Inorganica Chimica Acta, 22 (1977) L39–L41

Role of Ph_3E (E = P, As and Sb) Ligands in the Syntheses of η-Cyclopentadienyliron Carbonyl Complexes

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Received February 12, 1977

Although several authors [1–8] have studied the reactions of Ph_3E ligands with $(\eta-C_5H_5)Fe(CO)_2X$ (X = Cl, Br or I) under various reaction conditions and different types of products, *viz.* $(Ph_3P)_2Fe(CO)_3$ [1], $[(\eta-C_5H_5)Fe(CO)_2Ph_3P)]Cl\cdot 3H_2)$ [2], $[(\eta-C_5H_5)Fe(CO)_2(Ph_3E)]PtCl_6$ [2], $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$ [3–5], $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$ [4], $(\eta-C_5H_5)Fe(CO)(Ph_3As)I$ [7], and $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]BF_4$ [8] were reported, the previously available experimental data in brief for the complexes $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$ and $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$ (which are obtained as reaction products in this work also) are not fairly reproducible in nature and no attempt has been made so far to study the role of Ph_3E ligands in reactions with $(\eta-C_5H_5)Fe(CO)_2X$ by varying time intervals, organic solvents, reactant's amounts and reaction conditions. In the present paper attempts have been made to study these reactions with the above points of view and much attention has also been paid to clarify some confusing problems arising during the syntheses and interpretation of results.

Treichel *et al.* [4] only studied the reaction of Ph_3P with $\eta-C_5H_5Fe(CO)_2I$ by reflux method in some detail but syntheses of their reported products, *viz.* $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$ and $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$ in fairly good agreement with the experimental data, particularly with respect to yields, are absolutely an art and not always true.

I have studied this reaction several times and concluded that the $(\eta-C_5H_5)Fe(CO)_2I$ on refluxing with Ph_3P in benzene for varying time intervals yielded a mixture of $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$ and $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$. The proportion of these two products depended upon the reaction period. Only long time reflux (*ca.* 220–22 h) gave $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$ in noticeable yield (it also happens occasionally) whereas $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$ was the main product of short time reflux (8–12 h). However, Angelici *et al.* [8] have reported a convenient synthetic route for the preparation of $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]BF_4$ in 52% yield by the oxidation of $[(\eta-C_5H_5)Fe(CO)_2]_2$ with acetone, followed by addition of triphenylphosphine (Ph_3P).

The most interesting point is the appearance of carbonyl stretching frequencies in the CO region of the mixture obtained in most experiments and separately isolated components of the mixture, *i.e.* $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$ and $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$, which are quite analogous in both cases. In the mixture three ν(CO) bands at *ca.* 2055s, 2010s and 1935vs cm^{-1} (in KBr disc) are observed among which the first two ν(CO) absorptions at *ca.* 2055s and 2010s cm^{-1} may be attributed to $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$, and the last ν(CO) absorption at *ca.* 1935vs cm^{-1} is due to $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$, respectively. In the mixture positions of the other bands in the i.r. spectra due to $(\eta-C_5H_5)$–Fe [9] and Ph–P [10, 11] vibrations are slightly shifted from their appearance in the separately isolated components, *i.e.* $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$ and $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$.

In the i.r. spectrum of the ionic complex $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$ the ν(CO) absorptions (*ca.* 2055s and 2010s cm^{-1}) are almost the same as the ν(CO) bands of $(\eta-C_5H_5)Fe(CO)_2I$ [12]. This similarity often prevented the detection of any different product such as $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$, from the reaction of $(\eta-C_5H_5)Fe(CO)_2I$ and Ph_3P, but the appearance of other bands due to Ph–P [10, 11] vibrations in the i.r. spectrum and estimation of phosphorus percentage confirmed its formation. The physical properties such as colour, m.p., and solubilities in organic solvents clearly differentiate between $(\eta-C_5H_5)Fe(CO)_2I$ and $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$.

$(\eta-C_5H_5)Fe(CO)_2I$ on refluxing with Ph_3P in benzene for *ca.* 20 hr under an atmosphere of dry nitrogen yielded three types of reaction products, *viz*:

Products	Colour	Yield	M.P.	ν(CO) cm^{-1}
1) $(\eta-C_5H_5)Fe(CO)(Ph_3P)I$	Green	60%	140 °C	1935 vs
2) $[(\eta-C_5H_5)Fe(CO)_2(Ph_3P)]I$	Yellow	25%	172 °C	2055s,2010s
3) $(\eta-C_5H_5)Fe(CO)_2I$ (unreacted portion)	Black	15%	120 °C	2044s,2000s

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The yields of these reaction products are found invariable for the same reaction conditions. A change in the order of yields as noticed in this work: (η-C_5H_5)Fe(CO)(Ph_3P)I > [(η-C_5H_5)Fe$(CO)_2$(Ph_3)]I > (η-C_5H_5)Fe$(CO)_2$I is an art and it mainly depends on the reactant's amount, reaction period and selection of organic solvents.

Several attempts were made to isolate the product [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I in larger amount (as reported by Treichel *et al.* [4]) than (η-C_5H_5)Fe(CO)(Ph_3P)I, but failed and in most cases only (η-C_5H_5)Fe(CO)(Ph_3P)I was isolated in major yield. This observation is in fair agreement with the results reported by Brown, Haines *et al.* [13, 14] from the reactions of η-C_5H_5Fe$(CO)_2$X (X = Br and I) and P$(OPh_3)_3$ in benzene under reflux which afforded η-C_5H_5Fe(CO)P(OPh_3)X in yields greater than 85–90%. An attempt was also performed to get [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I by refluxing the (η-C_5H_5)Fe(CO)(Ph_3P)I for another 20 hr but it was not recovered. This attempt only produced better crystals of (η-C_5H_5)Fe(CO)(Ph_3P)I. The possibility of formation of [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I in some larger amount was noticed when Ph_3P was in excess over the required 1:1 molar ratio with (η-C_5H_5)Fe$(CO)_2$I, which also reduced the amount of unreacted portion of (η-C_5H_5)Fe$(CO)_2$I observed in the reaction. Hot benzene is found most suitable to separate the (η-C_5H_5)Fe(CO)(Ph_3P)I from [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I, while a large volume of unwarmed benzene was consumed for the same purpose. A mixture of hexane and benzene (80:20) is found more appropriate and less time consuming for the removal of unreacted portions of (η-C_5H_5)Fe$(CO)_2$I. Dichloromethane was found suitable for crystallisation of [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I.

Use of a high boiling solvent such as xylene in the reaction of Ph_3P and η-C_5H_5Fe$(CO)_2$I led to the decomposition of resulting substances into unidentified products. The examination of the i.r. spectra of the resulting products indicated that they did not contain CO groups.

I have also carried out photochemical syntheses to study the reaction of Ph_3P with (η-C_5H_5)Fe$(CO)_2$I. U.V. irradiation period of up to 18 hr in benzene solution yielded a mixture of (η-C_5H_5)Fe(CO)(Ph_3P)I and [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I in which the former was the major part. Longer irradiation period (*ca.* 60 hr) only yielded noticeable amount of [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I. Very fine crystals of both products were obtained by this method.

Probably the compound (η-C_5H_5)Fe(CO)(Ph_3P)I isolated by Polovyanyuk *et al.* [3, 5] from the reaction of Ph_3P and (η-C_5H_5)Fe$(CO)_2$I by using u.v. irradiation method (irradiation period 17 hr) which decomposed at 178–9 °C is a mixture of (η-C_5H_5)Fe(CO)(Ph_3P)I and [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I. They might have observed the presence of three C–O stretching frequencies in the carbonyl region of the i.r. spectrum of the complex but the similarities of the first two bands (above 2000 cm^{-1}) with the νCO bands of η-C_5H_5Fe$(CO)_2$I which remained as unreacted, prevented them from detecting the formation of another product, [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I, alongwith (η-C_5H_5)Fe(CO)(Ph_3P)I. I have isolated both components separately and characterized by elemental analyses, m.p. and i.r. spectra. The isolated products (η-C_5H_5)Fe(CO)(Ph_3P)I and [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I clearly melt at 140 °C and 172 °C respectively.

I have also recorded the ^{1}H n.m.r. spectrum of (η-C_5H_5)Fe(CO)(Ph_3P)I, the data for which are not available so far in the literature. The values of τ for C_5H_5 and phenyl protons are *ca.* 5.53 and 2.49–2.72, respectively. A resonance at *ca.* 5.50 τ may be attributed to the coupling of the protons with ^{31}P nucleus. These values are in fair agreement with the values for neutral triphenylphosphine substituted η-cyclopentadienyliron carbonyl complexes.

The products (η-C_5H_5)Fe(CO)(Ph_3P)I and [(η-C_5H_5)Fe$(CO)_2$(Ph_3P)]I showed an unexpected behaviour with nitrogen donor ligands. They do not react under normal conditions with mono-dentate nitrogen donor ligands such as aliphatic and aromatic amines but with bi-dentate ligands such as 1,10-phenanthroline or 2,2′-bipyridine they immediately yielded CO free stable products of the type [(η-C_5H_5)Fe(B)(Ph_3P)]I [15] (B = *o*-phen or 2,2′-bipy).

We have observed the formation of two products, (η-C_5H_5)Fe(CO)(Ph_3E)I [15] and [(η-C_5H_5)Fe$(CO)_2$(Ph_3E)]I [15] (E = P, As and Sb) from the reaction of (η-C_5H_5)Fe$(CO)_2$I with Ph_3E ligands while Davison *et al.* [2] reported only [(η-C_5H_5)Fe$(CO)_2$(Ph_3E)]PtCl_6 from the reaction of Ph_3E with (η-C_5H_5)Fe$(CO)_2$Cl.

Two more ligands, *viz.* bis(diphenylarsino)methane (DAM) and trimethylolpropane phosphite (Tmpp) behave like Ph_3E ligands in the reaction with η-C_5H_5Fe$(CO)_2$I. Four new complexes of the same type: [(η-C_5H_5)Fe$(CO)_2$(L)]I and (η-C_5H_5)Fe(CO)(L)I (L = DAM and Tmpp) were obtained from the reaction of these ligands (L) and η-C_5H_5Fe$(CO)_2$I in benzene under reflux for *ca.* 20h. These complexes have been characterised by their elemental analyses and i.r. spectral studies.

Complex	Colour	ν(CO) (cm^{-1})
(η-C_5H_5)Fe(CO)(DAM)I	Green	1952 vs
[(η-C_5H_5)Fe$(CO)_2$(DAM)]I	Yellow	2050s,2005s
(η-C_5H_5)Fe(CO)(Tmpp)I	Green	1960 vs
[(η-C_5H_5)Fe$(CO)_2$(Tmpp)]I	Yellow	2048s,2010s

The isolation procedures were quite parallel with the above discussed experimental observations.

Acknowledgment

Financial support from the University Grants Commission, New Delhi, India, is greatly appreciated.

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