

Photochemical interaction of molybdenum and tungsten phosphine hydride complexes with carbon dioxide

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UV, IR, and ¹H NMR spectra of photoproducts obtained by irradiation of phosphine hydride complexes MH_4L_4 ($M = Mo$ and W ; $L = PPh_2$, $PMcPh_2$, $PEtPh_2$, PEt_2Ph , and $PBuPh_2$) in an atmosphere of CO_2 , $^{13}CO_2$, and $C^{18}O_2$ have been studied. The photoproducts can be formed due to the insertion of carbon dioxide both into the $M-H$ bond and $M-C$ and $M-Ph$ bonds.

Key words: photochemistry; coordination compounds, small molecules.

It has been shown previously that carbon dioxide reduces to formate in the coordination sphere of $MoH_4(PPh_2CH_2CH_2PPh_2)_2$ (**1**) upon irradiation.¹ In this work, the photochemical interaction of the complexes of MH_4L_4 ($M = Mo$ and W ; $L = PPh_2$, $PMcPh_2$, $PEtPh_2$, PEt_2Ph , and $PBuPh_2$) with CO_2 has been studied.

Experimental

Phosphine hydride complexes MH_4L_4 (**2–7**) were prepared by a procedure described previously² and recrystallized from a benzene–methanol mixture. Benzene and toluene (for UV spectroscopy grade) purified from oxygen were used as solvents. All procedures were carried out in a metallic box filled with argon that was purified from oxygen and moisture.

Carbon dioxide of various isotopic compositions was obtained by the treatment of Na_2CO_3 , $Na_2^{13}CO_3$, $Ba^{13}CO_3$, and $BaC^{18}O_3$ with sulfuric acid.

In a typical photochemical experiment, a solution of the MH_4L_4 complex in benzene or toluene was irradiated in an atmosphere of CO_2 in a quartz cell with monochromatic or nonfiltered light ($\lambda < 450$ nm). The reaction was monitored by the change in the UV absorption spectra of the reaction mixture. To isolate the photolysis products, the solvent was removed by lyophilic evaporation. The IR and UV spectra of the initial MH_4L_4 complexes and their photoproducts were recorded on Specord 75 IR, Perkin-Elmer 325, Unicam SP 800, and Specord M 40 instruments. ¹H NMR spectra were recorded on a Bruker MSL-300 instrument (in C_6D_6).

Results and Discussion

The irradiation of solutions of MH_4L_4 in a CO_2 atmosphere was accompanied by a change in their color

from bright-yellow to reddish. After removal of the solvent, the photoproducts obtained, unlike complex **1**, were oily; therefore, they were deposited onto KBr plates for IR spectroscopy.

The most characteristic changes in the IR absorption spectra observed after irradiation of complexes **2–4** in a carbon dioxide atmosphere of various isotopic compositions are presented in Fig. 1 using complex **3** as an example. In the IR spectra of the photoproducts, the absorption bands of $W-H$ stretching vibrations (1834 and 1778 cm^{-1}) disappear, and three absorption bands appear at 1645 , 1359 , and 817 cm^{-1} , which undergo characteristic isotopic shifting to the low-frequency re-

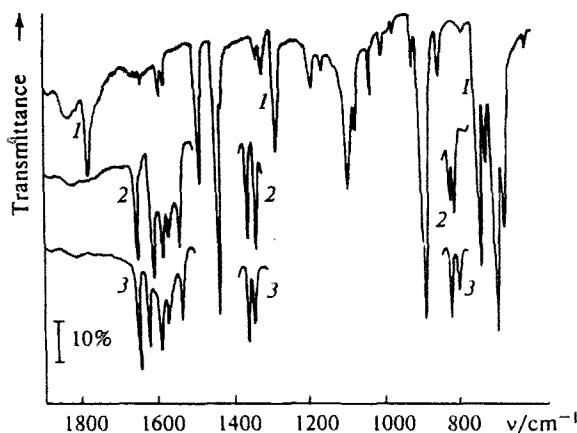


Fig. 1. IR absorption spectra: **1**, $WH_4(PMePh_2)_4$ (**3**) (in pellets with KBr); **2**, photoproduct obtained by the irradiation of compound **3** in an atmosphere of 40% CO_2 + 60% $^{13}CO_2$ (in a thin layer on KBr glass); **3**, photoproduct obtained by the irradiation of compound **3** in an atmosphere of 58% CO_2 + 42% $C^{18}O_2$ (in a thin layer on KBr glass).

* Deceased.

Table 1. Absorption bands and values of isotopic shifts in IR spectra of photoproducts obtained by the irradiation of complexes 1–7 in an atmosphere of CO₂, ¹³CO₂, and C¹⁸O₂

Complex	ν/cm^{-1}			$\Delta\nu/\text{cm}^{-1}$	
	CO ₂	¹³ CO ₂	C ¹⁸ O ₂	CO ₂ → ¹³ CO ₂	CO ₂ → C ¹⁸ O ₂
MoH ₄ (PPh ₂ CH ₂ CH ₂ PPh ₂) ₂ (1) ¹	1553,	1513,	1543,	40	10
	1364,	1341,	1348,	23	16
	797	790	781	7	16
MoH ₄ (PMePh ₂) ₄ (2)	1636,	1596,		40	
	1357,	1336,		21	
	808	800		8	
WH ₄ (PMePh ₂) ₄ (3)	1645,	1605,	1617,	40	28
	1359,	1335,	1342,	24	17
	817	810	800	7	17
WH ₄ (PEt ₂ Ph) ₄ (4)	1633,				
	1352,				
	813				
WH ₄ (PEtPh ₂) ₄ (5)	1637,				
	1351,				
	810				
WH ₄ (PBuPh ₂) ₄ (6)	1643,				
	1357,				
	810				
WH ₄ (PHPh ₂) ₄ (7)	1633,				
	1353,				
	797				

gion when ¹²C is replaced by ¹³C and ¹⁶O is replaced by ¹⁸O. In addition, the IR spectra of the photoproducts contain new absorption bands at 1583, 1570, and 1541 cm^{-1} , which remain unchanged when ¹²C is replaced by ¹³C or ¹⁶O is replaced by ¹⁸O.

Similar changes are observed in the IR spectra of the photoproducts for the other MH_4L_4 complexes studied: the absorption bands of $\nu(\text{M—H})$ stretching vibrations in the 1900–1700 cm^{-1} region disappear and new absorption bands, which differ somewhat depending on the initial MH_4L_4 , appear in fairly narrow spectral ranges, at 1645–1633, 1359–1351, and 817–797 cm^{-1} . These absorption bands in the IR spectra of the photoproducts undergo characteristic shifting to the low-frequency range due to the isotopic replacement of CO₂ by ¹³CO₂ or C¹⁸O₂. The positions of the new absorption bands sensitive to isotopic replacement and the values of the isotopic shifts in the IR spectra of the photoproducts are presented in Table 1. These data testify convincingly that the photoproduct contains CO₂.

In addition, along with the aforementioned absorption bands sensitive to isotopic replacement, additional absorption bands appear in the 1580–1577, 1569–1536, and 1542–1533 cm^{-1} regions, which do not change when ¹²C is replaced by ¹³C or ¹⁶O is replaced by ¹⁸O. The appearance of these bands is likely related to the formation of *ortho*-metallated Mo and W alkylarylpophosphines due to the intramolecular rearrangement of the primary products of the photochemical dehydrogenation of complexes 2–7. For example, the appearance of

similar bands at 1575, 1557, and 1542 cm^{-1} was observed in the IR spectra of *ortho*-metallated rhenium arylphosphines.³

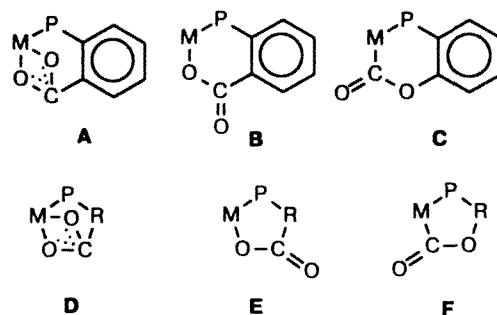
The published data¹ for complex 1, which has bidentate ligands, and whose irradiation in a carbon dioxide atmosphere results in the reduction of CO₂ to formate in the coordination sphere of the metal due to the insertion into the Mo—H bond, are presented in Table 1 for comparison. It can be seen that there is a great similarity between both the number and positions of the new absorption bands and their isotopic shifts in the IR spectra of the photoproducts obtained by the irradiation of complexes with monodentate ligands in a CO₂ atmosphere and in the spectrum¹ of compound 1. In addition, in the ¹³C{¹H} NMR spectra of the photoproduct obtained, for example, from complex 2, a new signal appears at 162.6 ppm, which is very close to the signal observed previously¹ for the formate product of photolysis (168.5 ppm). Therefore, based on this analogy, we can propose that the irradiation of Mo and W polyhydride complexes with monodentate alkylarylpophosphine ligands in a CO₂ atmosphere also results in the formation of photoproducts of the formate type. However, the following fact is noteworthy. It can be seen from the data in Table 1 that, on going from the photoproducts with bidentate ligands to the products with monodentate ligands, the difference between the frequencies of the stretching symmetric (1364 and 1359–1351 cm^{-1}) and the deformational (797 and 797–817 cm^{-1}) vibrations is not greater than 10–13 cm^{-1} , while the frequencies

of the stretching antisymmetric vibrations (1553 and 1633–1645 cm^{−1}) shift by 80–92 cm^{−1} (*i.e.*, almost by one order of magnitude greater).

It is known^{1,3–5} that the nature of the ligand (PPh₂CH₂CH₂Ph₂, PPh₃, Cl, or H) or metal (Mo, Rh, Ir, or Re) of formate complexes has a weak effect on the positions of the frequencies of, *e.g.*, $\nu_{as}(\text{CO}_2)$ vibrations ranging from 1550 to 1565 cm^{−1}. Thus, the frequencies at 1633–1645 cm^{−1} in the IR spectra of the photoproducts presented in Table 1 are almost 100 cm^{−1} greater than the frequencies of the stretching antisymmetric vibrations in the spectra of known formate complexes. Probably, this is related to the fact that the IR spectra of the photoproducts obtained, *e.g.*, from complex 1, were detected in crystals, while those obtained from compounds 2–7 were detected in a thin layer for oily substances.

As an alternative, it seems reasonable to discuss the possibility of the formation of photoproducts with other structures different from formates. As mentioned above, the CO₂-containing photoproducts obtained from complexes 2–7 also contain photoproducts of *o*-metallation containing no CO₂, in which the M–Ph bond is formed through the intramolecular hydrogen transfer from the *o*-C atom of the phenyl cycle to the metal. In addition, upon the photochemical dehydrogenation of Mo and W polyhydride complexes with monodentate alkylarylpophosphine ligands, as shown previously,⁶ the intramolecular transfer of a H atom from the α - or β -C atom of the alkyl substituent of the phosphine ligand to the metal occurs along with *o*-metallation to form the M–R bond.

Thus, during the photoreductive dehydrogenation of similar complexes, unlike complexes with bidentate ligands, it is possible to insert CO₂ not only to the M–H bond, but also to the M–Ph and M–R bonds. The formation of the compounds with the following hypothetical fragments can be proposed:



In this case, when the photoproduct has, for example, one of the structures B, C, E, or F, the assignment of the frequencies in the IR spectra of the photoproducts can be the following: 1633–1645 cm^{−1} ($\nu(\text{C}=\text{O})$); 1351–1359 cm^{−1} ($\nu(\text{C}=\text{O})$); and 797–817 cm^{−1} ($\delta(\text{CO}_2)$).

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