Journal of Organometallic Chemistry, 134 (1977) 381–389

Photoreactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with Potential Hydrogen Donors

J.A. Labinger* and S. Madhavan
Department of Chemistry and Radiation Laboratory
University of Notre Dame, Notre Dame, Indiana 46556

(Received March 11th, 1977)

Summary

Photolysis of the metal-metal bonded dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in the presence of a variety of potential hydrogen atom donors leads to net hydrogen abstraction only in the case of benzaldehyde, for which $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_5)$ is the only product formed. Photolysis in acetonitrile gives the monosubstitution product $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CH_3CN)$.

Introduction

It has been well established that the photochemistry of metal-metal bonded carbonyls usually involves homolytic cleavage of the metal-metal bond, followed by radical-type reactions of the resulting fragments (1-3), although other mechanisms have been established in some cases (4-6). Recently the high selectivity of the metal-centered radicals has been noted: only halogen atom abstraction from partially halogenated hydrocarbon solvents is observed, in contrast to the behavior of alkyl radicals which give hydrogen abstraction as well** (3). Presumably this is related to the relative

---

*To whom correspondence should be addressed.

**Formation of a metal hydride has been reported in the photolysis of $Re_2(CO)_{10}$ with water (7).

strength of M-X and M-H bonds. In principle, hydrogen atom abstraction by a photochemically-produced metal radical could be incorporated into a scheme for conversion of light energy, as follows:

$$M_2 \xrightarrow{h\nu} 2M\cdot$$

$$M\cdot + QH \longrightarrow HM + Q\cdot$$

$$2HM \longrightarrow M_2 + H_2$$

where M_2 represents the dimeric metal-metal bonded complex and QH the hydrogen source. Since several metal hydrides (e.g., $HMn(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$) thermally decompose to hydrogen and the dimeric species under relatively mild conditions, this cycle would effect the storage of light energy in the form of hydrogen, with the metal complex functioning as a catalyst. We have initiated an investigation into the feasibility of such a scheme, and here report preliminary results on reactions involving $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (Fp_2).*

Results

Irradiation of solutions of Fp_2 containing a wide variety of potential hydrogen donors, including toluene, diphenylmethane, triphenylmethane, cyclohexene, THF, benzyl methyl ether, isopropanol and hydroquinone, either neat or in benzene solution, gave no reaction detectable by IR or NMR. A reaction was observed for acetonitrile but, not surprisingly, this gave a substitution reaction, replacing one CO to form

---

*Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$.

$(\eta^5\text{-}C_5H_5)(CO)Fe(\mu\text{-}CO)_2Fe(CH_3CN)(\eta^5\text{-}C_5H_5)$. Structural characterization of this product follows from its IR and NMR spectra (see Experimental), which are quite similar to the analogous monosubstituted phosphine and phosphite complexes (8). Unlike the latter, the CH_3CN derivative is thermally quite unstable: a photolyzed solution in neat CH_3CN begins slowly reverting to Fp_2 as soon as the light is turned off, while a solution of the isolated product in other solvents decomposes substantially in minutes, leading to Fp_2, free CH_3CN and an insoluble, iron-containing solid.

Only for benzaldehyde was a product resulting from hydrogen abstraction found. Irradiation of a benzene solution of Fp_2 and PhCHO results in gradual formation of the known phenyl compound FpPh (9), along with evolution of gas. The overall stoichiometry is:

$$Fp_2 + 2PhCHO \rightarrow 2FpPh + 2CO + H_2$$

The product was obtained in >70% yield; no other species could be detected by IR or NMR either during, or after completion of, the reaction. The reaction is rather slow and inefficient: under conditions used (see Experimental) about four hours irradiation were required for complete conversion; the quantum yield was determined to be about 10^{-2}, considerably lower than values measured for halogen atom abstraction in related systems (1). Under the same conditions, isobutyraldehyde, crotonaldehyde, cinnamaldehyde and p-anisaldehyde all failed to react. p-Nitrobenzaldehyde reacted rapidly, but only a black, insoluble solid was obtained.

Discussion

It is apparent that hydrogen atom abstraction by Fp• is not at all a favorable process, in comparison with other radical-type reactions. Presumably the abstraction reaction, even for substrates which are generally excellent hydrogen donors, is not capable of competing with the recombination of Fp• to regenerate the starting dimer. The acetonitrile photosubstitution reaction most probably proceeds via Fp• in the following manner:

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \xrightarrow{h\nu} 2(\eta^5\text{-}C_5H_5)Fe(CO)_2\cdot$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2\cdot + CH_3CN \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)(CH_3CN)\cdot + CO$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2\cdot + (\eta^5\text{-}C_5H_5)Fe(CO)(CH_3CN)\cdot \rightarrow (\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CH_3CN)$$

Substitution via labile 17-electron intermediates has been implicated for both photochemical (1,10) and thermal (11) reactions of metal-metal bonded carbonyls.

The observation of products resulting from hydrogen abstraction only for benzaldehyde is not readily explainable. In the absence of detectable intermediates it is not possible to reach any definite conclusions about the mechanism of this reaction. Two basic mechanistic types appear reasonable; one involves the hoped-for hydrogen atom abstraction:

$$Fp_2 \xrightarrow{h\nu} 2Fp\cdot$$

$$Fp\cdot + PhCHO \rightarrow FpH + PhCO\cdot$$

$$Fp\cdot + PhCO\cdot \rightarrow FpCOPh$$

$$FpCOPh \xrightarrow{h\nu} FpPh + CO$$

$$2FpH \rightarrow Fp_2 + H_2$$

Variations on this scheme might also be envisioned. The failure to observe the benzoyl compound FpCOPh, suggested in this scheme, does not rule it out as an intermediate: photodecarbonylation of this species is very fast compared to the photoreaction of Fp_2 and PhCHO under the same conditions. Another possible mechanism is reminiscent of decarbonylation of aldehydes by coordinatively unsaturated complexes (12):

$$Fp_2 \xrightarrow{h\nu} 2Fp\cdot$$

$$Fp\cdot + PhCHO \rightarrow (C_5H_5)Fe(CO)(PhCHO)\cdot + CO$$

$$(C_5H_5)Fe(CO)(PhCHO)\cdot \rightarrow (C_5H_5)Fe(CO)(H)(COPh)\cdot$$

$$(C_5H_5)Fe(CO)(H)(COPh)\cdot \rightarrow (C_5H_5)Fe(CO)(COPh) + 1/2H_2$$

$$(C_5H_5)Fe(CO)(COPh) \rightarrow (C_5H_5)Fe(CO)_2Ph$$

This scheme appears more consistent with the extreme selectivity of the reaction, since i) the substrate must first displace CO from Fp·, restricting reaction to potential ligands (such as aldehydes); and ii) the oxidative addition step is more likely to be highly sensitive to substituents on the substrate than a radical hydrogen atom abstraction would be (e.g., the rate of H-abstraction from RCHO by phenyl radicals is virtually independent of R for both aliphatic and aromatic aldehydes (13)). Loss of H_2 might occur either directly or via H-abstraction by Fp· followed by decomposition of FpH as in the previous scheme.*

We are currently extending our studies to other metal systems in order to define the scope of these reactions and answer some of the open mechanistic questions.

Experimental

Photolyses were carried out in serum-capped pyrex or sealed NMR tubes, using a 100 watt medium pressure mercury lamp. Several of the unreactive mixtures were photolyzed in quartz tubes as well; no difference was found. Infrared spectra were obtained using a Perkin-Elmer 457 instrument; NMR on a Varian A-60; mass spectra on an AEI MS9. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals and used without further purification; recrystallization did not appear to affect results noticeably. $(\eta^5\text{-}C_5H_5)Fe(CO)_2(COC_6H_5)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_5)$ were prepared by literature methods (9).

With most of the substrates investigated (see above), prolonged irradiation caused no change in either the NMR or IR; only peaks from the starting materials could be observed. A small amount of insoluble brown solid was formed; the amount varied inversely with the degree of care taken in deoxygenating the solution.

---

*Still another possibility is that the benzaldehyde, not Fp_2, is the light-absorbing species leading to reaction; this appears to be ruled out by the fact that no benzoin (the product of photolysis of benzaldehyde (14)) is formed, even though the reaction mixtures contain large excesses of benzaldehyde.

$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CH_3CN)$

Irradiation of a solution of Fp_2 in neat CH_3CN (ca. 10^{-2} M) caused a gradual color change from red through brown to dark green. After 4-5 hours, IR and NMR showed complete disappearance of Fp_2. Evaporation of solvent gave a greenish-black solid. IR(Nujol mull): 2170 (vw, CN stretch); 1950 (s, terminal CO stretch); and 1725 cm^{-1} (bridging CO stretch). NMR (benzene): 5.53 (5 H), 5.65 (5 H) and 9.65 τ(3 H). Within minutes the benzene solution began showing NMR peaks characteristic of Fp_2 and free CH_3CN, accompanied by formation of a brown precipitate. Decomposition is slower in CH_3CN solution. Because of this instability in solution, a recrystallized sample giving satisfactory elemental analysis could not be obtained. The solid appears to be indefinitely stable under N_2. The mass spectrum showed no parent ion, but the peaks observed were very similar to the fragmentation products reported for Fp_2 (15), in addition to a peak at m/e = 41 (free CH_3CN).

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Ph$ from Fp_2 and PhCHO

Solutions of Fp_2 (10^{-2} M) and PhCHO(0.5 M) in benzene were irradiated until the red color was converted to a pale yellow-brown. After filtration to remove small amounts of brown solid, evaporation of solvent and recrystallization from pentane afforded FpPh in >70% yield, with spectral parameters (IR and NMR) identical to those previously reported (9). About four hours irradiation was required for complete reaction; monitoring by IR or NMR during reaction showed only signals due to starting materials and FpPh. Gas evolution was followed by carrying out the photolysis in a tube connected to an oil manometer by Tygon tubing; about

2-2½ moles of gas per mole of Fp_2 were evolved. Mass spectral analysis showed this to be a mixture of CO and H_2; because of instrumental instability at very low m/e values, meaningful quantitative data could not be obtained.

A similar solution containing, in addition, FpCOPh (2 x 10^{-3} M) was photolyzed in a sealed NMR tube. The NMR signal for FpCOPh was completely gone, replaced by that for FpPh, within 30 minutes; only about 20% of the Fp_2 had reacted during this time.

The quantum yield for this reaction was determined by carrying out the irradiation of a similar solution in a quartz cuvette, using a filter (Corning glass #5840) passing only light of wavelength in a narrow band around 350 nm. The reaction was monitored by following the decrease in the absorption peak at 510 nm (due to Fp_2) up to ca. 10% conversion to products. Ferrioxalate actinometry was used; under the conditions of the experiment essentially all of the light transmitted by the filter was absorbed by both the actinometer and reaction solutions.

Acknowledgements

The research described herein was supprted by the Division of Physical Research of the U.S. Energy Research and Development Administration. This is Radiation Laboratory Document No. NDRL-1739. We thank Dr. A.M. Trozzolo for helpful discussions, and Mr. Don Schifferl for assistance with mass spectral measurements.

References

1. M. Wrighton, Chem. Rev., 74 (1974) 401, and references therein.

2. C. Giannotti and G. Merle, J. Organometal. Chem., 105 (1976) 97.

3. R.M. Laine and P.C. Ford, Inorg. Chem., 16 (1977) 388.

4. A.R. Burkett, T. J. Meyer and D.G. Whitten, J. Organometal. Chem., 67 (1974) 67.

5. A. Hudson, M.F. Lappert, J.J. Macquitty, B.K. Nicholson, H. Zainal, G.R. Luckhurst, C. Zannoni, S.W. Bratt and M.C.R. Symons, J. Organometal. Chem., 110 (1976) C5.

6. D.M. Allen, A. Cox, T.J. Kemp, Q. Sultana and R.B. Pitts, J. Chem. Soc., Dalton Trans., (1976) 1189.

7. M. Herberhold and G. Süss, Angew. Chem., 87 (1975) 710.

8. R.J. Haines and A.L. du Preez, Inorg. Chem., 8 (1969) 1459.

9. R.B. King and M.B. Bisnette, J. Organometal. Chem., 2 (1964) 15.

10. B.H. Byers and T. L. Brown, J. Am. Chem. Soc., 97 (1975) 947.

11. J.P. Fawcett, R.A. Jackson and A. Poë, J. Chem. Soc., Chem. Commun., (1975) 733.

12. M.C. Baird, C.J. Nyman and G. Wilkinson, J. Chem. Soc. (A), (1968) 348.

13. M.V. Basilevskii and N.I. Piskun, Zh. Fiz. Khim., 39 (1965) 951.

14. M. Cocivera and A.M. Trozzolo, J. Am. Chem. Soc., 92 (1970) 1772.

15. A. Efraty, M.H.A. Huang and C.A. Weston, Inorg. Chem., 16 (1977) 79.