Insertion of Carbon Dioxide into a Molybdenum–Hydrogen Bond. Photochemical Formation of Hydridoformato Complex of Molybdenum(II)

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The reaction of $[MoH_4(dppe)_2]$ (**1**; dppe = $Ph_2PCH_2CH_2PPh_2$) with CO_2 in benzene under irradiation by light yielded $[MoH(O_2CH)(dppe)_2]$ (**2**), which was characterised spectroscopically. Complex (**2**) is slowly protonated by HCO_2H to give the known cationic complex $[MoH_2(O_2CH)(dppe)_2][HCO_2]$.

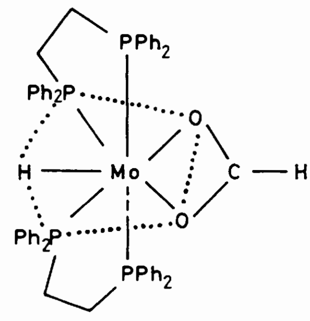
Activation of carbon dioxide with transition-metal complexes is becoming one of the most intriguing research problems aimed at the efficient utilisation of organic carbon resources.[1] Following our first report on the reduction of carbon dioxide to carbon monoxide by the use of the molybdenum(O) complex $[Mo(C_2H_4)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$),[2] several examples of the reaction of carbon dioxide with molybdenum complexes have been reported.[3–10] These include, in addition to the reduction to carbon monoxide similar to that mentioned above,[3–5] co-ordination of a CO_2 molecule to the molybdenum(O) species to give complexes of the type $[Mo(CO_2)_2(PR_3)_4]$,[6,7] and the insertion into molybdenum–nitrogen and –hydrogen bonds to yield carbamato[8] and formato derivatives, respectively.[9,10] Here we report the reaction of carbon dioxide with $[MoH_4(dppe)_2]$ (**1**), under irradiation by light, to give the hydridoformato complex $[MoH(O_2CH)(dppe)_2]$ (**2**). During the course of this investigation, Lyons *et al.*[10] reported the formation of the analogous formato complex with unidentate tertiary phosphine ligands starting from $[MoH_2(PMe_3)_5]$.

Results and Discussion

Irradiation of a yellow suspension of compound (**1**) in benzene with a 100-W high-pressure mercury lamp in an atmosphere of CO_2 at room temperature for 1 h afforded a dark red solution, from which a reddish brown solid was obtained on evaporating the solvent. Recrystallisation of the solid from toluene–hexane gave deep brown crystals, which analysed as the hydridoformato complex (2). The reaction was accompanied by the evolution of H_2 [64% on the basis of (**1**)] together with trace amounts of ethene and ethane [equation (1)].

$$\underset{(1)}{[MoH_4(dppe)_2]} + CO_2 \xrightarrow{h\nu} \underset{(2)}{[MoH(O_2CH)(dppe)_2]} + H_2 \qquad (1)$$

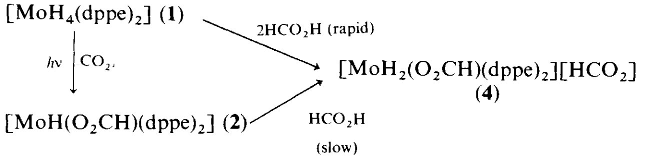
Complex (**2**) is highly soluble in aromatic hydrocarbons, moderately soluble in acetone and diethyl ether, and scarcely soluble in aliphatic hydrocarbons. It is stable to air to some extent in the solid state but is readily decomposed in solution. The i.r. spectrum of (**2**) contains bands at 1 360s and 1 550m cm^{-1} assignable to symmetric and antisymmetric CO_2 stretchings, respectively, of a bidentate carboxylato ligand.[11] Other characteristic bands are observed at *ca.* 1 810w,br and at 2 800m cm^{-1} which are assigned to Mo–H and aldehydic C–H stretchings, respectively. Similar i.r. bands have been reported for the closely related formato complex $[MoH(O_2CH)(PMe_3)_4]$ (**3**).[10] The proton n.m.r. spectrum of complex (**2**) in C_6D_6 showed an unresolved broad multiplet signal centred at δ 8.83 (1 H) and a triplet of triplets (J = 27.1 and 66.9 Hz) at -6.47 (1 H), which can be assigned to aldehydic C–H and hydridic Mo–H protons, respectively. The considerable low-field shifts of these signals as compared with those of the analogous complex (**3**) (δ 8.05 and -8.66, respectively)[10] reflect the poorer electron-donating ability of the dppe ligands in (**2**) than that of PMe_3 in (**3**).



Similarities in both the i.r. and ^1H n.m.r. characteristics of complexes (**2**) and (**3**) suggest that the former possesses the pentagonal bipyramidal structure shown above as determined for (**3**) by X-ray diffraction,[10] in which the hydride ligand and two of the four phosphorus atoms are in a pentagonal plane and the other phosphorus atoms occupy apical positions. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of complex (**2**) in toluene–C_6D_6 which consisted of A_2X_2 double triplets [δ 71.1 and 96.3 p.p.m. for the external PPh_3 reference, $^2J(P_{axial}\text{–}P_{equatorial})$ = 14.7 Hz] is also consistent with this formulation. The sharp triplet signals at 30 °C broadened as the temperature was increased to give two broad singlets at 80 °C. This temperature-dependent pattern was reversible, and complex (**2**) is considered to be fluxional in solution as is often encountered for seven-co-ordinate complexes.[12] The diformato complex $[Mo(O_2CH)_2(CO)_2(PEt_3)_2]$ was reported recently to possess formato ligands bonded to the metal in both bidentate and unidentate modes in the solid state.[13]

Since the tetrahydrido complex (**1**) has been known to release H_2 quantitatively on irradiation by light in benzene solution,[14] it is natural to consider that carbon dioxide in the present reaction system may interact with the co-ordinatively unsaturated dihydrido intermediate $[MoH_2(dppe)_2]$ formed upon irradiation. Subsequent insertion of CO_2 into one of the two Mo–H bonds in the reactive intermediate may result in the formation of the stable, eighteen-electron hydridoformato complex (**2**).[10]

Recently we have reported that the reaction of (**1**) with carboxylic acid RCO_2H gives the cationic dihydridocarboxylato complexes $[MoH_2(O_2CR)(dppe)_2][RCO_2]$ (**4**) (Scheme).[15] Although the acetato derivative of this cationic complex (**4**; R = Me) can be photochemically converted into the neutral monohydridoacetato complex $[MoH(O_2CMe)(dppe)_2]$,[15] such a reaction did not take place for the formato analogue. However, the reaction of (**1**) with allyl formate under irradiation by light yielded (**2**),[16] which provides an alternative pathway for the preparation of (**2**) from (**1**). The neutral hydridoformato complex (**2**) was converted into the cationic dihydridoformato complex (**4**; R = H) very slowly on reaction with formic acid (Scheme). Since the reaction of (**1**) with formic acid is very rapid,[15] the present results afford further evidence that the reaction of (**1**) with formic acid to yield cationic complex (**4**) does not involve the intermediate formation of (**2**), which is consistent with the reaction path proposed.[15]



Scheme.

Experimental

Most manipulations were carried out under nitrogen or argon or under vacuum using Schlenk-type flasks. U.v.–visible light irradiation was performed by using a Riko 100-W high-pressure mercury lamp through a Pyrex glass filter. Infrared (KBr disk) and n.m.r. spectra were recorded on JASCO A-202 and JEOL JNM-FX-90Q spectrometers, respectively. Gases evolved during the reaction were analysed by g.l.c. using molecular sieve 5A and Gaskuropack-54 columns. The complex $[MoH_4(dppe)_2]$ (**1**) was prepared as previously reported.[17]

Preparation of Bis[1,2-bis(diphenylphosphino)ethane]formatohydridomolybdenum(II) (**2**).—A yellow suspension of $[MoH_4(dppe)_2]$ (**1**) (0.279 g, 0.308 mmol) in benzene (20 cm^3) was irradiated by the light under an atmosphere of CO_2 in a closed flask with stirring at room temperature for 1 h to give a dark red solution. The release of H_2 [0.64 mol per mol of (**1**)] and traces of ethene and ethane was observed. From the resulting solution, solvent was removed by a trap-to-trap method to leave a reddish brown solid (0.290 g). This was dissolved in toluene (10 cm^3) and the solution was filtered. To the deep reddish brown filtrate was added hexane (10 cm^3) and the mixture was filtered to remove a yellow precipitate. From the filtrate, solvent was removed by evaporation and the residue was dissolved in toluene (20 cm^3). The solution was filtered and hexane was added. Keeping the mixture at −78 °C for several days yielded deep brown prisms of complex (**2**) (0.090 g, 31%), m.p. 222—224 °C (Found: C, 67.90; H, 5.50. $C_{53}H_{50}MoO_2P_4$ requires C, 67.80; H, 5.35%). When the reaction was carried out in an open system under a stream of CO_2 and nitrogen, (**2**) was obtained in higher yield (55%).

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