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THE TRANSITION METAL-CATALYSED REACTION BETWEEN $Fe(CO)_5$ AND GROUP V DONOR LIGANDS. A FACILE, HIGH YIELD SYNTHESIS OF $Fe(CO)_4PPh_3$

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Summary

The reaction of $Fe(CO)_5$ and L (L = Group V donor ligand), in the presence of $CoCl_2 \cdot 2\ H_2O$ or $CoI_2 \cdot 4\ H_2O$ as catalyst, results in the synthesis of $Fe(CO)_4L$ in good yield. Unusual reactivity patterns for the substitution of CO on $Fe(CO)_5$ by L have been found; for CoI_2 as catalyst the reaction rate increases in the order $PPh_3 \sim AsPh_3 \sim P(OPh)_3 > SbPh_3 > PPh_2Me > PPhMe_2 > P(C_6H_{11})_3 > P(OEt)_3 > P(n\text{-}Bu)_3 > P(OMe)_3$. These results are interpreted in terms of the variation of the catalyst through interaction of CoX_2 with L.

Introduction

Since the first reported synthesis of $Fe(CO)_4PPh_3$ in 1948 [1] there have been many attempts to prepare this complex in high yield and free from contamination with $Fe(CO)_3(PPh_3)_2$. Synthetic procedures have included the direct thermal reaction between PPh_3 and $Fe(CO)_5$ [2] and $Fe_3(CO)_{12}$ [3], as well as the photochemical reaction between PPh_3 and $Fe(CO)_5$ [4]. An alternate method has been the reduction of iron carbonyl halide complexes with PPh_3 in the presence of phenyl lithium [5]. More recently, synthetic procedures have included the use of a combination of high temperature and photochemical irradiation [6], metal hydrides [7], $RhCl(PPh_3)_3$ as a decarbonylation reagent [8] and iron carbonyl anions as catalysts [9].

A consideration of the above synthetic procedures reveals that they all suffer from at least one of the following disadvantages; (a) long reaction times and

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TABLE 1

REACTION CONDITIONS AND SPECTROSCOPIC DATA FOR THE COMPLEXES REPORTED IN THIS STUDY

	$CoCl_2$		CoI_2		$\nu(CO)$ [a] (cm^{-1})			Mol. mass [b]	Refs.
	Yield (%)	Time (h)	Yield (%)	Time (h)					
$Fe(CO)_4PPh_3$ [c]	83	2	99	0.5	2052	1978	1940	430	1–10
$Fe(CO)_4AsPh_3$	86	2	99	0.5	2048	1972	1942	474	3, 6, 7
$Fe(CO)_4SbPh_3$	90	5	97	1	2045	1970	1938	521	3, 6, 7
$Fe(COO_4PPh_2Me$	98	1	78	1.5	2058	1977	1947	368	11
$Fe(CO)_4PPhMe_2$	90	1.3	93	4	2055	1973	1937	306	11
$Fe(CO)_4P(C_6H_{11})_3$	60	3	58	5	2043	1964	1930	448	4
$Fe(CO)_4P(n\text{-}Bu)_3$	38	6	50	6	2045	1968	1932	370	4, 6
$Fe(CO)_4P(OPh)_3$	79	4	95	0.5	2067	1997	1960	478	7, 12
$Fe(CO)_4P(OEt)_3$	15 [d]	6	59	6	2062	1983	1950	334	7, 12
$Fe(CO)_4P(OMe)_3$	n.r. [e]	6	n.r.	6	—	—	—	—	6
$Fe(CO)_3(PPh_3)_2$	75	32 [f]	53	24 [g]	1883			664	2, 3, 5
$Fe(CO)_3(PPh_2Me)_2$	—	—	57	24	1874			540	13
$Fe(CO)_3(PPhMe_2)_2$	—	—	51	27	1868			416	6

[a] Recorded in $CHCl_3$. [b] Obtained by mass spectrometry. [c] For catalyst = $CoBr_2 \cdot 3\ H_3O$: yield 98%, time 1.25 h. [d] Maximum yield estimated by IR. [e] No reaction. [f] Experiment 2a. [g] Experiment 2b.

forcing conditions, (b) expensive reagents, (c) stringent procedures involving the exclusion of air and, most significantly, (d) the formation of mixtures of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$.

We wish to report that transition metal salts, most notably $CoX_2 \cdot n\ H_2O$ (X = Cl, Br, I) readily catalyse the reaction between $Fe(CO)_5$ and PPh_3 in refluxing toluene to give $Fe(CO)_4PPh_3$ in near quantitative yield with little formation of $Fe(CO)_3(PPh_3)_2$ [10]. The disubstituted derivative can be obtained in moderate yield by modifying the reaction conditions. We have generalized the reaction to other Group V donor ligands, L, and our results using $CoCl_2 \cdot 2\ H_2O$ and $CoI_2 \cdot 4\ H_2O$ as catalyst are reported.

Experimental

$Fe(CO)_5$ (Strem Chemicals) and the Group V donor ligands (obtained from various sources) were used as purchased. $CoX_2 \cdot n\ H_2O$ (X = Cl, Br, I) (BDH Chemicals) were dried in vacuo (0.1 mmHg) to give the complexes $CoCl_2 \cdot 2\ H_2O$, $CoBr_2 \cdot 3\ H_2O$ and $CoI_2 \cdot 4\ H_2O$. IR spectra were recorded on a PE 521 IR spectrometer and mass spectra were obtained from a Varian MAT CH5 spectrometer operating at 70 eV.

All reactions were routinely performed in degassed solvents under a nitrogen atmosphere.

1. Preparation of $Fe(CO)_4L$ [L = PPh_3, $AsPh_3$, $SbPh_3$, PPh_2Me, $PPhMe_2$, $P(C_6H_{11})_3$, $P(n\text{-}Bu)_3$, $P(OPh)_3$, $P(OEt)_3$]

Ligand, L, (10 mmol) and catalyst ($CoCl_2$, $CoBr_2$, CoI_2; 0.3 mmol) were added to toluene (30 ml) and the stirred solution brought to reflux. $Fe(CO)_5$ (20 mmol) was added to this solution and the reaction followed by monitoring changes in the ν(CO) region of the IR spectrum. Reflux was continued until the spectrum remained invariant with time or for a period of 6 h (Table 1). Catalyst and excess L were removed by eluting the cold reaction solution through a $CoCl_2 \cdot 6\ H_2O$/neutral alumina/silica gel column (three layers ~5 g/20 g/20 g), with benzene. Solvent and excess $Fe(CO)_5$ were then removed on a rotary evaporator and the required product was crystallised (where appropriate) from CH_2Cl_2/hexane mixtures.

2. Preparation of $Fe(CO)_3(PPh_3)_2$

(a) $Fe(CO)_4PPh_3$ (2 mmol), PPh_3 (2 mmol) and $CoCl_2 \cdot 2\ H_2O$ (0.2 mmol) were added to toluene (10 ml) and the solution refluxed for 32 h. The reaction mixture was eluted down a silica gel column (CH_2Cl_2/hexane, 1/1 as eluent) and gave $Fe(CO)_3(PPh_3)_2$ in 75% yield.

(b) $Fe(CO)_5$ (10 mmol), $CoI_2 \cdot 4\ H_2O$ (0.3 mmol) and PPh_3 (20 mmol) were added to methyl ethyl ketone (30 ml) and refluxed for 24 h. After solvent removal, the reaction mixture was purified as above to give $Fe(CO)_3(PPh_3)_2$ (53% yield).

3. Preparation of $Fe(CO)_3L_2$ (L = PPh_2Me, $PPhMe_2$)

$Fe(CO)_5$ (10 mmol), $CoI_2 \cdot 4\ H_2O$ (0.3 mmol) and L (20 mmol) were refluxed in methyl ethyl ketone (30 ml) for ~24 h. At the end of the reaction, catalyst and excess phosphine were removed on a column (see 1 above). The solvent was reduced to <5 ml and the product then crystallized from CH_2Cl_2/pentane at −78°C.

Discussion

The reaction between $Fe(CO)_5$ and Group V donor ligands, L, in refluxing toluene was carried out in the presence of catalytic amounts of $CoX_2 \cdot n\ H_2O$ (X = Cl, I). The reaction was monitored by the decrease in intensity of the $\nu(CO)$ absorption bands of $Fe(CO)_5$ and the increase of the A_1 band (~2050 cm^{-1}) of the required product, $Fe(CO)_4L$. Excess $Fe(CO)_5$ was used in the reactions to overcome difficulties experienced with volatility losses and to ensure that $Fe(CO)_4L$ would be the major product produced in the reaction. The excess $Fe(CO)_5$ can readily be removed, e.g. on a rotary evaporator at the end of the reaction.

An important feature of the catalysed reaction is the ability to prepare $Fe(CO)_4L$ in high yield with little contamination by $Fe(CO)_3L_2$. We have found that the final reaction mixture contains <5% $Fe(CO)_3L_2$ (except for L = $P(OEt)_3$ where ~10% $Fe(CO)_3[P(OEt)_3]_2$ was produced) and this is thought to be a consequence of the relatively short reaction times. In the absence of catalyst, reactions are poor and mixtures of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ are formed.

Purification of the product requires removal of both unreacted L and catalyst. This has been achieved by use of a column made up of three layers. The top layer consists of $CoCl_2 \cdot 6\ H_2O$ and is used to remove excess phosphine via the reaction $CoX_2 + 2\ L \rightarrow CoX_2L_2$ [14]. This is followed by a layer of silica-gel and a layer of alumina which remove catalyst from the required product.

The products were characterized by IR and mass spectra (Table 1) and their melting points. The IR data, ($\nu(CO)$ region) typically show three bands consistent with previously reported values [2]. The mass spectra all show parent ions and fragmentation patterns showing consecutive loss of CO.

The reactivity pattern for the replacement of CO on $Fe(CO)_5$ by L (CoI_2 as catalyst) was found to be $PPh_3 \sim AsPh_3 \sim P(OPh)_3 > SbPh_3 > PPh_2Me > PPhMe_2 > P(C_6H_{11})_3 > P(OEt)_3 > P(n\text{-}Bu)_3 > P(OMe)_3$ (Table 1). Since the effect of the catalyst must be to weaken the M—CO bond the above reactivity pattern must reflect this phenomena.

The exact nature of the catalyst in solution is unknown but it is thought to be a CoX_2L_2 complex formed from CoX_2 and phosphines in toluene [14]. These complexes are readily detected by the brown (CoI_2) or blue ($CoCl_2$) colour of the solutions obtained in the catalytic reactions. This formulation is further suggested by the addition of $CoCl_2(PPh_3)_2$ [14] to $Fe(CO)_5$ and PPh_3 which gives similar colour changes (and catalysis). A blue solution was also obtained on addition of $P(OEt)_3$ to $CoCl_2$.

Since attack of catalyst occurs at $Fe(CO)_5$ (most probably at a coordinated CO, as previously suggested [10,15]) the reaction will depend on the nature of L, the incoming ligand, and/or the nature of the catalyst. The effect of the nucleophilic character of L on the substitution reactions of transition metal carbonyls has been documented [16] and any deviation observed from an expected reactivity pattern must therefore result from the nature of the catalyst. For instance, the rate of the catalysed reaction follows the sequence $CoI_2 > CoBr_2 > CoCl_2$ for L = PPh_3 but this sequence is inverted for L = PPh_2Me. This effect could be due to either steric or electronic effects of the L or X ligands around cobalt or the catalyst—reagent interaction. Steric effects influence the equilibrium [17] $CoX_2L_2 + L \rightleftharpoons CoX_2L_3$ and we suspect that the 5 coordinate Co^{II} complex will be a poor catalyst. The more bulky CoX_2L_3 complex will have difficulty in interacting with the iron (or CO ligand) and if attack is at a coordinated CO, formation of a $CoX_2(CO)L_3$ complex is improbable. The steric influence on the equilibrium is not, however, the only effect as $P(C_6H_{11})_3$, which has a large cone angle [18] and should favour 4-coordinate Co^{II}, undergoes a slow substitution reaction relative to $PPhMe_2$ which has a smaller cone angle. Further studies will be needed to clarify the effect of the catalyst on the reaction. What is clear, however, is that minor modifications to the catalyst allows for reactivity pattern changes and this could have important consequences in the synthesis of hitherto unknown (or unobtainable) organometallic complexes.

The disubstituted products $Fe(CO)_3L_2$ have been prepared from either $Fe(CO)_5$ and 2 equivalents of L or $Fe(CO)_4L$ and 1 equivalent of L (L = PPh_3). The reactions are slow and yields moderate to poor. Attempts to prepare mixed disubstituted derivatives $Fe(CO)_3LL'$ (L = $AsPh_3$, $P(C_6H_{11})_3$; L' = PPh_3) have met with limited success, the reactions producing a number of products due to ligand exchange i.e. to form $Fe(CO)_3L_2$, $Fe(CO)_3L'_2$, and $Fe(CO)_3LL'$, as detected by IR and mass spectrometry.

Although all reactions were routinely carried out under nitrogen we have found that the use of non-dried and non-degassed toluene has little effect on the product yield unless the reaction times are long or the products air-sensitive. In an attempt to increase product yield or reduce the reaction time (especially for the synthesis of $Fe(CO)_3L_2$) we have carried out the reaction of $Fe(CO)_5$ and PPh_3 ($CoCl_2 \cdot 2\,H_2O$ as catalyst) in a variety of different solvents. These have included CH_3CN, $CHCl_3$, THF, hexane, C_2Cl_6, CH_3NO_2 and C_2H_5OH, but in all these solvents minimal catalysis was observed. Although the reaction did proceed in chlorobenzene, extensive decomposition occurred. In methylethylketone (MEK) the reaction between $Fe(CO)_5$ and PPh_3 (CoI_2 as catalyst) produced $Fe(CO)_3(PPh_3)_2$ in 53% yield. The reaction product precipitated from solution during the reaction and the reaction solution was found to contain small amounts of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$. Attempts to prepare $Fe(CO)_3(PPh_3)_2$ from $Fe(CO)_4PPh_3$ and PPh_3 in MEK gave a poor reaction (<10% reaction, 24 h) suggesting that reaction in MEK involves solvent participation. Reaction of L = PPh_2Me and $PPhMe_2$ with $Fe(CO)_5$ in MEK also gave $Fe(CO)_3L_2$ with little evidence of $Fe(CO)_4L$ formation.

We have also investigated the use of a range of transition metals as potential catalysts for this CO substitution reaction. Only nickel salts ($NiX_2 \cdot n\,H_2O$ (X = Cl, Br, I), $NiCl_2(PPh_3)_2$ and $NiSO_4$) and the iron dimers $[C_5H_5Fe(CO)_2]_2$, $[MeC_4H_5Fe(CO)_2]_2$ and $[(Me_5C_5)Fe(CO)_2]_2$, were found to catalyse the reaction. Other transition metal salts e.g. $Co(acetate)_2 \cdot 4\,H_2O$, $Co(NO_3)_2 \cdot 6\,H_2O$, $CoSO_4 \cdot 7\,H_2O$, $MnCl_2 \cdot 6\,H_2O$, $CuCl_2$ and $CrCl_3 \cdot 6\,H_2O$ as well as $RhCl(PPh_3)_2$ [8] showed no catalytic behaviour. It is thus apparent that the correct choice of metal ion and counterion are required for efficient catalysis.

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