

## Visible Light Enhanced Selective Reductive Elimination of a Methylmanganese Complex from a Heterodinuclear Dimethylphenyl-(4,4'-di-*tert*-butyl-2,2'-bipyridine)platinum—Pentacarbonylmanganese Complex

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Summary: Novel visible light induced reductive elimination of a heterodinuclear triorganoplatinum-manganese complex,  $({}^{t}Bu_{2}bpy)Me_{2}PhPt-Mn(CO)_{5}$ , gives a methylmanganese complex,  $MnMe(CO)_{5}$ , and a methylphenylplatinum complex,  $PtMePh({}^{t}Bu_{2}bpy)$ .

Use of light energy in controlling the selectivity and activity of chemical reactions is a highly fascinating method, but it is in generally very difficult, since irradiation frequently causes homolytic bond cleavage, dissociation of ligands, etc. or sometimes even luminescence.<sup>1,2</sup> On the other hand, reductive elimination is one of the most important key steps in organo-transition-metal chemistry in relation to transition-metal-mediated organic reactions and catalyses.<sup>3</sup> Among them,

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A series of (2,2'-bipyridine)- or (4,4'-di-*tert*-butyl-2,2'-bipyridine)triorganoplatinum-manganese pentacarbonyl complexes were prepared by the simple metathetical reactions of the corresponding triorgano(nitrato)platinum(IV) species with sodium pentacarbonylmanganate in THF (eq 1).

$$R^{1} \longrightarrow NO_{3} = Na[Mn(CO)_{5}] \xrightarrow{-NaNO_{3}} R^{1} \longrightarrow Na[Mn(CO)_{5}] \xrightarrow{-NaNO_{3}} R^{1} \longrightarrow Na[Mn(CO)_{5}] \xrightarrow{-NaNO_{3}} R^{1} \longrightarrow Na[Mn(CO)_{5}] \xrightarrow{-NaNO_{3}} R^{1} = H R^{2} = Me (1a), Et (1b), Ph (1c) R^{1} = Bu R^{2} = Me (2a), Et (2b), Pr (2c) Np (2d), Ph (2f) C_{g}H_{4}OMe_{-p} (2g)$$
(1)

In these heterodinuclear complexes, a large R<sup>2</sup> group is always placed trans to Mn, probably due to steric hindrance between the square-planar Pt coordination plane and the four equatorial carbonyl ligands at Mn. **1a** in THF shows two absorption bands at 533 ( $\varepsilon = 2900 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 325 nm ( $\varepsilon = 15000 \text{ M}^{-1} \text{ cm}^{-1}$ ), which are ascribed to MLCT bands from the HOMO orbital based on the Pt–Mn bond to the LUMO assignable to two empty  $\pi^*$  orbitals of the bpy ligand.<sup>8</sup>

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<sup>(8)</sup> DFT calculations of **1a** and **1c** and their corresponding products, which were performed by using Spartan 06 Windows from Wavefunction, Inc. at the B3LYP/LACVP/6-31G\* level of theory, reveal that reductive elimination of the former is endothermic but that of the latter is exothermic. The calculated wavelengths of two MLCT bands of **1a** were 554 and 400 nm. See the Supporting Information.



Figure 1. Molecular structure of  $(bpy)Me_3Pt-Mn(CO)_5$  (1a). All hydrogen atoms are omitted for clarity. Ellipsoids are given at the 50% probability level.

X-ray structure analysis revealed the molecular structure of **1a** (Figure 1).<sup>9</sup> The geometry at the Pt metal is essentially octahedral, where the Mn(CO)<sub>5</sub> moiety and bpy ligand are placed cis to each other. The Mo moiety possesses a pseudosquare-pyramidal structure, which is similar to that of the known Mn(-I) anionic complex [Ph<sub>4</sub>P][Mn(CO)<sub>5</sub>].<sup>10</sup> The Pt–Mn bond distance (3.0337(8) Å) in **1a** is significantly longer than those observed in other heterodi- or heterotrinuclear complexes containing platinum and manganese,<sup>11,12</sup> suggesting effective steric repulsion between the Pt and Mn moieties. In fact, four ligands at Pt and the carbonyl ligands cis to Pt in Mn are placed in a staggered conformation in order to minimize their steric congestion.

When the dimethylphenyl(4,4'-di-*tert*-butyl-2,2'-bipyridine)platinum-manganese complex **2f** was heated in benzene at 20 °C, selective and smooth cis reductive elimination of the methylmanganese(I) complex **3** took place, giving PtMePh('Bu<sub>2</sub>bpy) (**4**) (eq 2).<sup>13</sup>



The reaction is first order in heterodinuclear complex concentration, and the estimated first-order rate constant  $k_{obsd}$  was independent of both the <sup>*t*</sup>Bu<sub>2</sub>bpy and [Mn(CO)<sub>5</sub>]<sup>-</sup>



**Figure 2.** First-order plots for reductive elimination of **2f** in the dark ( $\bigcirc$ ) and under visible light irradiation ( $\bigcirc$ ) in benzene at 20 °C ([**2f**] = 0.300 mM).

concentrations, suggesting that the reaction proceeds without prerequisite prior 'Bu<sub>2</sub>bpy and heterolytic Mn anion dissociations (Figure 2 and Figures S3 and S4 in the Supporting Information). The first-order rate constant ( $k_{obsd} = (1.60 \pm 0.00) \times 10^{-4} \text{ s}^{-1}$ ) at 20 °C in benzene is significantly larger than those of reductive elimination of the corresponding monomethylplatinum-manganese complex (dppe)MePt-Mn(CO)<sub>5</sub>, which gives no methylmanganese complex.<sup>7c</sup> This reflects that the electron deficiency at Pt due to high metal valency favors reductive elimination.<sup>4a-4c</sup> Although interaction of electron-deficient olefin is known to enhance reductive elimination, and a significant acceleration effect of added acrylonitrile on the rate was observed in the present case. This may be due to coordinative saturation of acrylonitrile.

Similarly, the *p*-anisyl analogue **2g** also caused smooth reductive elimination. Attempted preparation of methyldiphenyl- and triphenylplatinum derivatives failed to give reductive elimination products, suggesting that high steric congestion around the Pt-Mn bond causes preferential cis reductive elimination. The trialkylplatinum-manganese complexes **2a**-e are relatively stable, and further heating of **2a** to 70 °C gave a complex mixture of MnMe(CO)<sub>5</sub> (37%), PtMe<sub>2</sub>(<sup>'</sup>Bu<sub>2</sub>bpy) (47%), PtMe<sub>2</sub>(CO)<sub>2</sub> (29%), and <sup>'</sup>Bu<sub>2</sub>bpy (8%). Theoretical calculations<sup>8</sup> revealed that reductive elimination of the dimenthylphenylplatinum complex is exothermic ( $\Delta E = -11.3$  kJ mol<sup>-1</sup> for **1b**), whereas the reaction of the trimethylplatinum complex is endothermic ( $\Delta E = 12.2$  kJ mol<sup>-1</sup> for **1a**), supporting the above facts.

The most notable fact in this reductive elimination of the M-C bond from the triorganoplatinum-manganese heterodinuclear complex is the unexpected acceleration effect of visible light irradiation on the reductive elimination. When **2f** (0.300 mM) was irradiated by visible light (> 500 nm) under the same conditions, reductive elimination was significantly enhanced ( $k_{obsd} = (24.6 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$ , ca. 15 times faster than the reaction in the dark), causing selective formation of the methylmanganese complex as shown in Figure 2. The quantum yield for this photoinduced reductive elimination of **2f** estimated as ca. 0.50 using chemical actinometry.<sup>14</sup> No significant effect of the added *t*-Bu<sub>2</sub>bpy ligand ( $k_{obsd} = (24.6 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$  for [*t*-Bu<sub>2</sub>bpy] = 0 mM,  $k_{obsd} = (22.8 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$  for [*t*-Bu<sub>2</sub>bpy] = 3.2 mM in benzene)

<sup>(9)</sup> Crystallographic data for **1a**:  $C_{18}H_{17}N_2O_5PtMn$ , monoclinic,  $P2_1/a$ , a = 13.574(3) Å, b = 10.5780(17) Å, c = 13.601(3) Å,  $\beta = 103.415(14)^\circ$ , V = 1899.6(6) Å<sup>3</sup>, Z = 4,  $D_{calcd} = 2.068$  g cm<sup>-3</sup>,  $F_{000} = 1128.00$ ,  $\mu$  (MoK $\alpha$ ) = 80.226 cm<sup>-1</sup>, 4523 reflections measured, 4340 independent reflections, R1 = 0.0293 ( $I > 2.00\sigma(I)$ ), wR2 = 0.0797 (all reflections).

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or added [Mn(CO)<sub>5</sub>]<sup>-</sup> anion ( $k_{obsd} = (19.4 \pm 0.3) \times 10^{-4} s^{-1}$ for [[PPN][Mn(CO)<sub>5</sub>]] = 0 mM,  $k_{obsd} = (14.2 \pm 0.2) \times 10^{-4} s^{-1}$  for [[PPN][Mn(CO)<sub>5</sub>]] = 3.4 mM in THF) on the rate was observed, excluding possible mechanisms involving prior ligand dissociation and heterolytic Pt–Mn bond cleavage processes. Addition of a large excess amount of a radical scavenger such as 2,6-di-*tert*-butylphenol (8.1 mM, 27 equiv/**2f**) or *p*-methxyphenol (3.00 mM, 10 equiv/**2f**) showed no effect on the rate, excluding radical processes. Substitution of the para position of the phenyl in **2g** by an OMe group also showed no significant effect.

We can speculate on a possible mechanism for this new photoinduced reaction from the above experimental facts. Since the irradiation causes electron promotion from the HOMO (Pt-Mn bond) to the LUMO (bpy),<sup>15</sup> the excited state of the complex involves a triplet Mn(I) cation with a bpy radical anion ligand (eq 3). Selective reductive elimination may take place from such an excited state. The origin of

this enhancement effect on reductive elimination by visible light is not completely understood at present, but the strong trans effect of the 'Bu<sub>2</sub>bpy anion radical ligand in the excited state could be responsible for it.<sup>16</sup>

$$2f \xrightarrow{vis} {}^{t}Bu \xrightarrow{i} N \xrightarrow{Ph} Me \xrightarrow{i} 3 + 4 \qquad (3)$$

In conclusion, we found the unprecedented visible light induced reductive elimination of a heterodinuclear triorganoplatinum-manganese complex. Although many light-induced reactions of organometallic compounds are known to cause ligand dissociation, homolytic bond cleavage, or luminescence, the present results illustrate the importance of light energy in fundamental organometallic elemental reaction processes, strongly related to catalyses.

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**Supporting Information Available:** Text, figures, tables, and a CIF file giving experimental details, an X-ray crystal structure analysis of **1a**, and details concerning the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

<sup>(15)</sup> Photoirradiation of **2f** with UV light was also performed, showing that both have an enhancement effect on the rate, though visible light has a stronger effect ( $k_{obs} = (24.6 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$  under visible light, (11.9  $\pm$  0.3)  $\times 10^{-4} \text{ s}^{-1}$  under UV light, (16  $\pm$  0.0)  $\times 10^{-4} \text{ s}^{-1}$  in the dark). Since **2f** has two MLCT bands at 546 and 323 nm in benzene assignable to electron promotion from the HOMO (Pt–Mn bond) to the first and second LUMOs (bpy), both irradiations would give similar bpy radical anion species eventually to cause reductive elimination. On the other hand, irradiation by our visible light having line spectra at 550 and 580 nm of a super-high-pressure 500 W UV lamp equipped with a Y-50 sharp cut filter and HA-50 heat-absorbing filter showed solvent effects. The MLCT band  $\lambda_{max}$  550 nm in benzene is sifted to  $\lambda_{max}$  450 nm in acetone, and accordingly the rate of reductive elimination under visible light irradiation is decreased from (24.6  $\pm$  0.4)  $\times 10^{-4} \text{ s}^{-1}$  in benzene to (10.4  $\pm$  0.1)  $\times 10^{-4} \text{ s}^{-1}$  in acetone. These results also support that the enhancement effect of visible light is due to absorption of the MLCT band.

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