Journal of Organometallic Chemistry, 282 (1985) C43—C45
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

CHIRALITY TRANSFER TO IRON IN A PHOTOCHEMICAL REACTION OF A GLUCOPYRANOSYLIRON COMPOUND

GEORGE L. TRAINOR

E.I. du Pont de Nemours & Company, Central Research & Development Department, Experimental Station, Wilmington, DE 19898 (U.S.A.)*

(Received October 23rd, 1984)

Summary

Photolysis (350 nm) of 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosyl(η^5-cyclopentadienyl)dicarbonyliron with triphenylphosphine in benzene results in ligand substitution affording 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosyl(η^5-cyclopentadienyl)(triphenylphosphine)carbonyliron in 85% yield. The process occurs with partial chirality transfer to iron giving a 70/30 mixture of diastereomers at that center. Circular dichroism spectroscopy was used to assign the (*R*) configuration to the iron center in the predominant diastereomer.

Asymmetric iron complexes of the type $CpFe(CO)(PR'_3)R$ have been useful as stereochemical probes for transformations at iron [1—5]. Such complexes have generally been prepared by photochemical replacement of a CO ligand in the corresponding $CpFe(CO)_2R$ complex. In cases where the R substituent is chiral the two CO ligands are chemically non-equivalent and some diastereoselectivity might be expected. In all previously reported cases, however, no stereochemical enrichment at iron has been noted [4—6]. We wish to report that in the highly asymmetric environment of a carbohydrate, a modest diastereoselectivity can be observed.

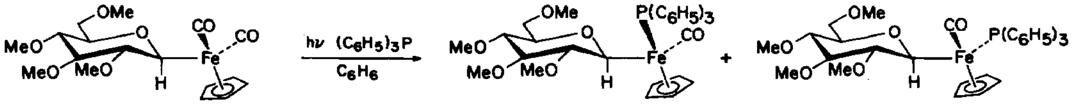
Irradiation (350 nm) of a solution of 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosyl(η^5-cyclopentadienyl)dicarbonyliron (I) [7] in deoxygenated benzene (50 m*M*) in the presence of triphenylphosphine (1.2 equiv.) led to the smooth conversion to a less polar, orange product. Excess triphenylphosphine and trace amounts of polar by-products were removed by column chromatography on silica gel in ethyl acetate/benzene (1/3) with particular care taken to avoid any possible fractionation of the orange product. Evaporation afforded the

---

*Contribution No. 3612.

0022-328X/85/$03.30

expected diastereomeric mixture of products (IIa + IIb) as an amorphous orange solid (85%).



I

IIa

IIb

70 : 30

The ^1H NMR spectrum (360 MHz) of the product is too complex to be completely assigned but is clearly indicative of a 70/30 mixture of diastereomers. Particularly diagnostic are the two sets of four singlets for the methoxyls and the two doublets (*J*(PH) 0.7 Hz) at δ 4.36 and 4.33 ppm for the cyclopentadienyl group in the major and minor diastereomers, respectively. Similarly, the proton decoupled ^{31}P NMR spectrum showed two singlets at δ 85.78 and 78.87 ppm in a 70/30 ratio. The infrared absorption spectrum had a single carbonyl band at 1916 cm^{-1}. Overall, the spectroscopic data are in full accord with the expected product (IIa + IIb).

The selectivity observed in this case is clearly not an artifact. A 70/30 product ratio combined with an 85% overall yield corresponds to a 60% absolute yield for the major isomer ruling out any fractionation or selective decomposition during work-up. To establish that the observed ratio is not the result of a slow, secondary isomerization under the reaction conditions, the reaction was carried out in benzene-d_6 and followed by ^1H NMR. The product ratio was constant throughout the course of the photolysis. No intermediates or by-products could be detected.

Circular dichroism (CD) spectroscopy has proven to be useful for the assignment of absolute configuration in systems of the type $CpFe(CO)(PR'_3)R$ when appropriate comparisons can be made to compounds of known configuration

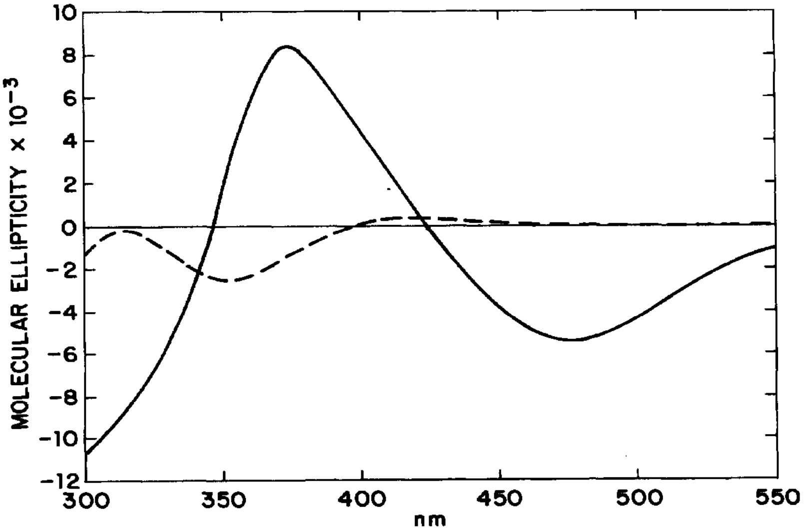
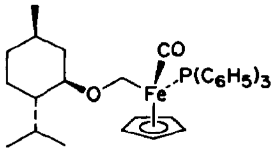


Fig. 1. (a) CD spectrum of complex I (— — — —); (b) CD spectrum of complex (IIa + IIb) (———). Spectra measured in ethanol solution (3 m*M*).

[8]. The starting complex I shows a weak CD spectrum characterized by extrema at 352 nm (−2400°) and 420 nm (+400°) (Fig. 1a). The product mixture (IIa + IIb) shows a stronger CD spectrum consistent with the generation of a chiral center at iron (Fig. 1b). The spectrum is characterized by extrema at 372 nm (+8300°) and 478 nm (−5500°). Morphologically, this spectrum is virtually the mirror image of that of complex III whose absolute configuration has been crystallographically determined [8]. On this basis it is possible to assign the (*R*)-configuration to the iron center of the major diastereomer IIa of our mixture.



III

Mechanistic studies on the $CpFe(CO)_2R$ system have implicated coordinatively unsaturated species of the type CpFe(CO)R in photochemically initiated ligand substitution and β-hydride-elimination reactions [9,10]. Such a species ($R = CH_3$) has recently been detected spectroscopically following photolysis in a PVC matrix at 12 K [11]. Although such species have not yet been structurally or stereochemically characterized, they are generally thought to be pyramidal and configurationally stable. Under these conditions, a net diastereoselectivity would require (i) diastereoselective CO dissociation and/or (ii) a differential partitioning between back reaction with nascent CO and cage escape for the two diastereomeric intermediates. Such processes might be mediated by specific intramolecular interactions with substituents on the carbohydrate portion of the molecule. Studies designed to probe these mechanistic possibilities are in progress.

Acknowledgements. R. Dale Collins is thanked for his technical assistance.

References

1 T.C. Flood, F.J. DiSanti and D.L. Miles, Inorg. Chem., 8 (1976) 1910.
2 S.L. Miles, D.L. Miles, R. Bau and T.C. Flood, J. Am. Chem. Soc., 100 (1978) 7278.
3 H. Brunner, B. Hammer, I. Bernal and M. Draux, Organometallics, 2 (1983) 1595.
4 T.C. Flood, K.D. Campbell, H.H. Downs and S. Nakanishi, Organometallic, 2 (1983) 1590.
5 P. Reich-Rohrwig and A. Wojcicki, Inorg. Chem., 13 (1974) 2457.
6 T.C. Flood and D.L. Miles, J. Am. Chem. Soc., 95 (1973) 6460.
7 G.L. Trainor and B.E. Smart, J. Org. Chem., 48 (1983) 2447.
8 C.-K. Chou, D.L. Miles, R. Bau and T.C. Flood, J. Am. Chem. Soc., 100 (1978) 7271.
9 R.J. Kazlaukas and M.S. Wrighton, Organometallic, 1 (1982) 602.
10 C.R. Folkes and A.J. Rest, J. Organomet. Chem., 136 (1977) 355.
11 R.H. Hooker, A.J. Rest and I. Whitewell, J. Organomet. Chem., 266 (1984) C27.