Photochemical reduction of carbon dioxide to formate in the coordination sphere of $MoH_4(Ph_2PCH_2CH_2PPh_2)_2$

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UV, IR, and NMR spectra of photolysis products obtained by irradiation of $MoH_4(Ph_2PCH_2CH_2PPh_2)_2$ (1) in an atmosphere of CO_2, $^{13}CO_2$, or $C^{18}O_2$ were studied. In the coordination sphere of 1, photochemical reduction of carbon dioxide occurs, yielding products of formate type. Treatment of photoproducts with acids affords formaldehyde.

Key words: carbon dioxide, photochemical reduction, photochemistry, phosphinehydride complexes of transition metals.

It has been shown previously[1—6] that irradiation of polyhydride complexes of transition metals MH_4L_4 (where M = Mo, W; and L are tertiary phosphines) with light results in coordinatively unsaturated species that can efficiently react with a variety of molecules, including relatively inert ones. For example, reaction of coordinatively unsaturated species with molecular nitrogen affords *trans*-dinitrogen complexes, whose treatment with HCl leads to reduction of the coordinated nitrogen to hydrazine[1—3]:

$$MH_4L_4 + N_2 \xrightarrow{h\nu} \textit{trans-}M(N_2)_2L_4 + HCl \longrightarrow N_2H_4.$$
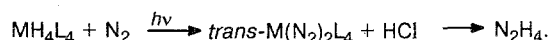
In a CO atmosphere these species are converted into phosphinecarbonyl complexes[4]:

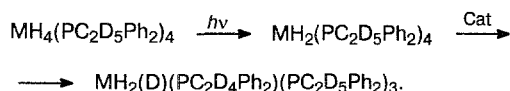$$MH_4L_4 + CO \xrightarrow{h\nu} M(CO)_xL_{6-x} + 2H_2 + (x-2)L.$$
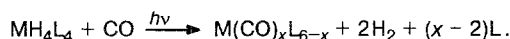
The degree of substitution (x) varies from 2 to 5 depending on the nature of the metal (M) and ligand (L) and the duration of irradiation. In benzene or cyclohexane, insertion into the metal—carbon bond occurs, giving products of intermolecular oxidative addition[5]:

$$MH_4L_4 + RD \xrightarrow{h\nu} H_2 + MH_2(D)(R)L_4,$$
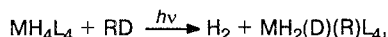
where R = C_6D_5 or C_6D_{11}

Coordinatively unsaturated species resulting from photolysis of MH_4L_4 can also be intramolecularly deactivated *via* oxidative addition of aryl or alkyl substituents of their own phosphine ligands[6]:

$$MH_4(PC_2D_5Ph_2)_4 \xrightarrow{h\nu} MH_2(PC_2D_5Ph_2)_4 \xrightarrow{Cat}$$

$$\longrightarrow MH_2(D)(PC_2D_4Ph_2)(PC_2D_5Ph_2)_3.$$

In the present work we studied photoreduction of carbon dioxide in the coordination sphere of $MoH_4(Ph_2PCH_2CH_2PPh_2)_2$ (1).

Experimental

Phosphinehydride complex 1 was prepared by a known procedure.[7] "For UV spectroscopy" grade benzene and toluene freed from oxygen were used as solvents. All of the operations were carried out in a box filled with oxygen-free dry argon.

Carbon dioxides of various isotopic compositions were prepared by treating Na_2CO_3, $Na_2^{13}CO_3$, $BaC^{18}O_3$, or $Ba^{13}CO_3$ with sulfuric acid.

In a typical photochemical experiment a solution of complex 1 in a CO_2 atmosphere was irradiated in a quartz cell with monochromatic or unfiltered light in the region below 450 nm. The course of the reaction was monitored by following the variations in the UV absorption spectra of the reaction mixture. To isolate the products of photolysis, the solvent was removed from the photolyzed solutions by lyophilic evaporation. The IR and UV spectra of the starting complex 1 and of the products of photolysis were recorded on Specord 75IR, Perkin-Elmer 325, Unicam SP800, and Specord M-40 instruments. NMR spectra were recorded in deuterobenzene on a Bruker MSL-300 spectrometer.

Results and Discussion

Irradiation of benzene or toluene solutions of complex 1 in a CO_2 atmosphere is accompanied by a change in their color from bright yellow to dark cherry. As this takes place, the band at 25640 cm^{-1} (390 nm) in the UV absorption spectra shifts to 24271 cm^{-1} (412 nm). Removal of the solvent from the irradiated solution of 1 ([1] = $2 \cdot 10^{-3}$ mol L^{-1}, toluene as the solvent, 1 atm of CO_2, 25 °C, ν_{irr} = 27397 cm^{-1} (365 nm), I_0 = $0.8 \cdot 10^{-8}$ Einstein (s mL)$^{-1}$, τ_{irr} = 107 min) gave a crystalline orange-colored product of photolysis in a yield of ~90 mol. %.

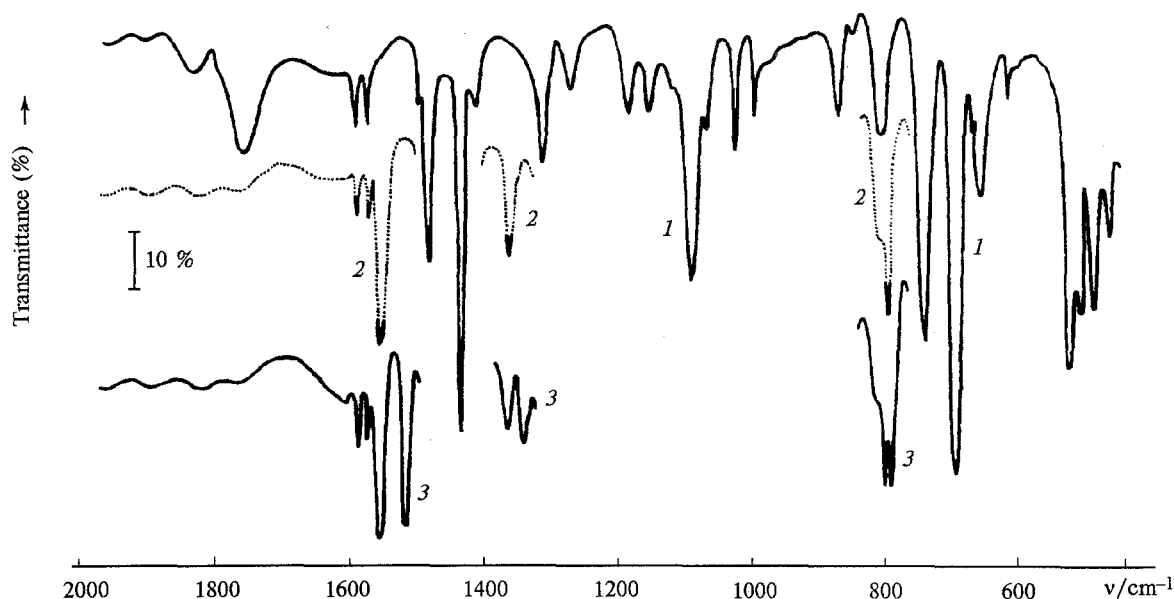**Fig. 1.** IR spectra of $MoH_4(Ph_2PCH_2CH_2PPh_2)_2$ (*1*) and the photoproducts obtained by irradiating **1** in a $^{12}CO_2$ atmosphere (*2*) in a mixture consisting of 40 % $^{12}CO_2$ and 60 % $^{13}CO_2$ (*3*).

The IR spectrum of this product as pellets with CsI displays the following most typical changes with respect to the spectrum of the starting complex **1** (Fig 1): the intensities of $\nu(Mo-H)$ stretching bands at 1830 and 1750 cm^{-1} decrease by an order of magnitude (spectra *1* and *2*), and three new bands (1553, 1364, and 797 cm^{-1}) appear (spectrum *2*). The latter absorption bands (AB) are absent from the IR spectrum of the photolysis product obtained in an argon atmosphere.

Figure 1 presents as well the IR spectrum of the photolysis product obtained by irradiation of **1** in an atmosphere of CO_2 containing ~60 % $^{13}CO_2$ (spectrum *3*). From Fig. 1 one can see that, along with the three above-mentioned AB arising in CO_2, this spectrum contains three similar lines shifted to the low-frequency region.

Isotope shifts of these bands were also observed in the IR spectrum of the photolysis product obtained in CO_2 enriched in ^{18}O. Experimental data on the positions of AB and their isotope shifts in the IR spectra of the photoproducts obtained by irradiation of compound **1** in CO_2, $^{13}CO_2$, and $C^{18}O_2$ are presented in Table 1. An analysis of these data makes it possible to assign the AB at 1553 cm^{-1} to stretching asymmetrical vibrations, the band at 1364 cm^{-1} can be assigned to stretching symmetrical vibrations, and the band at 797 cm^{-1} corresponds to bending vibrations of CO_2. This assignment is in good agreement with both characteristic positions of AB and the differences between the isotope shifts of these bands resulting from $^{12}C \rightarrow {}^{13}C$ or $^{16}O \rightarrow {}^{18}O$ isotope substitution.

One may assume that the photoproduct is a formate type complex. This is confirmed by examination of the NMR spectra. The ^{13}C and $^{13}C\{^1H\}$ NMR spectra of the photoproduct obtained from complex **1** in an
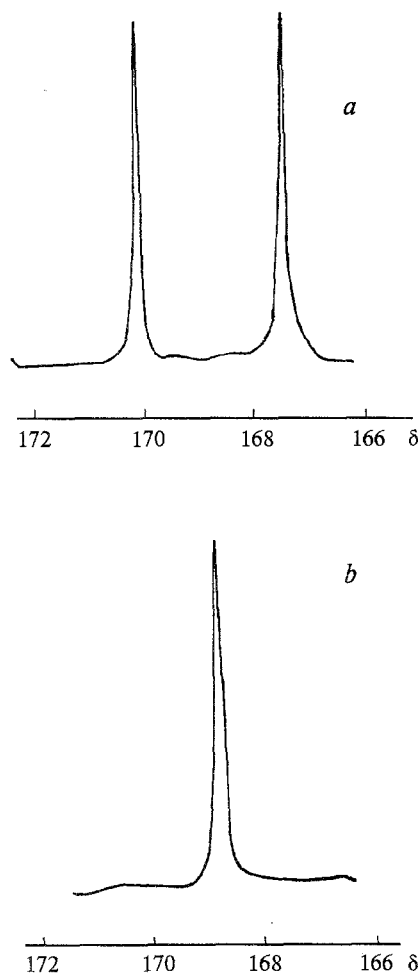
atmosphere of $^{13}CO_2$ are shown in Fig. 2. The $^{13}C\{^1H\}$ NMR spectrum exhibits a new intense line at δ 168.5, which is split into a doublet with a constant of 203 Hz in the ^{13}C NMR spectrum. The value of the chemical shift, δ 168.5, and the hyperfine coupling constant, $J_{C-H} = 203$ Hz, in the $^{13}C\{^1H\}$ and ^{13}C NMR spectra lie in the normal regions found for organic formates.[8] For example, for $Re(O_2{}^{13}CH)(Ph_2PCH_2CH_2PPh_2)_2$ formate complexes, these values are 171.9 ppm and $J_{C-H} = 202$ Hz,[9] which is very close to our results.

Thus, the data of IR and NMR studies indicate that CO_2 is photochemically reduced in the coordination sphere of $MoH_4(Ph_2PCH_2CH_2PPh_2)_2$ to formate.

It is noteworthy that when benzene or toluene solutions of complex **1** are boiled in a CO_2 atmosphere, the complex is reduced to give dicarbonyl complexes.

Table 1. Absorption bands (ν) and isotopic shifts ($\Delta\nu$) in the IR spectra of complex **1** irradiated in atmospheres of CO_2 of various isotopic compositions

Atmosphere	ν/cm^{-1}	$\Delta\nu/cm^{-1}$
CO_2	1553	—
	1364	—
	797	—
$^{13}CO_2$	1513	40
	1341	23
	790	7
$C^{18}O_2$	1543	10
	1348	16
	781	16

172   170   168   166 δ

172   170   168   166 δ

Fig. 2. ^{13}C NMR (*a*) and $^{13}C\{^{1}H\}$ NMR (*b*) spectra of the photoproduct obtained by irradiating **1** in a $^{13}CO_2$ atmosphere (deuterobenzene as the solvent).

Thus, the reaction of complex **1** with CO_2 occurring under irradiation is a photochemical process yielding formate type photoproducts, which differ from the products of the "dark" reaction.

The formate nature of the photoproduct is also confirmed by the fact that treatment of this product with HCl or H_2SO_4 gives formaldehyde. Formaldehyde was identified from its reaction with 4-amino-3-hydrazine-5-mercapto-1,2,4-triazole, which is known[10] to yield a colored complex characterized by an AB at 545 nm. The yield of formaldehyde based on starting complex **1** was ~10 mol. %. When the photoproduct is treated with

HCl in the presence of magnesium, the yield of formaldehyde increases to 17 mol. %, which implies that treatment of the photoproduct with acids yields, along with formaldehyde, formic acid, which is reduced to formaldehyde in the presence of magnesium.

It may be assumed that the photoproduct is a diformate molybdenum complex $Mo(O_2CH)_2(Ph_2PCH_2CH_2PPh_2)_2$. This is consistent with the following facts: the photoproduct incorporates a formate molecule; the $v(Mo-H)$ stretching bands disappear; complex **1** tends to form dinitrogen or dicarbonyl compounds.[1—3] As an alternative, formation of binuclear formate complexes may be assumed.

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