Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The reaction between di-iron enneacarbonyl and phosphines

P.S. BRATERMAN and W.J. WALLACE*
Department of Chemistry, University of Glasgow, Glasgow (Great Britain)

(Received May 10th, 1971)

Di-iron enneacarbonyl, $Fe_2(CO)_9$, reacts readily at room temperature with (*p*-tolyl)phosphine, L, dissolved in toluene or methylcyclohexane, to give mixtures of $Fe(CO)_5$, $Fe(CO)_4L$ and $Fe(CO)_3L_2$. We have followed the progress of this reaction by IR spectroscopy, and have studied the influences of light, temperature, and carbon monoxide on the product ratios.

Separate experiments show that in the dark the products do not react with each other, with carbon monoxide or with the starting materials under our conditions. In the presence of UV light, we have observed a variety of reactions, which will be reported later.

Typical reaction runs were carried out in a black-painted flask, mounted in a temperature-controlled water bath within a light-excluding box, under a slow stream of nitrogen. The rate of nitrogen flow did not affect the results, and trapping experiments showed that loss of $Fe(CO)_5$ from the reaction mixture was negligible. IR spectra were recorded at intervals, and product concentrations determined from non-overlapping peaks of the three species involved, using Beer's law plots obtained in the same cells as those used.

The product ratio $Fe(CO)_5/Fe(CO)_4L/Fe(CO)_3L_2$ was found to be $1/1 \pm 0.05/0.40 \pm 0.01$ in toluene at 26° under nitrogen; this ratio was constant throughout each run, reproducible from one run to another, and independent of the amounts of starting materials. At 16° and 36° the ratio $Fe(CO)_5/Fe(CO)_4L$ was unchanged, while the ratio $Fe(CO)_4L/Fe(CO)_3L_2$ took the values $1/0.35 \pm 0.01$ and $1/0.42 \pm 0.04$. Absolute rates were less reproducible, and would vary erratically within a single run.

When the reaction was carried out at 26° under one atmosphere of CO, the ratio $Fe(CO)_5/Fe(CO)_4L$ was again unchanged, while the ratio $Fe(CO)_4L/Fe(CO)_3L_2$ was found to be $1/0.30 \pm 0.01$.

A suspension of $Fe_2(CO)_9$ in toluene under carbon monoxide reacted quantitatively to give $Fe(CO)_5$. Under nitrogen, $Fe_2(CO)_9$ dissolved with decomposition to give $Fe(CO)_5$ (approx. 1.4 moles for each mole of $Fe_2(CO)_9$ taken) and a red, flocculent

---

*On sabbatical leave from Muskingum College, New Concord, Ohio 43762, U.S.A.

precipitate of, presumably oxidised material★. Such a precipitate was not observed in the other reactions, which led to the formation of clear solutions. The rate of disappearance of $Fe_2(CO)_9$ in these reactions is comparable with the rate of disappearance in the presence of L.

Our data indicate that $Fe_2(CO)_9$ reacts with L by at least two different pathways and are consistent with the following reaction scheme:

Reaction A: $Fe_2(CO)_9$ (solid) $\rightleftharpoons Fe(CO)_5 + Fe(CO)_4$ (slow)
$Fe(CO)_4 + L \rightarrow Fe(CO)_4L$ (very fast)
$Fe(CO)_4 + CO \rightarrow Fe(CO)_5$ (fast)
$Fe(CO)_4 + O_2 \rightarrow$ oxidised products + CO
(slow under our conditions)

Reaction B: $Fe_2(CO)_9$ (solid) $\rightleftharpoons$ [unknown] + CO
[unknown] $+ 2L \rightarrow \rightarrow Fe(CO)_3L_2 + yFe(CO)_5 + yFe(CO)_4L$
(y probably zero)

$Fe(CO)_4$ is thought to be an intermediate in the photochemical reactions of $Fe(CO)_5$ [1], and $Os(CO)_4$ has been postulated as an intermediate in the formation of osmium carbonyl hydrides[2].

Our scheme explains the observation of Noack and Ruch[3] that $Fe_2(CO)_9$ reacts with excess $C^{18}O$ to give $Fe(CO)_5$ containing 10–15% $C^{18}O$, both mono- and di-substituted species being present from the beginning of the reaction. Our data, however, argue against a scheme in which $[Fe(CO)_4]$ is the precursor of the disubstituted material, since the 1/1 ratio of $Fe(CO)_5$ to $Fe(CO)_4L$ would then be inexplicable. While it would be tempting to invoke a tricarbonyliron toluene complex as the unknown species in reaction sequence B, we have found that the course of the reaction in methylcyclohexane is at least qualitatively similar.

Further studies are in progress to determine the behaviour of $Fe_2(CO)_9$ with other ligands, and the nature of the intermediates in the light-promoted reactions.

REFERENCES

1 L.E. Orgel, *Metal-Ligand Bonds, Coordination Chemistry,* Special Publication No. 13, The Chemical Society, London, 1959, p.93.
2 J.R. Moss and W.A.G. Graham, *J. Organometal. Chem.,* 23 (1970) C47.
3 K. Noack and M. Ruch, *J. Organometal. Chem.,* 17 (1969) 309.

★At 26° analytically unimportant quantities of $Fe_3(CO)_{12}$ are also formed in this reaction as shown by a greenish colour in the reaction mixture.

J. Organometal. Chem., 30 (1971) C17–C18