Journal of Organometallic Chemistry, 168 (1979) 197—202
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REACTIONS OF DI-η^5-CYCLOPENTADIENYLTRICARBONYLTRIPHENYLPHOSPHINEDIIRON; AN IMPROVED SYNTHESIS OF THE CYCLOPENTADIENYLCARBONYLIRON TETRAMER *

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(Received September 8th, 1978)

Summary

The compound $(C_5H_5)_2Fe_2(CO)_3PPh_3$, previously obtained by the photolysis of $(C_5H_5)_2Fe_2(CO)_4$ with PPh_3, may also be obtained by refluxing these same reactants in benzene. The compound was isolated in pure form by means of low temperature column chromatography. It is unstable in solution in the absence of added PPh_3. Solid samples also are unstable over long periods of time. Decomposition in solution is complete within one hour at 80°C yielding a mixture of $(C_5H_5)_2Fe_2(CO)_4$ and $(C_5H_5)_4Fe_4(CO)_4$. This reaction is suppressed by excess PPh_3. Heating a mixture of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ and $P(OEt)_3$ gives a nearly quantitative yield of $(C_5H_5)_2Fe_2(CO)_3P(OEt)_3$. Refluxing a xylene solution of $(C_5H_5)_2Fe_2(CO)_4$ containing a slight molar excess of PPh_3 for 7 h results in the isolation of $(C_5H_5)_4Fe_4(CO)_4$ in 56% yield, making this reaction by far the most convenient method for the preparation, in gram quantities, of this transition metal cluster.

Introduction

Di-η^5-cyclopentadienyltetracarbonyldiiron, $(C_5H_5)_2Fe_2(CO)_4$, undergoes a number of varied reactions with phosphorus donor ligands. For example, at temperatures above 160°C in an autoclave, PPh_3 and $Ph_2PCH_2CH_2PPh_2$ react to cleave the iron dimer and displace the C_5H_5 groups giving $Fe(CO)_3(PPh_3)_2$ [1] and $Fe(CO)_3(Ph_2PCH_2CH_2PPh_2)$ [2], respectively. In refluxing toluene, ligands of the type R_4P_2 ($R = CH_3, C_6H_5$) react to form compounds of stoichiometry $(C_5H_5)_2Fe_2(CO)_2(R_2P)_2$ in which the metal—metal bond is cleaved and the two $(C_5H_5)Fe(CO)$ moieties are held together by a pair of bridging dialkyl phosphido groups [3].

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* Presented in part at the 147th National Meeting of the American Chemical Society, A.J. White, INORG 147.

At lower temperatures, such as in refluxing benzene solvent, $(C_5H_5)_2Fe_2(CO)_4$ reacts with $Ph_2P(CH_2)_nPPh_2$ (n = 1—3) to yield $(C_5H_5)_2Fe_2(CO)_2[Ph_2P(CH_2)_n\text{-}PPh_2]$ in which the diphosphine replaces both terminal CO ligands [4]. Under similar conditions, the iron dimer reacts with most monodentate phosphines and phosphites to replace only one CO yielding $(C_5H_5)_2Fe_2(CO)_3L$ as product [5]. The one known exception is the recently developed ligand Et_2NPF_2 which reacts to produce both mono- and di-substituted products [6].

One interesting and unexplored aspect of the chemical behavior of the monophosphine and -phosphite derivatives of $(C_5H_5)_2Fe_2(CO)_4$ is the variation in thermal stability exhibited by some of the members of the series. In the course of a ^{13}C variable temperature NMR study, the compound $(C_5H_5)_2Fe_2(CO)_3P(OEt)_3$ was observed to irreversibly decompose at 127°C to a carbonyl containing species thought to be $(C_5H_5)_2Fe_2(CO)_4$ [7]. In contrast, other workers noted that $(C_5H_5)_2Fe_2(CO)_3PPh_3$ was so unstable in solution above 50°C that it could not be synthesized by the thermal reaction of $(C_5H_5)_2Fe_2(CO)_4$ with PPh_3, and a room temperature photolysis of the two reactants had to be employed [5].

This paper describes the results of an investigation into the thermal decomposition of $(C_5H_5)_2Fe_2(CO)_3PPh_3$. As an outgrowth of this study, a third, previously unreported, type of reaction between $(C_5H_5)_2Fe_2(CO)_4$ and triphenylphosphine has been discovered which results in the production of $(C_5H_5)_4Fe_4(CO)_4$ rapidly and in high yield, and which represents a dramatic improvement over previously published routes to this cluster.

Experimental

All operations involving air sensitive compounds were conducted under an atmosphere of prepurified nitrogen using standard techniques. Solvents were ACS Reagent grade and were, in general, dried over molecular sieves and saturated with N_2 before use. More rigorous procedures for the deoxygenation of solvents are mentioned where used. Triphenylphosphine and triethyl phosphite were purchased from Strem Chemicals Inc. and were used as received, while $(C_5H_5)_2Fe_2(CO)_4$ were prepared and purified by literature methods [8]. Column chromatography was performed using J.T. Baker silica gel, 40—140 mesh, as adsorbant. Infrared spectra were recorded in solution using 1 mm cells on a Pye-Unicam SP 1100 spectrophotometer and were calibrated against polystyrene. NMR spectra were obtained at 60 MHz on a Perkin—Elmer R24A spectrometer using samples containing internal TMS as a reference.

Photochemical synthesis of $(C_5H_5)_2Fe_2(CO)_3PPh_3$. This reaction was carried out by the literature procedure [5] using a Pyrex flask and a Norelco Sunlamp. The reaction solvent was removed under high vacuum and the resultant solid taken up in the minimum volume of benzene and chromatographed on a 2.5 cm by 25 cm column which had been packed in hexane. The column was equipped with a water jacket and cooling system which maintained a column temperature of ca. 10°C during the chromatography. The column was developed first with hexane, then with 1/4 benzene/hexane until the unreacted $(C_5H_5)_2Fe_2(CO)_4$ had been eluted. The remaining green band was eluted with pure benzene and collected in a flask cooled in an ice/water bath. The solution was frozen and the solidified solvent removed under high vacuum (freeze-drying) to yield $(C_5H_5)_2$-

$Fe_2(CO)_3PPh_3$ as a green powder in 34% yield. The compound was characterized by its infrared spectrum in hexane ν(CO) observed 1960, 1937, 1740 cm^{-1}; reported [5] 1960, 1936, 1740 cm^{-1}; and by its NMR spectrum in $C_6D_5CD_3$ which has not previously been reported: τ (ppm) 2.60 (multiplet, 15 H, C_6H_5), 5.43 (slightly broadened singlet, 5 H, C_5H_5), 5.48 (doublet J 1 Hz, 5H, C_5H_5).

Thermal synthesis of $(C_5H_5)_2Fe_2(CO)_3PPh_3$. A mixture of 3.0 g (8.5 mmol) of $(C_5H_5)_2Fe_2(CO)_4$ and 16.1 g (61.5 mmol) PPh_3 was refluxed under N_2 in 125 ml benzene for 24 h. The solvent was removed under high vacuum and the resulting solid chromatographed in several portions as described above. After removal of solvent, the combined fractions contained 1.2 g (24% yield) of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ which gave NMR and infrared spectra identical to those described above.

Thermolysis of $(C_5H_5)_2Fe_2(CO)_3PPh_3$. In a typical reaction, 1.0 g (1.7 mmol) of freshly prepared $(C_5H_5)_2Fe_2(CO)_3PPh_3$ was dissolved in 100 ml of benzene which had been freshly distilled from Na/K benzophenone ketyl. The solution was held at reflux temperature for 1 h. The reaction mixture was reduced in volume to ca. 15 ml and then applied to the top of a 2.5 cm by 25 cm column, packed in hexane and precooled to 10° C. Elution with hexane brought down a faint orange band which was not collected. Elution with 1/4 benzene/hexane brought down a red-brown band which, after removal of solvent, was identified as $(C_5H_5)_2Fe_2(CO)_4$ by its NMR and infrared spectra [8]. No trace of the starting material was observed on the column, but a green band, immobile with pure benzene as solvent remained at the top of the column. Elution with $CHCl_3$ resulted in the recovery of $(C_5H_5)_4Fe_4(CO)_4$, identified by its NMR and infrared spectra [9]. The yields of these two products for five representative reactions are presented in Table 1. In all trials, a considerable amount of intractable brown decomposition material remained at the top of the column.

One thermolysis reaction was conducted in the following manner. A thick walled Carius tube with an internal volume of 60 ml was filled with 0.690 g (1.17 mmol) of freshly prepared $(C_5H_5)_2Fe_2(CO)_3PPh_3$, connected to a vacuum line, evacuated, then cooled in a liquid nitrogen bath. About 30 ml of toluene, which had been distilled from Na/K benzophenone ketyl, was distilled in under high vacuum and the tube sealed. After careful warming to room temperature, the tube was placed in an oven at 80° C for 2 h. The tube was then cooled to room temperature, broken open in a glove bag, the solution transferred, and

TABLE 1

PRODUCT DISTRIBUTION FROM $(C_5H_5)_2Fe_2(CO)_3PPh_3$ REACTIONS

Trial	$(C_5H_5)_2Fe_2(CO)_3PPh_3$ (g(mmol))	$(C_5H_5)_2Fe_2(CO)_4$ (g(mmol))	$(C_5H_5)_4Fe_4(CO)_4$ (g(mmol))	Molar ratio [a]	Yield [b] (%)
1	1.00 (1.70)	0.204 (0.577)	0.172 (0.289)	2.0/1	68
2	1.00 (1.70)	0.213 (0.602)	0.124 (0.208)	2.9/1	60
3	1.00 (1.70)	0.280 (0.792)	0.118 (0.198)	4.0/1	70
4	1.00 (1.70)	0.243 (0.687)	0.114 (0.191)	3.6/1	63
5	1.00 (1.70)	0.199 (0.563)	0.146 (0.245)	2.3/1	62
6 [c]	0.69 (1.17)	0.299 (0.845)	<0.001		72

[a] Ratio of mol $(C_5H_5)_2Fe_2(CO)_4$ recovered to mol $(C_5H_5)_4Fe_4(CO)_4$ recovered. [b] Based upon mol Fe recovered as either $(C_5H_5)_2Fe_2(CO)_4$ or $(C_5H_5)_4Fe_4(CO)_4$. [c] Reaction performed in sealed tube (see Experimental).

reduced in volume to ca. 15 ml. This solution was chromatographed as described above. The product distribution, reported in Table 1, was quite different than that observed for reactions in open vessels, with only a very small amount of $(C_5H_5)_4Fe_4(CO)_4$ being formed along with a higher yield of $(C_5H_5)_2Fe_2(CO)_4$ than had been observed previously.

Thermolysis of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ in the presence of excess PPh_3. A mixture of 1.0 g (1.7 mmol) of freshly prepared $(C_5H_5)_2Fe_2(CO)_3PPh_3$ and 2.2 g (8.4 mmol) PPh_3 was refluxed in 100 ml of benzene, which had been distilled from Na/K benzophenone ketyl, for 1 h. The solution was reduced in volume to ca. 15 ml and chromatographed at 10°C as described above. No $(C_5H_5)_2Fe_2(CO)_4$ was observed on the column during development with hexane or 1/4 benzene/hexane solution. Elution with pure benzene brought down a green band which was collected in a flask cooled to 0°C. Removal of the solvent by freeze drying resulted in recovery of 0.94 g (94% yield) of $(C_5H_5)_2Fe_2(CO)_3PPh_3$. No green band corresponding to $(C_5H_5)_4Fe_4(CO)_4$ could be eluted with $CHCl_3$. A small amount of brown decomposition material remained at the top of the column.

Thermal reaction of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ and $P(OEt)_3$. A mixture of 1.5 g (2.6 mmol) freshly prepared $(C_5H_5)_2Fe_2(CO)_3PPh_3$ and 0.43 g (2.6 mmol) $P(OEt)_3$ was refluxed in benzene, which had been distilled from Na/K benzophenone ketyl, for 1 h. The solution was reduced in volume to ca. 20 ml and chromatographed at 10°C on a 2.5 cm by 25 cm column packed in hexane. Elution with hexane and benzene/hexane mixtures of gradually increasing benzene content resulted in recovery of a single violet band. Evaporation of solvent resulted in the isolation of 1.23 g (96% yield) of $(C_5H_5)_2Fe_2(CO)_3P(OEt)_3$ which was identified by a comparison of its NMR and infrared spectra with those of an authentic sample prepared by the literature method [5].

Synthesis of $(C_5H_5)_4Fe_4(CO)_4$. In a typical reaction, a solution of 5.0 g (14.1 mmol) $(C_5H_5)_2Fe_2(CO)_4$ and 4.3 g (16.5 mmol) PPh_3 in 150 ml xylene was refluxed vigorously for 7 h. The solution was reduced in volume to about 50 ml and 50 ml of hexane was added. After overnight storage in a freezer at —10°C, filtration yielded a green-brown solid which was washed three times with 25 ml portions of hexane. The solid was dissolved in 50 ml of CH_2Cl_2 and the solution filtered through Celite. Fifty ml of hexane were then added, and the solution reduced to about one-half its volume on a rotary evaporator. During this process dark green crystals appeared which were collected on a glass frit and washed three times with hexane to give 2.4 g (56% yield) of pure $(C_5H_5)_4Fe_4(CO)_4$, characterized by its NMR and infrared spectra.

Results and discussion

In contrast to the previous report [5], it has now been observed that $(C_5H_5)_2Fe_2(CO)_3PPh_3$ can be prepared, albeit in only modest yield, by the reaction of $(C_5H_5)_2Fe_2(CO)_4$ with a large excess of PPh_3 in refluxing benzene. This compound may be isolated in reasonably pure form by low temperature column chromatography followed by removal of solvent at low temperatures. The infrared spectrum of this compound has been discussed previously [5]. The proton NMR spectrum is similar to those reported for other mono-phosphine derivatives of $(C_5H_5)_2Fe_2(CO)_4$ displaying two sets of separate cyclopentadienyl proton resonances, a singlet at lower field assignable to the ring on the unsubstituted iron and a doublet J(P—H) 1 Hz at higher field assignable to the ring on the iron atom bearing the phosphorus ligand, along with resonances for the protons on the coordinated phosphorus ligand [5,7,10].

Solid samples of $(C_5H_5)_2Fe_2(CO)_3PPh_2$ are extensively decomposed after several weeks, even when stored at —10° C under a nitrogen atmosphere. In the absence of excess PPh_3, solutions of the compound in carefully deoxygenated hydrocarbon solvents decompose within a period of hours at room temperature and above. NMR spectra, unless taken very quickly or at below ambient temperature, often contain an impurity peak at τ 5.21 ppm which grows in with time and is due to formation of $(C_5H_5)_2Fe_2(CO)_4$ (vide infra).

When benzene solutions of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ are heated to reflux in vessels open to a nitrogen atmosphere decomposition is complete within 1 h. The distribution of isolable products for five representative reactions is shown in Table 1. In general, 60—70 mol% of the starting iron may be isolated as either $(C_5H_5)_2Fe_2(CO)_4$ or $(C_5H_5)_4Fe_4(CO)_4$. The relative amounts of these two compounds formed during the decomposition varies erratically between experimentally observed limits of a 2/1 molar ratio and a 4/1 molar ratio. Such a variation is not totally surprising, considering that the rate of CO loss from the refluxing reaction solution could be quite variable.

One thermolysis reaction was performed in a sealed tube in order to determine the product distribution under conditions which minimized CO loss and to identify the impurity peak formed by decomposition of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ in sealed NMR tubes. As may be seen from Table 1, only a trace of green material, presumably $(C_5H_5)_4Fe_4(CO)_4$, was produced, with $(C_5H_5)_2Fe_2(CO)_4$ being the predominant isolable product. The observed yield of $(C_5H_5)_2Fe_2(CO)_4$ (72%) is close to the theoretical maximum if CO is considered to be the limiting reagent in the reaction 1,

$$4(C_5H_5)_2Fe_2(CO)_3PPh_3 \rightarrow 3(C_5H_5)_2Fe_2(CO)_4 + \text{decomposition products} \qquad (1)$$

where the maximum yield of the iron dimer is 75%. The attempted thermolysis of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ in the presence of a five-fold excess of triphenylphosphine yielded only unreacted starting material after 1 h. The reaction is thus inhibited by excess phosphine indicating that phosphorus ligand dissociation is perhaps an important step in the mechanism of decomposition.

The reaction of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ with a molar equivalent of $P(OEt)_3$ in refluxing benzene proceeds to completion within 1 h to give a nearly quantitative yield of the known compound $(C_5H_5)_2Fe_2(CO)_3P(OEt)_3$. No formation of either $(C_5H_5)_2Fe_2(CO)_4$ or $(C_5H_5)_4Fe_4(CO)_4$ was observed during the workup of this reaction. The rapid rate and high yield of this substitution reaction relative to analogous reactions of $(C_5H_5)_2Fe_2(CO)_4$ itself [5] indicates again that PPh_3 is an excellent leaving group. The use of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ as a synthetic intermediate should be considered when the synthesis of derivatives of $(C_5H_5)_2Fe_2(CO)_4$ involving scarce or unreactive two-electron donor ligands is considered.

The observation that the rapid thermal decomposition of $(C_5H_5)_2Fe_2(CO)_3PPh_3$ leads to its precursor, $(C_5H_5)_2Fe_2(CO)_4$, as well as the tetranuclear cluster $(C_5H_5)_4Fe_4(CO)_4$ led to the hope that the otherwise slow conversion of the iron dimer to the tetramer [9,11] might be promoted or even "catalyzed" by PPh_3.

Conditions were sought, therefore, under which $(C_5H_5)_2Fe_2(CO)_3PPh_3$ could be rapidly generated from the iron dimer and then decomposed in situ. Since it appeared that the slow step in this process would be the reaction of $(C_5H_5)_2Fe_2(CO)_4$ with PPh_3, a slight excess of the latter was used. After a reaction period of only 7 h, $(C_5H_5)_4Fe_4(CO)_4$ was isolated in 56% yield. No attempt has been made to determine the ultimate fate of the triphenylphosphine, or to learn whether the conversion of $(C_5H_5)_2Fe_2(CO)_4$ to $(C_5H_5)_4Fe_4(CO)_4$ could be appreciably promoted by truly catalytic amounts of triphenylphosphine.

Prior to this work, there were two literature procedures for the synthesis of $(C_5H_5)_4Fe_4(CO)_4$. The original method, due to King, involved refluxing $(C_5H_5)_2Fe_2(CO)_4$ in xylene for 12 days followed by exhaustive Soxhlet extraction of the solid product with ethyl ether for a further seven days to give the tetramer in about 14% yield [9]. More recently, Symon and Waddington reported that a 56% yield of the tetramer could be obtained by photolyzing a refluxing xylene solution of the dimer for seven days [11]. The procedure for synthesis of $(C_5H_5)_4Fe_4(CO)_4$ employed in this paper requires only a 7 h reaction period, and thus production and isolation of pure cyclopentadienylcarbonyliron tetramer in gram quantities may be accomplished in only 2 working days, as compared to a minimum of 19 and 8 working days for the previously reported methods.

It should also be noted that the course of thermal reactions between triphenylphosphine and $(C_5H_5)_2Fe_2(CO)_4$ is quite dependent upon the reaction conditions employed. Under the mildest temperature conditions, ca. 80°C, and with a large excess of phosphine, simple substitution of a PPh_3 for a carbonyl ligand occurs. More vigorous heating, to ca. 140°C, and a reduction in the amount of excess phosphine results in condensation of the iron dimer to the tetrameric cluster. Under the most extreme conditions, heating at 160°C in a sealed vessel to prevent escape of CO, even more extensive rearrangement of the coordination sphere around iron occurs, yielding $Fe(CO)_3(PPh_3)_2$ [1].

Acknowledgements

The support of this research by a grant from the Professional Development Fund at Agnes Scott College is gratefully acknowledged. I would also like to express gratitude to Prof. C.T. Sears for the use of the low temperature chromatography equipment, and to Prof. M.D. Curtis for helpful discussion.

References

1 B.F. Hallam and P.L. Pauson, J. Chem. Soc., (1956) 3030.
2 H. Behrens and W. Aquila, Z. Naturforsch. B, 22 (1967) 454.
3 R.G. Hayter, J. Amer. Chem. Soc., 85 (1963) 3120.
4 R.J. Haines and A.L. duPreez, J. Organometal. Chem., 21 (1970) 181.
5 R.J. Haines and A.L. duPreez, Inorg. Chem., 8 (1969) 1459.
6 R.B. King, W.C. Zipperer and M. Ishaq, Inorg. Chem., 11 (1972) 1361.
7 D.C. Harris, E. Rosenberg and J.D. Roberts, J. Chem. Soc. Dalton, (1974) 2398.
8 R.B. King, Organometallic Syntheses, Volume 1, Academic Press, New York, 1965. p. 114.
9 R.B. King, Inorg. Chem., 5 (1966) 2227.
10 F.A. Cotton, L.J. Kruczynski and A.J. White, Inorg. Chem., 13 (1974) 1402.
11 D.A. Symon and T.C. Waddington, J. Chem. Soc. Dalton, (1973) 1879.