Inorganica Chimica Acta, 47 (1981) 187–189

The Optimization of Yield in Cluster Synthesis. The Preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$

SHAYNE J. LANDON and ARNOLD L. RHEINGOLD*

Department of Chemistry, State University of New York, Plattsburgh, N.Y. 12901, U.S.A.

Received July 15, 1980

Yields of nearly 80% of the tetrameric cluster, $[CpFe(CO)]_4$ can be obtained from the dimer, $[CpFe(CO)_2]_2$, through the catalytic action of triphenylphosphine combined with uv irradiation. Conduction of the reaction in m*-xylene proved critical to obtain high yields. In halocarbon solvents, triphenylphosphine was catalytically ineffective, and the tetramer was obtained as its radical cation.*

Introduction

Transition-metal clusters containing four or more metal atoms are formed frequently in low yield along minor pathways of complex reactions. Consequently, few details of cluster formation mechanisms are generally well understood. We wish to report that yields approaching 80% can be obtained in the synthesis of the cyclopentadienyl iron carbonyl tetramer $(CpFeCO)_4$ *I* (Cp = η^5-C_5H_5) from the iron dimer $[CpFe(CO)_2]_2$ II. Several of the factors which proved critical to obtaining optimum yields provide knowledge of the initial aspects of the *II* → *I* conversion.

$$\underset{(II)}{2[CpFe(CO)_2]_2} \rightarrow \underset{(I)}{[CpFeCO]_4} + 4CO$$

The initial procedure for this conversion [1], a thermal method, proceeded in low yield (14%) and required a tedious workup following a 14-day reflux period in xylene. Symon and Waddington with the addition of UV irradiation increased the yield to ~50% and decreased the reflux time to seven days [2]. White has very recently reported that the presence of triphenylphosphine in stoichiometric quantities assists a strictly thermal conversion providing a 56% yield in seven hours [3].

Results and Discussion

Waddington reports that from the photolysis of *II* in xylene, a yellow intermediate tentatively identified as $[Cp(xylene)Fe(CO)_2]$ could be isolated, and that the eventual disappearance of this intermediate after prolonged irradiation paralleled the formation of *II* [4]. The apparent importance of this intermediate as an initial step in dimer to tetramer conversion and the apparent σ-bonded nature of the arene ligand suggested to us that the individual xylene isomers might behave differently. In fact, in both *o* and *p*-xylene, no *II* → *I* conversion occurred, whereas yields approaching 80% were common in *m*-xylene in the presence of varying quantities of triphenylphosphine [5]. The primary photolytic event may therefore involve the formation of a σ-bonded xylene complex (from the only isomer possessing doubly activated substitution sites) with the concomitant cleavage of the dimer.

In halocarbon solvents, $CHCl_3$ and CCl_4, we have obtained conversions of *II* → *I* of up to 52% with UV irradiation and without triphenylphosphine. (In trials without UV irradiation, no conversion occurred; the addition of triphenylphosphine in halocarbon solvents did not improve yield). Under these conditions *I* is obtained as its radical cation, $(CpFeCO)_4^{+}$, which upon treatment with hydrazine is quantitatively converted to *I*. We note that these results are in conflict with an earlier report [6] of the photochemical behavior of *II* in halocarbon solvents in which $CpFe(CO)_2Cl$ was observed as the primary product, but decomposed to form ferrocene. The formation of *I* was not reported. Although Boch and Wrighton have shown that *I* can be photooxidized to I^{+} in the presence of halocarbons [7], it is not conclusive in the *II* → *I* conversion that *I* is formed first and subsequently photooxidized. If this sequence were valid, one would expect to find evidence for the formation of *I* in solvents having physical properties in common with halocarbons, and such has not been our observation. These results

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*Author to whom correspondence should be addressed.

TABLE I. Reactions of $[CpFe(CO)_2]_2$ in the Presence of $(C_6H_5)_3P$.

Trial	(Fe:P)	Rx Time (hours)*	% Yield $(CpFeCO)_4$
1	1:0.1	22.0	53
2	1:1.2	7.5	77
3	1:2.0	7.5	52
4	1:5.0	8.0	42

*Reaction times were adjusted to achieve maximum yield.

lead us to speculate that in halocarbon media the primary photochemical event is carbonyl dissociation.

The lower conversion yields found in halocarbons (in comparison to xylene) also arise from the partial photodecomposition of *II* to form ferrocene, as also observed by others [2, 6]. In halocarbons ferrocene is also photooxidized and we have isolated it directly as ferrocenium tetrachloroferrate $(Cp_2Fe)^+FeCl_4^-$ [8]. Attempts to decrease the yield of ferrocene by the addition of styrene (to act as a free-radical trap) resulted only in inhibition of the formation of the ferrocenium salt. Instead, equivalent quantities of unoxidized ferrocene were found.

The effectiveness of triphenylphosphine in promoting the conversion of *II* → *I* suggests that other Group V ligands might also serve the same purpose. White has shown convincingly that the formation of the mono(triphenylphosphine) derivative of *II*, $[Cp_2Fe_2(CO)_3(C_6H_5)_3P]$, precedes formation of *I* [3,9].

$$[CpFe(CO)_2]_2 + (C_6H_5)_3P \rightarrow [Cp_2Fe_2(CO)_3(C_6H_5)_3P]$$

$$2[Cp_2Fe_2(CO)_3(C_6H_5)_3P] \rightarrow [CpFeCO]_4 + 2CO + 2(C_6H_5)_3P$$

We reasoned initially that poorer donor ligands might further facilitate the formation-decomposition cycle of the mono-substituted derivative. A yield of only 41% of *I* could be obtained, however, when $(C_6H_5)_3As$ was substituted for $(C_6H_5)_3P$, and no conversion was found in the presence of $(C_6H_5)_3Sb$. Moreover, in the presence of the As and Sb ligands, substantial decomposition of *II* occurred (chiefly as the formation of elemental iron). In the open systems in which these reactions were conducted, it can be safely assumed that CO displacement is irreversible, and that enhanced decomposition results from the instability of repetitively and successively substituted products. Reactions occurring in the presence of ligands which form very stable, mono-substituted derivatives of *II*, *e.g.*, $(C_6H_5O)_3P$ and $(C_2H_5O)_3P$, also lead to no formation of *I*. We are currently studying whether further improvements in yield can be obtained through the use of other arylphosphines.

Table I displays representative data used to determine the optimum Fe:P ratio in UV-irradiated *II* → *I* conversion reactions in the presence of $(C_6H_5)_3P$. While an approximate 1:1 ratio produces the greatest yield, reasonable yields are still obtained at catalytic levels of $(C_6H_5)_3P$ if reaction times are extended. Very high levels of $(C_6H_5)_3P$ appear to inhibit the reaction due, presumably, to the increased ability of the mono$(C_6H_5)_3P$ derivative of *II* to reform rather than decompose along a pathway leading to formation of *I*. The nearly quantitative recovery of $(C_6H_5)_3P$ by liquid chromatography also supports the catalytic involvement of the phosphine ligand in the *II* → *I* conversion.

Experimental

All operations were conducted under an atmosphere of dried nitrogen. *Meta*-xylene (Eastman) and the halocarbons were dried over Linde 3A molecular sieve and saturated with nitrogen before use. Triphenylphosphine was recrystallized twice from methanol, and *II* was prepared and purified by a standard procedure [10]. Liquid chromatographic separations were performed on deactivated alumina (Merck, μ25) on a modified Michel–Miller, low pressure system (Ace).

Reaction of $[CpFe(CO)_2]_2$ and $(C_6H_5)_3P$

M-xylene

A solution of 1.06 g *II* (3.0 mmol) and 0.94 g $(C_6H_5)_3P$ (3.6 mmol) in 80 ml *m*-xylene was heated at reflux for 7.5 hr in a Pyrex vessel while irradiated by a Spectroline 100 UV lamp at a distance of 10 cm. The solution was filtered hot, concentrated, and chromatographed on alumina eluted with an 80/20 (v/v) chloroform/benzene mixture. Collection of the dark green band and removal of solvent afforded 0.69 g *I*, 77% yield identified by its spectral properties (nmr and ir) [1]. In separate fractions, 0.90 g $(C_6H_5)_3P$ and a trace of *II* were also collected.

Reactions employing either other Fe:P molar ratios or other group-V ligands were performed similarly.

Chloroform

A solution of 0.90 g *II* (7.5 mmol) in 30 ml $CHCl_3$ was photolyzed (as above) for 5 hr in a Pyrex tube at room temperature. During irradiation the initially purple-red solution changed to brown-green and was accompanied by the formation of a black ppt. The ppt. was identified as the molecular cation of *I*, based upon its ir absorption at 1703 cm^{-1} (neutral form, 1640 cm^{-1}) [7]. The solvent volume was reduced to 5 ml and the solution treated with 0.75 g hydrazine. Chromatographic fractionation of the resulting solution (as above) produced a dark green band (*I*), a pink band (*II*), and a yellow band (ferrocene). The yield of *I* was 52%.

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