

THE SYNTHESIS OF GROUP V SUBSTITUTED DERIVATIVES OF IRON PENTACARBONYL IN HIGH YIELD

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(Received July 17th, 1973)

Summary

A simple, high yield, general synthesis of an extensive collection of mono-substituted derivatives of iron pentacarbonyl is based on the use of $\text{Fe}(\text{CO})_5$ as solvent, substrate and carbonylating agent.

Introduction

Iron pentacarbonyl reacts with the appropriate ligand ($\text{L} =$ arylphosphines or arylarsines) in refluxing cyclohexanol to give the corresponding $\text{LFe}(\text{CO})_4$ and $\text{L}_2\text{Fe}(\text{CO})_3$ typically in yields of 15% each [1]. Use of the more expensive $\text{Fe}_3(\text{CO})_{12}$ as parent carbonyl increases the yield of substituted products considerably, approximately 34% of the mono- and 27% of the disubstituted products are obtained ($\text{L} = \text{PPh}_3$) [1,2]. Strohmeier and Müller have been able to extend the range of substituted $\text{Fe}(\text{CO})_5$ complexes to include phosphites, alkylphosphines, and isonitriles under conditions of prolonged photolysis of the ligand and $\text{Fe}(\text{CO})_5$ in hydrocarbon solvent [3]. Again the increased yields observed in their preparation (typical yields are 30 to 40% for both mono- and disubstituted products; up to 60% to 70% for the more basic phosphine and isonitrile complexes) is due to the production of the aggregate $\text{Fe}_2(\text{CO})_9$. Indeed $\text{Fe}_2(\text{CO})_9$ has been used as a starting material to prepare various $\text{LFe}(\text{CO})_4$ and $\text{L}_2\text{Fe}(\text{CO})_3$ complexes [4]. However, this involves either the purchase of the much more expensive $\text{Fe}_2(\text{CO})_9$ or its prior preparation. Several other approaches to Group V substituted iron carbonyls exist in the literature [5,6]. None of these however possess the convenience of the preparation described herein.

Use of expensive or difficult to obtain ligands warrants a higher yield synthesis. Furthermore separation difficulties especially of the mono- from the disubstituted products as well as excess ligand from the products are frequently

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TABLE I
PERCENT YIELDS AND SOME PHYSICAL PROPERTIES OF $LFe(CO)_4$ AND $L_2Fe(CO)_3$ COMPLEXES
PREPARED IN THIS STUDY

Complex	Yield ^a (%)	M.p. (°C)	$\nu(CO)^b$ (cm^{-1})	Ref.
$[Ph_3P]Fe(CO)_4$	85	196 - 198	2051.0, 1979.0, 1945.3	[1]
$[(p-MeC_6H_4)_3P]Fe(CO)_4$	60	180 - 182.5	2048.5, 1976.0, 1943.0	<i>d</i>
$[(o-MeC_6H_4)_3P]Fe(CO)_4$	94	148 (dec.)	2048.5, 1973.0, 1945.0	[2]
$[Ph_3As]Fe(CO)_4$	96	170 - 175	2049.3, 1976.3, 1945.8	[1]
$[Ph_3Sb]Fe(CO)_4$	52	133 - 135	2046.5, 1975.8, 1944.3	[1]
$[Diphos][Fe(CO)_4]_2$	79	182 - 184	2050.0, 1980.8, (1946.3, 1938.3)	[13]
$[Me_2PhP]Fe(CO)_4$	70	47.5- 48.5	2050.5, 1978.6, 1939.9	[14]
$[Me_2PhP]_2Fe(CO)_3^c$	11	85 - 87 (dec)	1882.8	<i>d</i>
$[(PhO)_3P]Fe(CO)_4$	47	68 - 69	2065.5, 1996.0, (1964.3, 1959.8)	[3]
$[(PhO)_3P]_2Fe(CO)_3$	14	114 - 114.5	(1933.3, 1924.3)	[3]
$[(MeO)Ph_2P]Fe(CO)_4$	60	68.5- 70	2054.2, 1984.0, (1948.2, 1945.6)	<i>d</i>
$[(MeO)Ph_2P]_2Fe(CO)_3$	22	140 - 143	1902.0	[2]
$[(MeO)_3P]Fe(CO)_4$	49	43 - 43.5	2063.2, 1992.7, (1963.3, 1950.6)	[11]
$[(MeO)_3P]_2Fe(CO)_3$	33	73 - 74	(1920.5, 1912)	[11]
$[n-Bu_3P]Fe(CO)_4$	34	25	2048.0, 1974.8, 1935.4	[3]
$[n-Bu_3P]_2Fe(CO)_3$	31	53 - 55	1873(br)	[3]
$[CH_2=CHCOOH]Fe(CO)_4$	22	103 - 104	2102(m), 2037(s), 2024(vs), 2004(vs)	[7]

^aIsolated and purified, based on L. ^bHexane solution, $\pm 0.5\text{ cm}^{-1}$. For $LFe(CO)_4$ low energy band (or bands if split, as denoted by parentheses) is strong, higher energy bands are medium to weak. ^cPrepared by irradiation only. ^dThis work.

encountered. The preparation described below illustrates a quick convenient high yield synthesis of a wide range of iron carbonyl derivatives, in many cases specific for the monosubstituted $LFe(CO)_4$ form.

Discussion

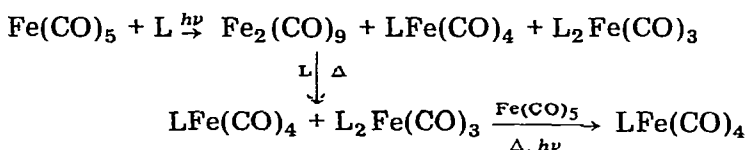
We have prepared an extensive series of $LFe(CO)_4$ complexes in high yield by a combination of photochemical and thermal reactions using $Fe(CO)_5$ both as solvent and reactant*. Thus a broad spectrum of ligands L (aryl- and alkyl-phosphines, phosphites, triphenylarsine, triphenylstibine and acrylic acid) were added to pure $Fe(CO)_5$ in approximately 1 to 15 molar ratios. Product yields (isolated and purified), melting points, and IR frequency data in the CO stretching region are recorded in Table 1. Products were characterized by comparison of their melting points and infrared spectra with literature values. New compounds were further characterized by elemental analysis. With the exception of the acrylic acid derivative which is equatorially substituted [7], all compounds have the axially substituted trigonal bipyramidal structures. These assignments are based on the IR absorptions in the CO stretching region [8]. In addition three crystal structures have been reported on typical axially substituted complexes corroborating the structural assignment inferred from infrared [9,10].

The conditions generally employed in this synthesis were room temperature irradiation followed by reflux without irradiation and a final reflux plus irradiation period. Reaction times of each process were selected to optimize the

*Extreme caution must be used in the handling of this reagent. Excess $Fe(CO)_5$ may be recovered in vacuo and reused.

yield of $\text{LFe}(\text{CO})_4$. Only in the case of the acrylic acid derivative did the initial irradiation process give the highest yield of product. In all other cases subsequent thermal reaction of the photochemically formed $\text{Fe}_2(\text{CO})_9$ is necessary [3,11]. [It should be noted that a distinct advantage of using $\text{Fe}(\text{CO})_5$ as solvent is that $\text{Fe}_2(\text{CO})_9$ is soluble in the pentacarbonyl, thus facilitating its reaction in this thermal process.] As an example of the importance of these steps an analysis of the reaction of Me_2PhP with $\text{Fe}(\text{CO})_5$ follows. When $\text{Me}_2\text{-PhP}$ and $\text{Fe}(\text{CO})_5$ are irradiated only for 1 h, a 54% yield of $\text{Me}_2\text{PhPFe}(\text{CO})_4$ and 11% yield of $[\text{Me}_2\text{PhP}]_2\text{Fe}(\text{CO})_3$ is obtained. Following this irradiation with a 1 h reflux increases the yield of monosubstituted complex to 80% with the amount of disubstituted complex remaining the same. The final 1 h reflux plus irradiation period decreased the $\text{Me}_2\text{PhPFe}(\text{CO})_4$ yield to 70% but also reduced the $[\text{Me}_2\text{PhP}]_2\text{Fe}(\text{CO})_3$ to zero, through the carbonylation action of $\text{Fe}(\text{CO})_5$ [12]. The final yield of monosubstituted complex at this step is of course dependent on its photochemical and thermal stability. In summary, the preparations whose experimental details are presented below utilize the following reaction scheme:

Scheme



Although the scheme indicates $\text{LFe}(\text{CO})_4$ to be the final product, which is the case for arylphosphines, -arsines, and -stibines, in several other cases $\text{L}_2\text{-Fe}(\text{CO})_3$ remains as a prominent impurity. For those cases convenient separation techniques are given in the experimental section.

Experimental

All reactions were carried out in a *well-vented hood*.

Material and equipment

Iron pentacarbonyl was used as purchased from Pressure Chemical Co. The following ligands were gifts of the sources cited and were generally used as received without further purification: $n\text{-Bu}_3\text{P}$ and Ph_3P (M & T Chemical Co.); $(\text{MeO})_3\text{P}$ (Mobil Chemical Co.); $(\text{MeO})\text{Ph}_2\text{P}$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (Diphos) (Arapahoe Chemical Co.). Acrylic acid was purchased from Aldrich Chemical Co. All other ligands were purchased from Strem Chemical Co.

Melting points were taken in open capillary tubes on a Thomas—Hoover apparatus and are uncorrected. Infrared spectra were taken on a Perkin—Elmer 521 grating spectrophotometer, calibrated in the CO stretching region with CO and H_2O vapor.

General preparation

The following description of the synthesis refers to all the complexes with

the exception of the acrylic acid derivative. A simple apparatus consisting of a one-necked 100 ml round-bottomed pyrex flask into which a magnetic stirring bar and 10 mmole of ligand had been placed was equipped with a condenser and N_2 inlet tube and was degassed several times. Twenty ml (150 mmole) of $Fe(CO)_5$ was carefully syringed into the flask via the N_2 inlet; the reaction was kept under N_2 at all times. The solution was stirred and irradiated for 2 h by a 450 watt Ace-Hanovia mercury arc lamp positioned 6 to 8 inches from the reaction flask; a reflector may be used. At the end of the irradiation the reaction solution was heated by an oil bath maintained at 150° for 1 h. The lamp was again turned on and a final irradiation period of 1 h at the high temperature completed the preparation. The solution was cooled to room temperature and excess $Fe(CO)_5$ removed in vacuo into a liquid N_2 cold trap. The recovered $Fe(CO)_5$ was stored and reused.

Isolation and purification of complexes with $L = Ph_3P, (p-CH_3C_6H_4)_3P, (o-CH_3C_6H_4)_3P, Ph_3As, Ph_3Sb, Me_2PhP,$ and $Ph_2PCH_2CH_2PPh_2$

The preparation is specific for the monosubstituted derivatives for these L groups. Upon removal of excess $Fe(CO)_5$ the residue was extracted with 50 - 100 ml THF and chromatographed on an F-20 Alumina column (1 X 8 inch), eluting with THF until the eluant was no longer yellow. The volume of the eluant was then reduced to approximately 100 and 50 ml of water added. The volume was further reduced until crystals began to form. The yellow crystals were collected and recrystallized from boiling heptane. Elemental analysis of the new $LFe(CO)_4$ complex is as follows: $L = (p-CH_3C_6H_4)_3P$, calcd.: C, 63.56; H, 4.49; found: C, 63.55; H, 4.55. Elemental analysis showed one diphos ligand per two $Fe(CO)_4$ groups; calcd. for $(CO)_4FePPh_2CH_2CH_2PPh_2-Fe(CO)_4$; C, 55.61; H, 3.27; mol. wt., 734; found; C, 55.82; H, 3.39; mol. wt., 698.

Isolation and purification of complexes containing $L = (PhO)_3P, (MeO)Ph_2P,$ or Me_2PhP

The residue remaining after removal of $Fe(CO)_5$ was placed on the alumina column. Elution with 150 to 200 ml pentane yields a yellow solution from which yellow crystals of pure $LFe(CO)_4$ were obtained upon reduction of the volume to 50 ml and cooling at -78° . Further elution of the column with 100 to 150 ml of THF yields a yellow solution containing $L_2Fe(CO)_3$. Removal of solvent under vacuum followed by recrystallization from boiling hexane yields light yellow crystals of pure $L_2Fe(CO)_3$. This procedure may also be used to separate the mono- from the disubstituted derivative (present after irradiation only) of Me_2PhP . Elemental analysis for the new compound is as follows: (Found: C, 53.23; H, 3.37. Mol.wt., 370. $[(MeO)Ph_2P]Fe(CO)_4$ calcd.: C, 53.35; H, 3.40%. Mol.wt., 384.)

Isolation and purification of complexes with $L = (MeO)_3P$

The residue was similarly washed onto the alumina column and eluted with pentane. Cooling of the eluant to -78° for 1 to 2 h produced light yellow crystals of pure $L_2Fe(CO)_3$. The mother liquor was taken to dryness and the yellow residue vacuum sublimed at 25° yielding bright yellow crystals of pure $LFe(CO)_4$.

Isolation and purification of complexes with L = n-Bu₃P

Similar pentane elution of the residue on the alumina column again yielded both mono- and disubstituted compounds in the eluant. The eluant was concentrated to dryness and the liquid products fractionally distilled in vacuo (≈ 0.1 mm) using a short path length, micro-distillation apparatus. The mono-substituted compound distilled very slowly (days) at 75°, however higher temperatures tend to decompose this product forming more of the disubstituted compound. The disubstituted complex distilled at temperatures greater than 90°.

Preparation, isolation, and purification of (CH₂=CHCOOH)Fe(CO)₄

The apparatus was again charged with ligand and Fe(CO)₅ as described previously. Irradiation at room temperature for 4 h with vigorous stirring produced the best yields of this thermally unstable LFe(CO)₄. Excess Fe(CO)₅ was removed and the residue washed with 10 ml H₂O before recrystallization of the golden yellow crystals from Et₂O/heptane.

Acknowledgements

The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society for a post-doctoral fellowship to H.L.C. and for support of this research. We are also appreciative to Research Corporation for a Cottrell Research Grant awarded to D.J. Darensbourg and M.Y.D. for the purchase of a Perkin-Elmer 521 infrared spectrophotometer.

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