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THE REACTION OF CARBON DIOXIDE WITH HYDRIDO- AND DINITROGEN COMPLEXES OF IRON

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SUMMARY

The insertion of CO_2 into the Fe–H bond of FeH_4L_3 and $FeH_2(N_2)L_3$ ($L = PEtPh_2$) is reported. The properties of the resulting complex $Fe(O_2CH)_2L_2$ are described and the chemical evidence for the presence of the $HCOO^-$ group in this complex is discussed.

INTRODUCTION

The only reaction of carbon dioxide with transition-metal complexes previously reported concerned the insertion of CO_2 into the cobalt–hydrogen bonds of the complexes $CoH_3(PPh_3)_3$ and $CoH(N_2)(PPh_3)_3$[1-3].

In the course of our research on hydrido and dinitrogen complexes of transition metals, we have found that FeH_4L_3 and $FeH_2(N_2)L_3$ ($L = PEtPh_2$) react with CO_2 under mild conditions to give to a diformate complex of formula $Fe(O_2CH)_2L_2$. We describe below the preparation and properties of this complex.

RESULTS AND DISCUSSION

Gaseous carbon dioxide reacts under mild conditions with $FeH_4(PEtPh_2)_3$ and $FeH_2(N_2)(PEtPh_2)_3$ in solution or in the solid state, according to the following equation:

$$FeH_2L'L_3 + CO_2 \rightarrow Fe(O_2CH)_2L_2 + L' + L$$
$$(L' = H_2 \text{ or } N_2;\ L = PEtPh_2)$$

The reaction of the solid, powdered iron complexes and CO_2 at atmospheric pressure takes place slowly (20 h) at room temperature in the sunlight, but no reaction is observed during 10 h at 0° in the light or at 20° in the dark. Hydrogen and nitrogen are present in the gaseous products (Table 1), and the solid product, after washing with n-pentane at low temperature, shows analytical results in agreement with the proposed formula. However, prolonged washing of the complex or attempted crystallisation causes decomposition.

TABLE 1

Complex	μmols	Reagent	Products (μmols)			H_2/Fe	N_2/Fe	CO/Fe
			H_2	N_2	CO			
FeH_4L_3	25.2	CO_2	23.8			0.94		
FeH_4L_3	50.8	CO_2	49.0			0.96		
$FeH_2N_2L_3$	27.3	CO_2		26.6			0.97	
$Fe(HCOO)_2L_2$	38.0	H_2SO_4			68.0			1.8

The reaction between a benzene solution of $FeH_2(N_2)(PEtPh_2)_3$ and CO_2 at atmospheric pressure and room temperature, monitored by recording of the IR spectrum of the mixture, requires few hours for completion, as shown by the disappearance of the strong ν(N–N) band of the original dinitrogen complex at 2060 cm^{-1}. This reaction leads, however, to a product containing small and variable amounts of phosphine; this is probably due to the instability of $Fe(O_2CH)_2(PEtPh_2)_2$, which in solution gives free phosphine along with the insoluble iron(II) formate. We thus failed to prepare the complex $Fe(O_2CH)_2L_2$ by treatment of $FeH_2(N_2)L_2$ with formic acid or of $Fe(O_2CH)_2 \cdot 2\,H_2O$ with phosphine in various solvents at several temperatures.

The presence of the formate group in the complex is indicated by the IR spectrum, which shows, in addition to bands due to the phosphine ligand, two strong bands at 1590 and 1370 cm^{-1}, assignable to the antisymmetric and symmetric stretching vibration of the coordinated HCOO group. These bands are similar to those found in the analogous cobalt formate $Co(O_2CH)(PPh_3)_3$[1,2] [ν(HCOO) 1620 and 1300 cm^{-1}]. Furthermore, $Fe(O_2CH)_2(PEtPh_2)_2$ reacts with C_2H_5Br to give ethyl formate:

$$Fe(O_2CH)_2L_2 + 4C_2H_5Br \rightarrow FeBr_2 + 2\,HCOOC_2H_5 + 2\,LC_2H_5Br$$

and with sulphuric acid to give carbon monoxide (see Table 1):

$$Fe(O_2CH)_2L_2 + H_2SO_4 \rightarrow FeSO_4 + 2\,CO + 2\,H_2O + 2\,L$$

EXPERIMENTAL

The complexes $FeH_4(PEtPh_2)_3$ and $FeH_2(N_2)(PEtPh_2)_3$ were prepared by published methods[4–6].

All solvents were of reagent grade quality and were dried, de-aerated and saturated with the appropriate gas before use. The products were manipulated in an atmosphere of pure nitrogen by standard vacuum-line techniques. Samples for m.p. determination were contained in evacuated tubes. Infrared spectra were measured using a Perkin–Elmer 337 spectrometer. Gas chromatographic determinations were carried out using Carlo Erba Fractovap Mod. B and Hewlett Packard Mod. 5750 B instruments.

Diformatobis(ethyldiphenylphosphine)iron(II); $Fe(O_2CH)_2(PEtPh_2)_2$

Finely powdered $FeH_4(PEtPh_2)_3$ (0.2 g) was kept under CO_2 at room temperature and atmospheric pressure for 16–20 h in the sunlight. The green waxy product was washed three times with 5 ml of n-pentane at −20° to −10°, and dried under vacuum. Decomp. point 135–140°.

The n-pentane solution from the washings was evaporated under reduced pressure to give an oil, identified as $PEtPh_2$ by means of its IR spectrum. (Found: C, 60.7; H, 5.6; Fe, 102; P, 10.5. $C_{30}H_{32}FeO_4P_2$ calcd.: C, 62.7; H, 5.6; Fe, 9.7; P, 10.8%.)

The analogous reaction carried out with solid $FeH_2(N_2)(PEtPh_2)_3$ and CO_2 gave identical results (found: Fe, 10.5; P, 9.7%).

Reaction of $FeH_4(PEtPh_2)_3$ and $FeH_2(N_2)(PEtPh_2)_3$ with CO_2

(*a*). A solution of the iron complex (0.2 g, 0.28 mmol) and $PEtPh_2$ (0.14 g, 0.65 mmol) in benzene (5 ml) was kept at room temperature under CO_2 at atmospheric pressure for 45 min in the sunlight. A little residue was filtered from the resulting red-brown solution. A sample of this solution was treated with an excess of C_2H_5Br and after several hours gave ethyl formate, detected by GLC. The solution was treated with n-pentane, and on standing a white powder separated. The analytical results (found: P, 4.5; Fe, 17.2%) are not consistent with any simple formulation. The product is almost insoluble in organic solvents. The IR spectrum of the product in Nujol showed two strong bands at 1590 and 1370 cm^{-1}, assignable to the HCOO group.

A similar reaction involving $FeH_2(N_2)(PEtPh_2)_3$ and CO_2 gave similar results.

(*b*). Solid samples of powdered iron complexes were kept for 3–4 days under CO_2 in a sealed tube at room temperature. Hydrogen and nitrogen in the gaseous products were detected by GLC as previously described[7]. The results are reported in Table 1.

Reaction of $Fe(O_2CH)_2(PEtPh_2)_2$ with C_2H_5Br

A solid sample of the iron complex (40 mg) in benzene (0.5 ml) was treated with an excess of C_2H_5Br (0.05 ml) at room temperature. The mixture was stirred for 24 h. Ethyl formate was detected in the benzene solution by GLC.

Reaction of $Fe(O_2CH)_2(PEtPh_2)_2$ and H_2SO_4

A solid sample of the iron complex was treated with an excess of concentrated de-aerated sulphuric acid at room temperature in an apparatus connected to the gas chromatographic apparatus. Carbon monoxide was detected by using a 4 m column, int. diam. 6 mm, filled with a molecular sieve (5A): column temperature, 100°; carrier gas: helium, 2 l/h. The results are reported in Table 1.

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