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THE CHEMISTRY OF METAL CARBONYL ANIONS

V *. INTERACTIONS OF CARBONYLMETALLATE MONOANIONS WITH QUARTERNARY ALKYL- AND ARYL-ONIUM IONS

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Summary

Tetraphenyl-phosphonium and -arsonium ions react with $C_5H_5Fe(CO)_2^-$ to give 35—45% yields of $PhFe(CO)_2C_5H_5$ and substantial amounts of dimer. Corresponding reactions of $Re(CO)_5^-$ are much slower and yield only $Re_2(CO)_{10}$. Tetraphenylarsonium salts of less nucleophilic carbonyl anions including $C_5H_5M(CO)_3^-$ (M = Mo, W), $Mn(CO)_5^-$, $Co(CO)_4^-$ and $V(CO)_6^-$ are isolable as crystalline solids and are stable at 25°C. Base sensitive quarternary ammonium ions, $PhMe_3N^+$ and $PhCH_2Me_3N^+$, also react slowly with $C_5H_5Fe(CO)_2^-$ to quantitatively yield $CH_3Fe(CO)_2C_5H_5$ and $PhCH_2Fe(CO)_2C_5H_5$, respectively. A comparison of the reactions of these organometallic bases and non-metallic bases such as hydroxide ion and carbanions with quarternary onium ions is presented.

Introduction

In connection with our studies on the reactivity patterns of metal carbonyl anions [1], we have discovered that certain quarternary alkyl- and aryl-onium ions react with the strongly nucleophilic anion $C_5H_5Fe(CO)_2^-$ [2] to produce $RFe(CO)_2C_5H_5$, where R = alkyl or aryl. Although previous reports have appeared on similar reactions of $C_5H_5Fe(CO)_2^-$ with more reactive onium ions including phenyldiazonium [3], triphenylsulfonium [3] and diphenyliodonium [3,4] ions, to our knowledge no reports on the reaction of any carbonyl anions with quarternary alkyl- and/or aryl-ammonium, -phosphonium and -arsonium ions have appeared in the scientific literature. The facile reactions of $C_5H_5Fe(CO)_2^-$ and $Re(CO)_5^-$ with $(C_6H_5)_4As^+$ are particularly noteworthy in that the

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* For part IV see ref. 27.

latter ion has been regarded as an unreactive counterion for the isolation of crystalline salts of carbonylmetallate ions [5]. For example, recently the isolation of thermally stable tetraphenylarsonium salts of $M(CO)_6^-$ (M = V, Nb, Ta) [6], $Ir(CO)_2Cl_2^-$ [7], $ReW(CO)_{10}^-$ [8] and $C_5H_5Fe(CO)(COC_2H_5)CN^-$ [9] has been described.

Experimental

General procedures and materials

All operations were carried out under an atmosphere of purified nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate and molecular sieves. Solutions were transferred by stainless steel cannulae and syringes; otherwise reactions were performed by using standard Schlenck apparatus [10]. Reagent grade tetrahydrofuran was freshly distilled from the benzophenone ketyl of potassium under an argon atmosphere. With exceptions noted below, all reagents and other solvents were obtained from commercial sources and used without further purification. The preparation of sodium/potassium alloy has been described previously [11]. Moisture was removed from $Ph_4AsCl \cdot xH_2O$ (Eastern Chemical Co.) by stirring a methylene chloride solution of this substance with magnesium sulfate for approximately one hour. (Infrared evidence indicates that negligible exchange of chloride and sulfate ions occurs under these conditions.) Subsequently, solid Ph_4AsCl was obtained by treatment of the filtered CH_2Cl_2 solution with excess anhydrous ethyl ether, followed by drying of the solid in vacuo. Solutions of carbonylmetallate anions were generated from corresponding neutral dimers either by reduction with Na/K or sodium amalgam (in the case of $Re_2(CO)_{10}$) as described previously [11].

IR spectra were recorded on a Perkin—Elmer 237B spectrometer. Solution spectra were obtained in sealed sodium chloride cells equipped with stainless steel Luer stopcocks to permit filling via syringe outside the glove box with essentially complete exclusion of air. Solutions of $C_5H_5Fe(CO)_2^-$ in THF could be kept for at least 1/2 h in these cells without significant oxidation occurring. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan and Galbraith Laboratories.

All reactions were carried out similarly and will be illustrated by that of Ph_4PBr with $C_5H_5Fe(CO)_2^-$: A solution of $KFe(CO)_2C_5H_5$ (8.7 mmol) prepared from the reduction of 1.54 g (4.33 mmol) of $[C_5H_5Fe(CO)_2]_2$ by 1 ml of sodium/potassium alloy ($NaK_{2.8}$) in 125 ml of tetrahydrofuran (THF) for 1.5 h [11] was filtered (medium porosity fritted disc) and cooled to ca. —70°C. Subsequently, the solution was rapidly added via a cannula to another flask containing a magnetically stirred slurry of $Ph_4P^+Br^-$, 3.64 g (8.66 mmol) in 15 ml of THF at —70°C. The deep red color of the $C_5H_5Fe(CO)_2^-$ slowly gave way to a deep brown when the solution was allowed to warm. Other experiments conducted at room temperature under similar conditions showed the reaction to be complete within 15 min. Infrared spectra of solutions obtained by mixing reactants at —70°C or room temperature were essentially identical and showed strong bands of almost equal intensity at 2015 cm^{-1} (due to $PhFe(CO)_2C_5H_5$) and 1994 cm^{-1} (due to $[C_5H_5Fe(CO)_2]_2$) and a weak band at 1925 cm^{-1} (due to $PhFe(CO)(PPh_3)C_5H_5$ [3]). The latter band grew upon prolonged exposure of the solution to fluorescent lamp radiation. After filtration of the reaction mixture (medium frit), it was evaporated to dryness, carefully extracted with 2 × 20 ml of warm petroleum ether/benzene (9 : 1, v : v), and chromatographed on a 2 × 12 cm alumina column. The first colored band (yellow) was eluted with 9 : 1 petroleum ether/benzene and gave upon evaporation $PhFe(CO)_2C_5H_5$ contaminated with triphenylphosphine. Subsequent chromatography of a hexane solution of the first fraction on an alumina column gave a single yellow band which was eluted with hexane. Evaporation of solvent from the eluate gave 0.95 g (43% yield) of yellow crystalline and spectroscopically pure $PhFe(CO)_2C_5H_5$. By using an increasingly benzene-rich petroleum ether/benzene solution, $[C_5H_5Fe(CO)_2]_2$, 0.69 g (45%), and $PhFe(CO)(PPh_3)C_5H_5$, 0.10 g (2%), were successively eluted and isolated as pure, crystalline substances. In other preparations, substantially larger yields of $PhFe(CO)(PPh_3)C_5H_5$, were obtained by exposing the crude reaction mixture to normal laboratory (fluorescent) light for several hours. In these preparations, infrared evidence for the presence of $PhCOFe(CO)(PPh_3)C_5H_5$ [3] was also obtained.

Analogous reactions of $KFe(CO)_2C_5H_5$ with Ph_4AsCl gave 40—45% yields of $PhFe(CO)_2C_5H_5$. In these preparations the yields of pnicogen-substituted product, $PhFe(CO)(AsPh_3)C_5H_5$, was often substantially greater (up to 10%) than those for corresponding reactions with Ph_4PBr. Reactions conducted at low temperatures (—78°C) with Ph_4AsCl and Ph_4PBr gave essentially the same yields of $PhFe(CO)_2C_5H_5$.

Thermally unstable orange-red crystalline solids, probably ionic $[Ph_4E][C_5H_5Fe(CO)_2]$(E = P or As), were isolated at —78°C but decomposed rapidly above 0°C to yield a mixture of $[C_5H_5Fe(CO)_2]_2$ and $PhFe(CO)_2C_5H_5$. An alternative formulation which seems less likely involves a pentacoordinate P covalently bonded to iron. However, related antimony compounds have been shown to exist [28].

Reaction of Me_3PhNBr *with* $C_5H_5Fe(CO)_2^-$

A solution of $KFe(CO)_2C_5H_5$ (5.2 mmol) in 100 ml THF (prepared by Na/K reduction of dimer) was added to 1.1 g (5.2 mmol) of dry Me_3PhNBr. After about 10 min the stirred solution had changed from the characteristic deep red of the iron anion to a yellow color due to $CH_3Fe(CO)_2C_5H_5$, as evidenced by an infrared spectrum in the carbonyl region which showed bands due only to product (2008, 1948 cm^{-1}). All but about 5 ml of solvent was removed under reduced pressure at or below 0°C. Subsequently 40 ml of 0.1 *M* HCl and 50 ml of pentane, both oxygen free, were added to the flask in order to separate *N,N*-dimethylaniline from $CH_3Fe(CO)_2C_5H_5$ by protonation of the former substance. The mixture was stirred vigorously for 2 h. The aqueous phase was carefully removed and 10 g of $CaCl_2$ added to dry the pentane layer. Removal of pentane provided 0.82 g (82% yield) of volatile $CH_3Fe(CO)_2C_5H_5$, spectroscopically free of other carbonyl-containing impurities. The properties of this substance were identical to those described earlier for bonafide $CH_3Fe(CO)_2C_5H_5$ [13]. Numerous other salts of the type $[Me_3ArylN]Br$ also provide essentially quantitative yields of $CH_3Fe(CO)_2C_5H_5$.

Reaction of $Me_3C_6H_5CH_2NCl$ *with* $C_5H_5Fe(CO)_2^-$

Room temperature reactions of this salt with $Fe(CO)_2C_5H_5^-$ in THF were quite slow and required approximately 1 h for completion. Infrared and NMR analysis of the reaction mixture showed the products to be principally $PhCH_2Fe(CO)_2C_5H_5$ [15] and Me_3N. No formation of the dimer, $[C_5H_5Fe(CO)_2]_2$, was detected in reactions of $RMe_3N^+X^-$ (R = phenyl, benzyl, X = Cl, Br) with $KFe(CO)_2C_5H_5$ in THF.

Results and discussion

Reactions of quarternary onium ions with $C_5H_5Fe(CO)_2^-$

Reactions of Ph_4PBr and Ph_4AsCl with $C_5H_5Fe(CO)_2^-$ have been found to be extremely rapid at room temperature in THF. They provide 40—45% yields of $PhFe(CO)_2C_5H_5$(I), substantial amounts of $[C_5H_5Fe(CO)_2]_2$, biphenyl and much smaller amounts of $PhFe(CO)(EPh_3)C_5H_5$ and $PhCOFe(CO)(EPh_3)C_5H_5$ (E = P, As). The pnicogen derivatives have been obtained previously in moderate yields from the photosubstitution of EPh_3 into I [3]. In view of the previously reported poor to moderate yields of I (summarized in Table 1) it would appear that Ph_4PBr (commercially available in more convenient form than corresponding Ph_3S^+ salts * and much less costly than Ph_4AsCl) is a valuable precursor to I. However, this method suffers from an additional chromatographic separation of I from PPh_3 which is not necessary in the corresponding triphenylsulfonium ion reaction. Diazonium, oxonium, sulfonium and halonium ions have been recognized for many years as being useful reagents for the synthesis of organometallic compounds [17]; however, apparently the value of corresponding phosphonium or arsonium ions in such syntheses has not been appreciated previously. This circumstance is somewhat surprising since it is known that tetraphenyl-phosphonium and -arsonium ions are unstable in the presence of strong bases such as hydroxide ion and carbanions. Thus, concentrated aqueous solutions of tetraphenylphosphonium hydroxide readily decompose according to eq. 1 [18,19]. Other reac-

$$Ph_4P^+OH^- \rightarrow Ph_3P{=}O + PhH \qquad (1)$$

tions of Ph_4P^+ with strong bases are summarized by eq. 2 and 3. All of these reac-

TABLE 1

SUMMARY OF SYNTHESES OF $PhFe(CO)_2C_5H_5$

Reaction	Yield (%)	Reference
$Fe(CO)_2C_5H_5^- + PhI$	2	12
$IFe(CO)_2C_5H_5 + PhMgBr$	3	12
$PhCOFe(CO)_2C_5H_5 + h\nu$	12	13
$Fe(CO)_2C_5H_5^- + C_6H_5N_2BF_4$	trace	3
$Fe(CO)_2C_5H_5^- + (C_6H_5)_2IBF_4$	18	3
$Fe(CO)_2C_5H_5^- + (C_6H_5)_3SBF_4$	40—45	3
$Fe(CO)_2C_5H_5^- + (C_6H_5)_4PBr$	35—45	This work
$Fe(CO)_2C_5H_5^- + (C_6H_5)_4AsCl$	35—45	This work

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* Triphenylsulfonium chloride is commercially available as highly impure 50% aqueous solutions (Aldrich). We have experienced considerable difficulty in obtaining solid Ph_3SBF_4 from these solutions. Since $C_5H_5Fe(CO)_2^-$ is immediately hydrolyzed to form $HFe(CO)_2C_5H_5$, the onium salts used in these preparations must be free of moisture.

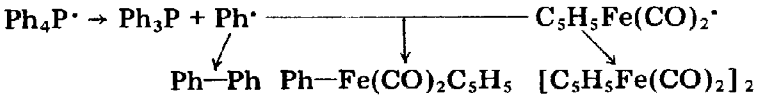
$$Ph_4PBr + LiPh \rightarrow Ph_5P + LiBr\ [20] \tag{2}$$

$$Ph_4PBr + LiCH_3 \rightarrow Ph_3P{=}CH_2 + PhH + LiBr\ [21] \tag{3}$$

tions, as exemplified by eq. 2, are likely to proceed via a 5-coordinate intermediate [21,22]. Very strong organometallic bases such as $C_5H_5Fe(CO)_2^-$ also undergo reactions with Ph_4P^+ and it seems possible that a similar intermediate (II) may be involved as shown in scheme 1.

SCHEME 1

$$Ph_4P^+ + C_5H_5Fe(CO)_2^- \rightleftharpoons \underset{\text{(II)}}{[Ph_4P{-}Fe(CO)_2C_5H_5]} \rightleftharpoons Ph_4P^\cdot + {}^\cdot C_5H_5Fe(CO)_2$$



Homolytic cleavage of the incipient P—Fe bond in II followed by a decomposition of $Ph_4P^\cdot$ and subsequent recombination of radicals accounts qualitatively for the formation of $[C_5H_5Fe(CO)_2]_2$, $PhFe(CO)_2C_5H_5$ and biphenyl, the principal products of this reaction. In accord with Scheme 1 it was found that moderately stable solutions of $Ph_4P^+Fe(CO)_2C_5H_5^-$ and $Ph_4As^+Fe(CO)_2C_5H_5^-$ could be obtained in acetonitrile/THF. For example, a solution of $Ph_4P^+Fe(CO)_2C_5H_5^-$, prepared by adding 8.5 mmol of Ph_4PBr in 30 ml of dry, oxygen-free acetonitrile to a solution of 8.5 mmol of $KFe(CO)_2C_5H_5$ in 100 ml of THF remained unchanged for at least 0.5 h at room temperature, as evidenced by its infrared spectrum which showed only two strong bands of equal intensity at 1867 and 1792 cm^{-1}. This was essentially identical in the carbonyl region to that obtained from a solution of $[Bu_4N][Fe(CO)_2C_5H_5]$ in THF [1865s, 1788s] [11]. Only after stirring the solution for over 48 h at room temperature did all $Fe(CO)_2C_5H_5^-$ disappear. The addition of acetonitrile had no significant influence on product distributions.

The only other phosphonium salt shown to react with $C_5H_5Fe(CO)_2^-$ was $PhCH_2$-Ph_3PCl. Reaction occurred immediately on mixing in THF at room temperature and provided mostly $[C_5H_5Fe(CO)_2]_2$ (yields up to 95%), only small amounts of $PhCH_2Fe(CO)_2C_5H_5$ [15] (yields to 5%) and traces of $PhCH_2Fe(CO)PPh_3C_5H_5$ [16] for reactions conducted in the dark. Surprisingly, a closely related cation, bis(triphenylphosphine)iminium ion, PPN^+, effectively a substituted phosphonium ion, was unreactive with $C_5H_5Fe(CO)_2^-$. Orange-brown, crystalline, solid $[PPN][C_5H_5Fe(CO)_2]$, only slightly soluble in THF, (ν(CO) in THF: 1864s, 1791s cm^{-1}) could be isolated from the metathesis of [PPN]Cl and $KFe(CO)_2C_5H_5$ in THF. Similar PPN^+ salts of $V(CO)_6^-$, $Mn(CO)_5^-$, $Co(CO)_4^-$, $Cr_2(CO)_{10}^{2-}$ and $Cr_2(CO)_{10}I^-$ have been described previously [23]. Quarternary alkylphosphonium salts of $Fe(CO)_2C_5H_5^-$ were also found to be thermally stable at room temperature. The preparation of related onium salts of $C_5H_5M(CO)_3^-$ (M = Cr, Mo, W) containing the cations R_4P^+ (R = alkyl), Me_3SO^+ and $Me_3PNH_2^+$ has been reported [26].

Although $C_5H_5Fe(CO)_2^-$ may be isolated as crystalline salts of R_4N^+ (R = Me, Et, Pr, Bu, etc.) which are stable indefinitely at room temperature under nitrogen

[11], especially base-sensitive quarternary ammonium ions such as $R'Me_3N^+$ ($R' = Ph, PhCH_2$) have been found to react with the iron anion within minutes (ca. 10 min for R = Ph and 1 h for $R = PhCH_2$) to give essentially quantitative yields of product according to eq. 4 and 5.

$$C_5H_5Fe(CO)_2^- + PhMe_3N^+ \rightarrow MeFe(CO)_2C_5H_5 + PhNMe_2 \tag{4}$$

$$C_5H_5Fe(CO)_2^- + PhCH_2Me_3N^+ \rightarrow PhCH_2Fe(CO)_2C_5H_5 + NMe_3 \tag{5}$$

Entirely analogous reactions of hydroxide ion with these and related ammonium ions are known (eq. 6 and 7) [25].

$$OH^- + PhMe_3N^+ \rightarrow MeOH + PhNMe_2 \tag{6}$$

$$OH^- + PhCH_2Me_3N^+ \rightarrow PhCH_2OH + NMe_3 \tag{7}$$

Although other strongly basic carbonyl anions are likely to react with such ammonium ions, these reactions have not been studied as they are unlikely to be of any synthetic value. Indeed, in the above examples, $PhCH_2Fe(CO)_2C_5H_5$ [15] and $MeFe(CO)_2C_5H_5$ [12] are more readily prepared by other methods.

Interactions of quarternary onium ions with $Re(CO)_5^-$ and other carbonylmetallate monoanions

The reaction of $NaRe(CO)_5$ with Ph_4E^+ (E = P, As) was much slower at room temperature in THF than corresponding reactions of $C_5H_5Fe(CO)_2^-$. For example, 12 h were required for the reaction between Ph_4AsCl and $NaRe(CO)_5$ to proceed to completion. For these reactions, no $PhRe(CO)_5$ [4] was formed; all $Re(CO)_5^-$ was converted to $Re_2(CO)_{10}$. Also Ph_4As^+ was shown to be converted quantitatively to Ph_3As and biphenyl.

All carbonylmetallate monoanions that are weaker nucleophiles than $C_5H_5Fe(CO)_2^-$ and $Re(CO)_5^-$ [2] including $Mn(CO)_5^-$, $C_5H_5M(CO)_3^-$ (M = Mo, W), $Co(CO)_4^-$ and $V(CO)_6^-$ are unreactive with Ph_4As^+ at room temperature. Treatment of THF solutions of these tetraphenylarsonium salts with an excess of diethyl ether provides crystalline salts which are stable indefinitely at room temperature under nitrogen; crystalline $[Ph_4As][V(CO)_6]$ is also stable for several hours in air. Infrared spectra in the carbonyl region of these salts in THF are shown in Table 2. The striking feature of the spectra is their simplicity. In

TABLE 2

INFRARED SOLUTION SPECTRA OF TETRAPHENYLARSONIUM CARBONYLMETALLATES IN THF IN THE CARBONYL REGION

Anion	C—O stretching frequencies (cm^{-1})
$C_5H_5Fe(CO)_2^-$ [a]	1867s, 1792s
$C_5H_5W(CO)_3^-$	1894s, 1781s
$C_5H_5Mo(CO)_3^-$	1898s, 1784s
$Mn(CO)_5^-$	1895s, 1861s
$Co(CO)_4^-$	1890s
$V(CO)_6^-$ [b]	1855vs

[a] Stabilized salt in 10 : 3, v : v THF/acetonitrile (see text). [b] Methylene chloride.

contrast to corresponding spectra of sodium or potassium salts in THF which often show more carbonyl stretching frequencies than expected on the basis of the local symmetry of the anion due to varying degrees of ion pairing [24], the spectra of Ph_4As^+ salts in THF are entirely consistent with that expected on the basis of local symmetry arguments. Thus, while THF solutions of Na^+ of K^+ salts of $Mo(CO)_3C_5H_5^-$ show three strong stretching frequencies in the carbonyl region [11], solutions of $[Ph_4As][Mo(CO)_3C_5H_5]$, which contain a roughly spherical cation, show only two bands of approximately equal intensity. Such a spectrum is consistent with an anion of C_{3v} local symmetry.

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