## Decomposition of electron-excited molecules of molybdenum and tungsten phosphine hydride and phosphine nitrogen complexes 1.\* Photodehydrogenation, photodenitrogenation, and formation of coordinatively unsaturated species

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The kinetics and mechanism of photodehydrogenation of the phosphine hydride complexes  $MH_4L_4$  (M = Mo, W; L are phosphine ligands) and the formation of coordinatively unsaturated species  $ML_4$  were studied by the absorbance of long-wavelength bands with  $\lambda_{max}$  at 450–460 nm appeared in the absorption spectra of the photoproducts. The rate constants of the reactions of the coordinatively unsaturated M(DPPE)<sub>2</sub> species (M = Mo, W; DPPE = Ph\_2PCH\_2CH\_2PPh\_2) with molecular nitrogen in benzene were determined ( $k_W = 200 \text{ s}^{-1}$ ,  $k_{Mo} = 8700 \text{ s}^{-1}$ ).

**Key words:** coordination compounds, photochemistry, primary mechanism of photodecomposition, activation and fixation of small molecules.

It has previously been shown<sup>1-7</sup> that the products of photodecomposition of the molybdenum and tungsten phosphine hydride complexes are able, under mild conditions, to efficient activation and fixation of various molecules, including rather inert molecules, such as N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, alkanes, cycloalkanes, alkenes, and arenes. Therefore, it was of interest to study the mechanism of decomposition of electron-excited molecules of the phosphine hydride complexes of transition metals  $MH_4L_4$  $(M = Mo, W; L = PHPh_2, PMePh_2, PEtPh_2, PEt_2Ph,$ PBuPh<sub>2</sub>, PPrPh<sub>2</sub>, P(OPr<sup>i</sup>)<sub>2</sub>Ph, P(OPr<sup>i</sup>)<sub>3</sub>, 1/2 DPPE  $(DPPE = Ph_2PCH_2CH_2PPh_2)$ , and others). In the present work, we studied the kinetics of photodehydrogenation of the phosphine hydride complexes upon irradiation in deuterated benzene  $(C_6D_6)$  and cyclohexane  $(C_6D_{12})$  and the formation of coordinatively unsaturated species from the Mo and W phosphine hydride  $(MH_4L_4)$  and phosphine nitrogen (*trans*-M(N<sub>2</sub>)<sub>2</sub>L<sub>4</sub>) complexes under the conditions of stationary and pulse irradiation at 77 and 300 K, respectively.

## Experimental

Solutions of the  $MH_4L_4$  complexes in a concentration of  $\sim 10^{-3}$  mol L<sup>-1</sup> in deuterated solvents were irradiated with the monochromatic light at  $\sim 300$  K in cylindrical quartz cells with continuous stirring of the solutions. The light intensity was measured by the ferrioxalate actinometer.<sup>8</sup> The gas phase over the photolyzed solutions was analyzed using a Töpler pump and a mass spectrometer. Solid solutions of  $MH_4L_4$  and *trans*-

 $M(N_2)_2L_4$  were irradiated in quartz cells placed in a Dewar vessel with liquid nitrogen. The electronic absorption spectra in the visible and near-IR regions were recorded during irradiation. The pulse irradiation of solutions of the  $MH_4L_4$  and *trans*- $M(N_2)_2L_4$  complexes at 300 K was studied on a laser pulse photolysis setup<sup>9</sup> using an YAG: Nd<sup>3+</sup> laser (alumoyttrium garnet with neodymium) and the harmonic with  $\lambda = 354$  nm.

## **Results and Discussion**

The irradiation of solutions of the phosphine hydride  $MH_4L_4$  complexes at 300 K results in the evolution of  $H_2$  into the gas phase over solutions, and free phosphine ligands L appear in the solution. The quantum yields for



**Fig. 1.** Photochemical dehydrogenation of a solution of  $MoH_4(DPPE)_2$  in  $C_6D_6$  upon irrdiation with  $\lambda = 254$  nm,  $I_0 = 1.5 \cdot 10^{-8}$  Einstein s<sup>-1</sup> mL<sup>-1</sup>, 25 °C.

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**Fig. 2.** Photochemical dehydrogenation of a solution of WH<sub>4</sub>(PMePh<sub>2</sub>)<sub>4</sub> in C<sub>6</sub>D<sub>12</sub> upon irradiation with  $\lambda = 254$  nm,  $I_0 = 1.5 \cdot 10^{-8}$  Einstein s<sup>-1</sup> mL<sup>-1</sup>, 25 °C.

the photoelimination of hydrogen ( $\phi_{H_2}$ ) and phosphine ligands ( $\phi_L$ ) are ~10<sup>-1</sup> and ~10<sup>-3</sup>—10<sup>-4</sup>, respectively; therefore, the main process of [MH<sub>4</sub>L<sub>4</sub>]\* decomposition is photodehydrogenation. As shown in Figs 1 and 2, HD and D<sub>2</sub> are formed along with H<sub>2</sub> by the photodehydrogenation of MH<sub>4</sub>L<sub>4</sub> in deuterated R—D solvents.

Possible primary photochemical reactions during the photodehydrogenation of  $MH_4L_4$  can be the heterolytic cleavage of the M-H with the formation of H<sup>+</sup> or H<sup>-</sup>, homolytic cleavage forming atomic hydrogen H', and finally, H<sub>2</sub> photoelimination via the molecular mechanism. The molecular mechanism seems to be the most probable. First, in such nonpolar media as benzene or cyclohexane the heterolytic cleavage of the M-H bond is improbable. Second, in the present study, no atomic hydrogen H<sup>•</sup> or radical products of its addition to molecules with unsaturated bonds and no other radical or radical ion products were observed by the ESR method upon the photolysis of MH<sub>4</sub>L<sub>4</sub> in solid solutions at 77 K. Third, the analysis of the kinetic curves presented in Figs 1 and 2 shows that  $H_2$  is formed in the primary photochemical processes and HD and D<sub>2</sub> are formed only after an induction period (~70-90 min), i.e., in the secondary (dark and photochemical) reactions. It is most likely that the coordinatively unsaturated species appeared due to the primary photochemical reactions can interact with the deuterated R-D solvents to give the oxidative addition products, whose irradiation can result in the formation of HD and  $D_{2}$ .

$$MH_{4}L_{4} \xrightarrow{hv} H_{2} + MH_{2}L_{4} \xrightarrow{RD} MH_{2}(D)(R)L_{4} \xrightarrow{hv} HD$$
(1)

$$MH_{4}L_{4} \xrightarrow{hv} 2 H_{2} + ML_{4} \xrightarrow{RD}$$
$$\longrightarrow MD_{2}R_{2}L_{4} \xrightarrow{hv} D_{2}$$
(2)



**Fig. 3.** Absorption spectra of MoH<sub>4</sub>(PMePh<sub>2</sub>)<sub>4</sub> ( $C_0 = 10^{-3} \text{ mol L}^{-1}$ ) in toluene at 77 K, d = 1 mm: initial spectrum (*I*), after irradiation with  $\lambda = 254$  nm for 1.5 h (2); different spectrum (2 - 1) (3), and the absorption spectrum of the coordinatively unsaturated photoproduct formed at 300 K after the pulse irradiation of a solution of *trans*-Mo(N<sub>2</sub>)<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub> (4).

It is shown in Fig. 3 that upon the irradiation of a solution of  $MoH_4(PMePh_2)_4$  at 77 K ( $\lambda = 254$  nm) the initial electronic absorption spectrum (curve *I*) is transformed into the overall spectrum of the photoproduct and residues of the initial complex (curve *2*). The difference curve *3* (*2* – *I*) represents the absorption spectrum with the absorption maximum at 450–460 nm. This long-wavelength absorption band presumably belongs to the coordinatively unsaturated species  $MoH_2(PMePh_2)_4$  or  $Mo(PMePh_2)_4$ .

Note that the long-wavelength absorption band, appeared after the pulse irradiation of a benzene solution of *trans*-Mo(N<sub>2</sub>)<sub>2</sub>(DPPE)<sub>2</sub>, coincides well with the band in the absorption spectra of the photoproducts formed upon the photolysis of MoH<sub>4</sub>(DPPE)<sub>2</sub> or *trans*-Mo(N<sub>2</sub>)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub> in a solid solution of toluene at 77 K (*cf.* curves 3 and 4 in Fig. 3). This means that the same coordinatively unsaturated ML<sub>4</sub> species are formed upon the photolysis of MH<sub>4</sub>L<sub>4</sub> and *trans*-M(N<sub>2</sub>)<sub>2</sub>L<sub>4</sub>.



**Fig. 4.** Pulse photolysis of a nitrogen-saturated benzene solution of *trans*-W(N<sub>2</sub>)<sub>2</sub>(DPPE)<sub>2</sub> at 300 K: kinetics of changes in the absorbance at  $\lambda = 550$  nm ( $D_{550}$ ) after a photolyzing pulse (*I*); ln $D_{550}$  (*2*).



**Fig. 5.** Pulse photolysis of a nitrogen-saturated benzene solution of *trans*-Mo(N<sub>2</sub>)<sub>2</sub>(DPPE)<sub>2</sub> at 300 K: kinetics of changes in the absorbance at  $\lambda = 500$  nm ( $D_{500}$ ) after a photolyzing pulse (*I*); ln $D_{500}$  (2).

For the pulse photolysis of *trans*-W(N<sub>2</sub>)<sub>2</sub>(DPPE)<sub>2</sub> in benzene at room temperature, a long-wavelength band at 400–600 nm appears in the absorption spectrum of the solution after a pulse with  $\lambda = 354$  nm. In this case, as shown in Fig. 4, the absorbance at  $\lambda = 550$  nm decays exponentially in an N<sub>2</sub> atmosphere with the rate constant k = 200 s<sup>-1</sup>.

It is known<sup>10</sup> that after a photolyzing pulse of the nitrogen-saturated solution of trans-W(N<sub>2</sub>)<sub>2</sub>(DPPE)<sub>2</sub> in THF the absorbance decreases at  $\lambda = 300$  nm, *i.e.*, in the maximum of the electronic charge-transfer transition from tungsten to nitrogen. After a pulse the absorbance at  $\lambda =$ 300 nm is recovered in the two-step process with the rate constants  $k_1 = 390 \text{ s}^{-1}$  and  $k_2 = 1.6 \text{ s}^{-1}$ . The results obtained can be explained<sup>10</sup> by the formation from trans- $W(N_2)_2(DPPE)_2$  (after a pulse) of the coordinatively unsaturated W(DPPE), species followed by their two-step interaction with N<sub>2</sub> to form  $W(N_2)(DPPE)_2$  in the first step, whereas *trans*-W(N<sub>2</sub>)<sub>2</sub>(DPPE)<sub>2</sub> is formed in the second step. The obtained rate constant for the decay of the long-wavelength absorption band appeared during the pulse photolysis of *trans*-W(N<sub>2</sub>)<sub>2</sub>(DPPE)<sub>2</sub> in benzene  $(k = 200 \text{ s}^{-1})$  is close to the rate constant for the addition of the first N<sub>2</sub> molecule to the coordinatively unsaturated  $W(DPPE)_2$  species in THF ( $k_1 = 390 \text{ s}^{-1}$ ). Based on our experimental results and known literature data, one may conclude that the long-wavelength absorption band at 400-600 nm, which appears after the pulse photolysis of trans-W(N<sub>2</sub>)<sub>2</sub>(DPPE)<sub>2</sub> in benzene, belongs to the W(DPPE), coordinatively unsaturated species. For the pulse photolysis of a benzene solution of trans- $Mo(N_2)_2(DPPE)_2$  under N<sub>2</sub> at 300 K, the absorbance at  $\lambda = 500$  nm decays exponentially (Fig. 5). Similar patterns were also observed for the absorbances at  $\lambda = 400$  and 600 nm. The average rate constant for the decay of the long-wavelength absorption band (k) measured at  $\lambda = 400$ , 500, and

600 nm was 8700 s<sup>-1</sup>. By analogy to the isoelectronic tungsten complex, this constant is the rate constant for the addition of the first N<sub>2</sub> molecule to the coordinatively unsaturated Mo(DPPE)<sub>2</sub> species. Note that the ratio of the rate constants for the addition of the first N<sub>2</sub> molecule to the isoelectronic coordinatively unsaturated M(DPPE)<sub>2</sub> species for Mo and W is 43.

Thus, the irradiation of the phosphine hydride (MH<sub>4</sub>L<sub>4</sub>) or phosphine nitrogen (*trans*-M(N<sub>2</sub>)<sub>2</sub>L<sub>4</sub>) complexes of Mo and W in the region  $\lambda < 350$  nm results in the elimination of two H<sub>2</sub> or two N<sub>2</sub> molecules, respectively, to form the primary coordinatively unsaturated ML<sub>4</sub> species characterized by the long-wavelength absorption bands with  $\lambda_{max}$  450–460 nm.

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