(1*H*)-ones, important synthetic targets. The dehydrogenation of DHPMs employs rhenium(I) complexes as photosensitizers, and the whole process is environmentally benign, i.e., with visible-light irradiation ($\lambda > 400$ nm)

SCHEME 2. Plausible Mechanism for the Dehydrogenation



of rhenium(I) complexes (**P1**−**P4**), 3,4-dihydropyrimidin-2(1*H*)-ones DHPMs can be successfully converted to pyrimidin-2(1*H*)-ones with good to excellent yields in CH_3CN−H_2O solution at room temperature, in which CCl_4 and K_2CO_3 are important for improving the reaction efficiency. Luminescence quenching study and product analysis reveal that photoinduced electron transfer between rhenium(I) complex **P** and DHPMs plays an important role in this reaction. Efforts toward further mechanistic understanding and extension of the dehydrogenation are currently underway.

Experimental Section

General Procedure for the Photochemical Preparation of Pyrimidin-2(1*H*)-ones. To a mixture of ethyl 1,2,3,4-tetrahydro-6-methyl-2-oxo-4-phenylpyrimidine-5-carboxylate **1a** (1.0 mmol), Re(I)(Phen)$(CO)_3$Br (0.15 mmol), and K_2CO_3 (9.0 mmol in 5 mL H_2O) were added CH_3CN (50 mL) and CCl_4 (5 mL). The solution was divided into two 50-mL Pyrex tubes and degassed for 40 min by Argon. The resultant mixture was then irradiated by a 500-W high-pressure mercury lamp at ambient temperature. A glass filter was employed to cut off light with wavelength below 400 nm. The progress of the reaction was monitored by thin-layer chromatography at regular intervals. Generally, after 12 h of irradiation the conversion was close to 100%. Upon removal of solvent in vacuo, the residue was diluted with 30 mL of CH_2Cl_2 and washed with saturated aqueous NH_4Cl (3 × 10 mL). The residue was purified by column chromatography on silica gel eluting with CH_2Cl_2/ethyl acetate = 4:1, and the fraction with R_f = 0.15 was collected and concentrated to give the target ethyl 1,2-dihydro-6-methyl-2-oxo-4-phenylpyrimidine-5-carboxylate **2a** as a pale yellow solid, which was identified by ^{1}H and ^{13}C NMR spectroscopy and MS spectrometry.

Ethyl 1,2-Dihydro-6-methyl-2-oxo-4-phenylpyrimidine-5-carboxylate (2a). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.82 (t, 3H, J = 7.1 Hz), 2.40 (s, 3H), 3.94 (q, 2H, J = 7.2 Hz), 7.39−7.51 (m, 5H), 12.39 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 13.2, 18.4, 60.8, 109.0, 127.5, 128.2, 128.7, 130.1, 138.2, 155.4, 160.8, 165.9, 171.7; EI-MS m/z (%) 258 (M^+, 45), 229 (100), 213 (67), 185 (34), 104 (28), 77 (11).

Ethyl 1,2-Dihydro-6-methyl-2-oxo-4-*p*-tolylpyrimidine-5-carboxylate (2b). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.88 (t, 3H, J = 7.1 Hz), 2.356 (S, 3H), 2.372 (S, 3H), 3.98 (q, 2H, J = 7.1 Hz), 7.26−7.36 (m, 4H), 12.37 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 13.4, 18.5, 20.9, 60.9, 109.1, 127.6, 128.8, 134.9, 140.2, 155.6, 161.1, 166.1, 171.6; EI-MS m/z (%) 272 (M^+, 32), 243 (100), 227 (27), 199 (9), 118 (7).

Ethyl 1,2-Dihydro-4-(4-methoxyphenyl)-6-methyl-2-oxopyrimidine-5-carboxylate (2c). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.94 (t, 3H, J = 8.0 Hz), 2.36 (s, 3H), 3.81 (s, 3H), 4.03 (q, 2H, J = 8.0 Hz), 7.02 (d, 2H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.0 Hz), 12.25 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 13.5, 18.2, 55.4, 60.9, 108.9, 113.7, 129.5, 130.2, 155.5, 159.8,

161.2, 166.3, 171.1; EI-MS m/z (%) 288 (M^+, 86), 259 (100), 243 (34), 219 (19), 134 (15), 69 (23).

Ethyl 4-(4-Chlorophenyl)-1,2-dihydro-6-methyl-2-oxopyrimidine-5-carboxylate (2d). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.88 (t, 3H, J = 7.1 Hz), 2.41 (s, 3H), 3.98 (q, 2H, J = 7.1 Hz), 7.45 (d, 2H, J = 8.4 Hz), 7.54 (d, 2H, J = 8,5 Hz), 10.74 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 13.3, 18.5, 60.9, 108.8, 128.0, 128.3, 129.4, 134.6, 135.0, 137.0, 155.3, 162.0, 165.6, 170.1; EI-MS m/z (%) 294 (M^+, 10), 292 (43), 263 (100), 247 (52), 219 (15), 206 (13), 138 (18).

Ethyl 4-(4-Bromophenyl)-1,2-dihydro-6-methyl-2-oxopyrimidine-5-carboxylate (2e). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.87 (t, 3H, J = 7.1 Hz), 2.40 (s, 3H), 3.98 (q, 2H, J = 7.1 Hz), 7.38 (d, 2H, J = 8.4 Hz), 7.68 (d, 2H, J = 8.4 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 13.3, 18.5, 60.9, 108.7, 123.6, 129.6, 131.3, 137.4, 155.4, 162.1, 165.6, 170.0; EI-MS m/z (%) 338 (M^+, 37), 336 (39), 308 (91), 306 (100), 293 (34), 291 (40), 184 (8), 182 (9).

Ethyl 1,2-Dihydro-2-oxo-4,6-diphenylpyrimidine-5-carboxylate (2f). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.74 (t, 3H, J = 8.0 Hz), 3.84 (q, 2H, J = 8.0 Hz), 7.48−7.57 (m, 10H), 12.59 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 13.1, 61.2, 111.7, 127.9, 128.5, 130.5, 135.2, 157.3, 165.3 (br), 166.4 ; EI-MS m/z (%) 320 (M^+, 18), 291 (100), 275 (15), 247 (72), 104 (12), 77 (5).

Ethyl 1,2-Dihydro-2-oxo-6-phenyl-4-*p*-tolylpyrimidine-5-carboxylate (2g). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.77 (t, 3H, J = 8.0 Hz), 2.37 (s, 3H), 3.85 (q, 2H, J = 8.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.0 Hz), 7.48−7.54 (m, 5H), 12.54 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 13.1, 20.9, 61.1, 111.5, 127.8, 127.9, 128.4, 129.0, 130.4, 132.2, 135.4, 140.5, 157.4, 166.5; EI-MS m/z (%) 334 (M^+, 63), 305 (M^+, 100), 289 (54), 261 (18), 118 (13), 104 (12), 77 (4).

Ethyl 4-(4-Chlorophenyl)-1,2-dihydro-2-oxo-6-phenylpyrimidine-5-carboxylate (2h). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.76 (t, 3H, J = 8.0 Hz), 3.86 (q, 2H, J = 8.0 Hz), 7.49−7.60 (m, 9H), 12.65 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 13.1, 61.2, 111.7, 127.9, 128.4, 128.5, 129.8, 130.5, 134.7 (br), 135.3, 157.5, 166.2; EI-MS m/z (%) 356 (M^+, 4), 354 (22), 327 (13), 325 (100), 309 (21), 104 (6).

Ethyl 4-Methyl-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (4a). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04 (t, 3H, J = 8.0 Hz), 2.57 (s, 3H), 2.62 (s, 3H), 4.15 (q, 2H, J = 8.0 Hz), 7.64 (d, 2H, J = 8.0 Hz), 7.40−7.47 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 22.7, 29.8, 61.8, 121.1, 128.5, 128.6, 130.2, 137.9, 163.7, 165.6, 168.3, 172.6; EI-MS m/z (%) 288 (M^+, 100), 259 (13).

Ethyl 2-(Methylthio)-4,6-diphenylpyrimidine-5-carboxylate (4b). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86 (t, 3H, J = 8.0 Hz), 2.62 (s, 3H), 4.01 (q, 2H, J = 8.0 Hz), 7.51−7.65 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.5, 29.7, 61.9, 120.9, 128.5, 130.2, 137.5, 164.4, 168.2, 172.8; EI-MS m/z (%) 350 (M^+, 100), 321 (91), 305 (56), 275 (45), 231 (65), 159 (32), 129 (84), 77 (54).

Acknowledgment. Financial support from Solar Energy Initiative of the Knowledge Innovation Program of the Chinese Academy of Sciences (KGCXZ-YW-389), the National Science Foundation of China (20732007, 21090343 and 50973125), the Ministry of Science and Technology of China (G2007CB808004 and 2009CB220008), and the Bureau for Basic Research of the Chinese Academy of Sciences is gratefully acknowledged.

Supporting Information Available: Experimental details, UV−vis spectra of **P2**, **1a**, **2a** and CCl_4, luminescence quenching experiments, ^{1}H, ^{13}C NMR spectra of dehydrogenation products and other data. This material is available free of charge via the Internet at http://pubs.acs.org.