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REACTIONS OF ORGANOLITHIUM AND GRIGNARD REAGENTS WITH THE CYCLOPENTADIENYLIRON TRICARBONYL CATION AND ITS DERIVATIVES

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SUMMARY

Reactions of CH_3Li, C_6H_5Li, and $C_6H_5CH_2MgCl$ with $[(C_5H_5)Fe(CO)_2Y]^+$-$[B(C_6H_5)_4]^-$ [$Y=CO$, $P(C_6H_5)_3$, and CS] have been investigated. The organolithium reagents used act either as reducing agents or as nucleophilic reagents towards the cyclopentadienyliron tricarbonyl cation and its thiocarbonyl analogue. Benzylmagnesium chloride reacts with the cyclopentadienyl ring of $[(C_5H_5)Fe(CO)_3]^+$ and $[(C_5H_5)Fe(CO)_2P(C_6H_5)_3]^+$ producing neutral cyclopentadiene complexes.

INTRODUCTION

Nucleophilic substitution and addition reactions of cyclopentadienyl-iron, -tungsten, and -molybdenum carbonyl cations have been investigated by Treichel and Shubkin[1]. Pentafluorophenyllithium, phenyllithium, and sodium borohydride were used as nucleophilic reagents. Isolation of several products in some reactions indicated the possibility of various modes of reaction. For example, cyclopentadienyliron tricarbonyl hexafluorophosphate reacted with pentafluorophenyllithium to yield a trace of *exo*-$(5\text{-}C_6F_5C_5H_5)Fe(CO)_3$, 12.7% $(C_5H_5)Fe(CO)_2C_6F_5$, and 17.6% $(C_5H_5)Fe(CO)_2C(O)C_6F_5$. Since decarbonylation of $(C_5H_5)Fe(CO)_2C(O)C_6F_5$ did not occur under similar reaction conditions, it would appear that the three products are direct reaction products.

Nucleophilic reagents such as hydrazine, N_3^-, amines and NCO^- attack the electrophilic C of the CO ligand of $[(C_5H_5)Fe(CO)_3]^+$ giving stable addition products[2].

$$(C_5H_5)Fe(CO)_3^+ + Nu \rightarrow (C_5H_5)Fe(CO)_2NCO + P \qquad (1)$$

$$Nu = N_3^-,\ N_2H_4,\ NCO^-;\quad P = N_2,\ NH_3 \text{ or } CO$$

$$(C_5H_5)Fe(CO)_3^+ + RNH_2 \rightarrow (C_5H_5)Fe(CO)_2C(O)NHR + H^+ \qquad (2)$$

Similar reactions with $[(C_5H_5)Fe(CO)_2CS]^+[PF_6]^-$ showed nucleophilic

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attack to occur at the thiocarbonyl carbon atom, thus suggesting the electrophilic character of the carbon of the CS ligand to be markedly greater than that of the CO carbon[3].

This study reports further investigations of organometallic nucleophilic reagents, specifically methyl- and phenyllithium and benzylmagnesium chloride, with $[(C_5H_5)Fe(CO)_2Y]^+[B(C_6H_5)_4]^-$ [Y=CO, CS, or $P(C_6H_5)_3$].

RESULTS AND DISCUSSION

Phenyllithium reacts with $[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$ via a carbonyl carbon attack to produce the neutral addition product $(C_5H_5)Fe(CO)_2C(O)C_6H_5$ and by a reductive process yielding $[(C_5H_5)Fe(CO)_2]_2$. These results differ somewhat from those of Treichel and co-workers who found only the dimeric product and biphenyl under similar reaction conditions[1]. Since decomposition of (C_5H_5)-$Fe(CO)_2C(O)C_6H_5$ was observed here it is likely that the column chromatography technique used by those workers to separate components obscured the initial results.

The reaction of methyllithium with $[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$ produced predominantly $[(C_5H_5)Fe(CO)_2]_2$. In order to check for multiple CO addition products as the mode for dimer formation, $(C_5H_5)Fe(CO)_2C(O)CH_3$ was prepared and reacted with CH_3Li. No $[(C_5H_5)Fe(CO)_2]_2$ was produced but rather infrared results suggested addition of CH_3Li either to a terminal CO group or to the metal (with elimination of CO)[4].

Various Grignard reagents, including benzylmagnesium chloride, have been found to react with metal carbonyls in a manner completely analogous to organolithium reagents[5]. With $[(C_5H_5)Fe(CO)_3]^+$ however benzylmagnesium chloride reacts at the ring producing the neutral cyclopentadiene complex as the only CO containing product. Analysis of the infrared spectra of both the inital reaction mixture and the isolated product indicated the presence of three terminal and no bridging or acyl carbonyl groups. Due to the air sensitivity of the complex an elemental analysis was not attempted; however the complete IR, NMR, and mass spectral data were consistent with formulation of the product as the cyclopentadiene complex, *exo*-$(5\text{-}C_6H_5CH_2C_5H_5)Fe(CO)_3$[6-8]. Similar ring addition products were obtained by Treichel *et al.* in the reaction of C_6F_5Li, C_6H_5Li, and $NaBH_4$ with $[(C_5H_5)Fe(CO)_2$-$P(C_6H_5)_3]^+$ [1]. Since C_6F_5Li and $C_6H_5CH_2MgCl$ are likely to be similar in nucleophilic properties, the addition of benzylmagnesium chloride to the cyclopentadienyl ring is not surprising. For the reaction of C_6F_5Li with $[(C_5H_5)Fe(CO)_3]^+$ however, only a small amount of ring addition was observed and 17.6 and 12.7% of (C_5H_5)-$Fe(CO)_2C(O)C_6F_5$ and $(C_5H_5)Fe(CO)_2C_6F_5$ were obtained as reaction products. It would appear that benzylmagnesium chloride is in its reaction with $[(C_5H_5)$-$Fe(CO)_3]^+$ more selective than C_6F_5Li.

In contrast to the low melting point and air sensitivity of *exo*-$(5\text{-}C_6H_5CH_2$-$C_5H_5)Fe(CO)_3$, *exo*-$(5\text{-}C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$ is quite stable and is the only carbonyl containing product in the $C_6H_5CH_2MgCl/[(C_5H_5)Fe(CO)_2P$-$(C_6H_5)_3]^+$ reaction. It has been suggested that in the case of $[(C_5H_5)Fe(CO)_2$-$P(C_6H_5)_3]^+$ steric hindrance by the large phosphine ligand might be responsible for the exclusive ring addition of C_6F_5Li and C_6H_5Li[1]. Since there are numerous examples of addition of RLi and RMgX reagents to the *cis* carbonyl carbon of M-

$(CO)_5PR_3$ complexes (M = Group VI metal; R = various aryl, alkyl and alkoxy groups, including the extremely bulky tricyclohexylphosphine groups)[9,10], it is more likely that electronic factors control the course of the reaction.

The reactions of CH_3Li or C_6H_5Li and $C_6H_5CH_2MgCl$ with $[(C_5H_5)Fe(CO)_2CS]^+$ under similar conditions as with the all carbonyl analogue appear to involve a different mode of reaction and/or the production of unstable addition products. Only in the case of CH_3Li reaction with $[(C_5H_5)Fe(CO)_2CS]^+$ are carbonyl-containing products identifiable; $[(C_5H_5)Fe(CO)_2]_2$ is formed in low yield. Although reaction of C_6H_5Li and $C_6H_5CH_2MgCl$ with $[(C_5H_5)Fe(CO)_2CS]^+[B(C_6H_5)_4]^-$ occurs, as evidenced by the dissolving of the insoluble salt in THF, it has been impossible to isolate any products of these reactions. The IR spectra of the reaction mixtures (and nujol mulls of the dried residues) show no absorptions attributable to CO stretching modes and, in the case of the benzylmagnesium chloride reaction, the CS band at 1348 is also clearly removed. A dark residue is obtained in both cases. The thiocarbonyl compound's reaction and products are thus definitely dependent on the nucleophilic reagent used, *i.e.*, stable products are obtained in the azide and amine reactions. On the other hand, the results reported here suggest that the substitution of a CS for a CO ligand produces an alteration of the electronic character of the molecule not so readily discerned in the reactivity studies with azides and amines.

EXPERIMENTAL

All reactions were carried out under nitrogen or argon at 0° or −78°. The solvent, tetrahydrofuran, freshly distilled from $LiAlH_4$, was flushed with inert gas before adding the solid carbonyl compound. The Grignard or organolithium reagent (purchased from Alfa Inorganics) was added via syringe in a THF or ether solution. An IR was taken of the reaction mixture to assure that the initial product was the same as the product after workup as well as to ascertain completeness of reaction. The reactions were then quenched with ethanol and the solvent removed at reduced pressures. $[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$ [11], $[(C_5H_5)Fe(CO)_2P(C_6H_5)_3]^+Cl^-$ [11], $[(C_5H_5)Fe(CO)_2CS]^+[B(C_6H_5)_4]^-$ [12] and $(C_5H_5)Fe(CO)_2C(O)CH_3$[13] were prepared as described in the literature.

Infrared spectra were recorded on a Perkin–Elmer 521 spectrophotometer. Sealed cells (0.1 mm) were used for THF solutions; 1 mm cells for hydro- and halocarbon solutions. A Jeolco Minimar MH100 was used for the proton NMR spectra. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York. Melting points were determined on a Hoover Unimelt apparatus and they are uncorrected.

Reaction of C_6H_5Li and $[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$

The IR spectrum of the THF solution containing a mixture of 0.15 mmole of $[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$ and 1.15 mmoles of C_6H_5Li taken after 15 min of reaction time at 0° has asymmetric absorbances in the CO stretching region centered at 2020 and 1965 cm^{-1}. Solvent was removed in vacuum and the residue was placed in a sublimator (80° and ca. 0.5 mm). Comparisons of the IR and NMR spectra of the sublimate with those of known compounds indicated the sublimate to be ca. 80% $(C_5H_5)Fe(CO)_2C(O)C_6H_5$ and ca. 20% $[(C_5H_5)Fe(CO)_2]_2$.

IR of sublimate in hexane (cm^{-1}); 2049 w, 2023 s, 2006 w, 1971 s, 1959 w, 1940 vw, 1791 w, 1592 br, m.

IR of pure $(C_5H_5)Fe(CO)_2C(O)C_6H_5$ in halocarbon mull: 2029 s, 1972 s, 1943 w, and 1603 m[14].

IR of pure $[(C_5H_5)Fe(CO)_2]_2$ in chloroform: 2005 vs, 1960 vs, 1793 vs.

The NMR of the sublimate $(C_5H_5)Fe(CO)_2C(O)C_6H_5$ in $DCCl_3$ (TMS=0 ppm): $\delta(C_6H_5)$ 7.47 (mult), $\delta(C_5H_5)$ 4.81 ppm (singlet); $[(C_5H_5)Fe(CO)_2]_2$: $\delta(C_5H_5)$ 4.71 (singlet) ppm. Decomposition was indicated in that the singlet at 4.71 was approximately 4 times that of the 4.81 resonance whereas the IR of the sublimate indicated the opposite distribution.

Reaction of CH_3Li *with* $[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$

Since $(C_5H_5)Fe(CO)_2C(O)CH_3$ is quite volatile, attempts were made to sublime this product out of reaction mixtures of CH_3Li (2.0 mmoles) and $[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$ (0.2 mmole). Traces of the acyl product were suggested by the IR of the reaction mixture however no sublimate (80–90°/0.1 mm) was obtained. The residue was predominantly $[(C_5H_5)Fe(CO)_2]_2$.

Reaction of CH_3Li *with* $(C_5H_5)Fe(CO)_2C(O)CH_3$

A known sample of $(C_5H_5)Fe(CO)_2C(O)CH_3$ was prepared as reported in the literature[13] (IR in CO region in THF: 2014 cm^{-1}, 1953.5, and 1659; in hexane, 2022, 1964, and 1669 cm^{-1}). $(C_5H_5)Fe(CO)_2C(O)CH_3$ (2.0 mmoles) were reacted with 2.3 mmoles CH_3Li in THF at $-78°$ for 30 min and then at 0° for another 30 min. The solution changed from bright yellow to red-black over the course of the reaction period. The IR of this reaction mixture showed new bands at 1890.5 and 1569 cm^{-1} in approximately 50% yield. Attempts to ethylate a possible addition product by the triethyloxonium fluoroborate method were unsuccessful[15]. No $[(C_5H_5)Fe(CO)_2]_2$ was observed under the reaction conditions. Attempts to decompose $(C_5H_5)Fe(CO)_2C(O)CH_3$ by holding at refluxing chloroform temperature for 18 h failed.

Reactions of $C_6H_5CH_2MgCl$ *with* $[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$

$[(C_5H_5)Fe(CO)_3]^+[B(C_6H_5)_4]^-$ (0.4 g; 0.74 mmole) were placed in 20 ml of THF at 0°. Upon addition of 4.5 mmoles of $C_6H_5CH_2MgCl$ the insoluble salt dissolved. The IR spectrum of this solution showed only 2 absorptions in the CO stretching region at 2042 and 1963 cm^{-1}, the latter broad and approximately doubling the intensity of the former. After quenching the reaction, solvent was removed *in vacuo*. Sublimation at 70–80° and 0.5 mm yielded a yellow, low-melting (ca. 30°), air-sensitive sublimate, ($\sim$50% yield). Elemental analysis was not attempted however the complete IR and NMR (see Table 1) as well as the mass spectral data indicated its formulation to be *exo*-$(5\text{-}C_6H_5CH_2C_5H_5)Fe(CO)_3$.

The mass spectrum of the sublimate did not show the parent molecular ion, rather the highest mass peak is at 205, $[(C_5H_5)Fe(CO)_3]^+$. Peaks at masses 91 and 182 indicate production of benzyl and bibenzyl. Other peaks indicate the typical successive loss of CO groups from $[(C_5H_5)Fe(CO)_3]^+$.

TABLE 1

INFRARED AND NMR DATA FOR CYCLOPENTADIENE COMPLEXES

	Proton NMR[a]	*IR* (cm^{-1})[b]	
		ν(CO)	*Other bands*
$C_6H_5CH_2C_5H_5Fe(CO)_3$	7.26 (m) C_6H_5	2046.6 vs	3085.5 w, 3063.0 w
	1.97 (d) CH_2	1978.5 vs	3027.5 w, 2940.0 w
	5.48 (m) H_β	1963.0 vs	2925.0 w, 2837.5 w
	3.05 (m) H_α		1602 m, 1496 m, 1455 m
	2.86 (s) H_{endo}	2051 vs[c]	
		1983 vs[c]	1602 m[c]
		1974 vs[c]	
$C_6H_5CH_2C_5H_5Fe(CO)_2P(C_6H_5)_3$	7.16 (m) $P(C_6H_5)_3$	1974.5 vs	3081 w, 3061 w, 2930 w,
	6.82 (m) C_6H_5	1918.5 vs	3027 w, 1495 m, 1436 m
	1.82 (d) CH_2		
	4.98 (m) H_β		
	2.40 (m) H_α		
	2.82 (s) H_{endo}		
$C_6H_5C_5H_5Fe(CO)_2P(C_6H_5)_3$[d,e]	7.03 (m) C_6H_5	1980 vs	3060 m, 2920 m,
	7.34 (m) $P(C_6H_5)_3$	1920 vs	1480 m, 1435 m
	5.15 (m) H_β		
	2.62 (m) H_α		
	3.85 (m) H_{endo}		

[a] Deuteriochloroform solution, TMS as internal standard, (TMS=0 ppm). (s), singlet; (d), doublet; (m), multiplet. [b] CCl_4 as solvent except where noted. [c] Hydrocarbon solvent. [d] Work of Treichel, see ref. 1. [e] Nujol mull, KBr cells.

Reaction of $[(C_5H_5)Fe(CO)_2P(C_6H_5)_3]^+Cl^-$ *with* $C_6H_5CH_2MgCl$

$(C_5H_5)Fe(CO)_2P(C_6H_5)_3^+Cl^-$ (0.46 g; 0.87 mmole) was reacted with 1.5 mmoles of $C_6H_5CH_2MgCl$. An IR of this solution (in THF) showed 2 main CO absorptions at 1968.5 and 1912.0 cm^{-1}. After quenching the reaction and removal of solvent the residue was dissolved in benzene and chromatographed on a 20 × 2 cm column of adsorption alumina with a 50/50 benzene/hexane mixture as eluant. A yellow band eluted and a green band stayed on the column. The eluant was concentrated and the compound precipitated as bright yellow crystals upon addition of hexane. Recrystallization from benzene/hexane yielded 0.35 g (75%) of *exo*-(5-$C_6H_5CH_2C_5H_5$)$Fe(CO)_2P(C_6H_5)_3$; m.p., 144.5–146°.

IR and NMR results may be found in Table 1. The mass spectrum indicated the highest mass fragment to be $[Fe(CO)_2P(C_6H_5)_3]^+$. A high intensity peak was seen for the expected organic fragment, $[C_6H_5CH_2C_5H_5]^+$, mol.wt., 156. (Found: C, 72.49; H, 5.11; P, 5.61. Mol.wt., 529. $C_{32}H_{27}O_2PFe$ calcd.: C, 72.47; H, 5.13; P, 5.84%. Mol.wt., 530.)

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REFERENCES

1 P. M. Treichel and R. L. Shubkin, *Inorg. Chem.*, 6 (1967) 1328.
2 L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, 2 (1968) 391.
3 L. Busetto, M. Graziani and U. Belluco, *Inorg. Chem.*, 10 (1971) 78.
4 R. G. Pearson and R. W. Johnson, *Inorg. Chem.*, 10 (1971) 2091.
5 D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, 5 (1971) 247.
6 M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, 279 (1964) 191.
7 N. W. Alcock, *Chem. Commun.*, (1965) 177.
8 M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1959) 3753.
9 D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, 9 (1970) 1691.
10 Unpublished results, this laboratory.
11 A. Davison, M. L. H. Green and G. Wilkinson, *J. Chem. Soc.*, (1961) 3172.
12 L. Busetto, U. Belluco and R. J. Angelici, *J. Organometal. Chem.*, 18 (1969) 213.
13 R. B. King, *J. Amer. Chem. Soc.*, 85 (1963) 1918.
14 R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 2 (1964) 15.
15 E. O. Fischer and V. Kiener, *J. Organometal. Chem.*, 23 (1970) 215.