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A Convenient Synthetic Route to Complexes of the Types $(\pi\text{-}C_5H_5)Fe(CO)_2X$ and $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$

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Oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ by molecular oxygen in acetone and aqueous fluoroboric acid followed by reaction with anionic or neutral ligands provides a convenient route to complexes of the type $(\pi\text{-}C_5H_5)Fe(CO)_2X$ and $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ (X = Cl, Br, NCO, CN, NO_3, N_3, O_2CH, $O_2C_2Cl_3$; L = $P(C_6H_5)_3$, C_5H_5N, H_2NNH_2, $S(C_4H_9)_2$). Spectroscopic evidence indicates that the intermediate in these reactions is the cationic aquo complex, $(\pi\text{-}C_5H_5)Fe(CO)_2(OH_2)^+$.

Introduction

Recently Meyer and coworkers reported[1] that oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ by ferric ion in acetone leads to a labile acetone complex which readily reacts with anionic or neutral ligands to give complexes of the types $(\pi\text{-}C_5H_5)Fe(CO)_2X$ and $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ (where X = anionic ligand and L = neutral ligand). We wish to report a similar but more convenient one-step synthesis of a wide variety of the $(\pi\text{-}C_5H_5)Fe(CO)_2X$ and $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ complexes.

Oxidation of $[(C_5H_5)Fe(CO)_2]_2$ by oxygen in acetone and aqueous fluoroboric acid produces a reactive cationic intermediate, identified as $(\pi\text{-}C_5H_5)Fe(CO)_2(OH_2)^+$.

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2+2HBF_4+H_2O+1/2O_2\rightarrow 2[(\pi\text{-}C_5H_5)Fe(CO)_2(OH_2)]BF_4 \qquad (1)$$

This aquo complex undergoes substitution upon reaction with anionic (equation (2)) or neutral ligands. This procedure differs from

$$[(\pi\text{-}C_5H_5)Fe(CO)_2(OH_2)]BF_4+X^-\rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2X+BF_4^-+H_2O \qquad (2)$$

previous preparations using acid wit hoxygen as the oxidant[2,3] in that the ligand is not present during the oxidation and therefore may be quite basic. This synthetic method does not require anaerobic or anhydrous reaction conditions or reagents, and appears to have a wide range of application.

Experimental Section

Bis(cyclopentadienyldicarbonyliron)(Pressure Chemical Co.) was recrystallized from dichloromethane-hexane before use. Other reagents were not purified further.

NMR spectra were recorded on a Perkin-Elmer Hitachi R20-B spectrometer in chloroform-d_1 or acetone-d_6 using tetramethylsilane as an internal standard. Infrared bands were measured using a Perkin-Elmer 237B grating spectrophotometer equipped with an expanded abscissa recorder, and are believed accurate within ± 2 cm^{-1}. Carbon monoxide was used for calibration. Elemental analyses were performed by Meade Microanalytical Laboratories, Amherst, Massachusetts. (a) *$(C_5H_5)Fe(CO)_2Cl$.* $[(C_5H_5)Fe(CO)_2]_2$ (2.00g, 0.57 mmol) was dissolved in 65 ml of acetone, and 48-50% aqueous HBF_4 (2.1g, 1.2 mmol) in 10 ml of acetone was added. Oxygen gas was bubbled through solution until the dimer had been consumed (*ca* 5-10 min). A drop of the reaction mixture added to several ml of water should give a clear orange solution. Cloudiness indicates the presence of starting material). A solution of NaCl (2.0g, 3.42 mmol) in 20 ml of water was added and the mixture was evaporated under water aspirator vacuum to remove the acetone. (Any excess starting material or dimer which has formed during the reaction precipitates at this point). The aqueous solution was filtered and extracted with 20 ml portions of CH_2Cl_2 until the extract was colorless. The combined extracts were dried over $MgSO_4$, filtered, concentrated on a rotary evaporator and crystallized with pentane by cooling at –20°C. Dark red crystals of $(C_5H_5)Fe(CO)_2Cl$ (1.20 g, 50%) were collected and washed with hexane. (b) *$(C_5H_5)Fe(CO)_2Br$.* This procedure is identical to that described in section (a). $[(C_5H_5)Fe(CO)_2]_2$ (2.00g, 0.57 mmol) was oxidized and reacted with an aqueous solution of NaBr (1.25g, 1.21 mmol) to yield dark purple $(C_5H_5)Fe(CO)_2Br$ (1.13g, 39%). (c) *$(C_5H_5)Fe(CO)_2CN$.* $[(C_5H_5)Fe(CO)_2]_2$ (2.65g, 0.75 mmol) was oxidized and treated with NaCN (2.0g, 4.08 mmol) by the method described in (a). Dark yellow $(C_5H_5)Fe(CO)_2CN$ (1.62g. 53%) was crystallized from a small volume of CH_2Cl_2 with ether and pentane. (d) *$(C_5H_5)Fe(CO)_2NCO$.* $[(C_5H_5)Fe(CO)_2]_2$ (2.00g, 0.57 mmol) was reacted as in (a) with KNCO (1.30g, 1.60 mmol). The product 0.80g, 32%) was crystallized from CH_2Cl_2-hexane. (e) *$(C_5H_5)Fe(CO)_2NO_3$.* $[(C_5H_5)Fe(CO)_2]_2$ (2.00g, 0.57 mmol) was oxidized and

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(1) E.C. Johnson, T.J. Meyer, and N. Winterton, *Inorg. Chem.*, *10*, 1673 (1971).

(2) T.S. Piper, F.A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *1*, 165 (1955).

(3) T.E. Sloan and A. Wojcicki, *Inorg. Chem.*, *7*, 1268 (1968).

reacted with KNO_3 (0.90g, 0.89 mmol) as in (a). Crystallization from CH_2Cl_2-hexane gave $(C_5H_5)Fe(CO)_2NO_3$ (1.33g, 49%). (f) *$(C_5H_5)Fe(CO)_2N_3$*. $[(C_5H_5)Fe(CO)_2]_2$ (7.00g, 1.97 mmol) was oxidized in 150 ml of acetone and 48-50% HBF_4 (7.4g, 4.2 mmol) with O_2. Sodium azide (10.0g, 15.4 mmol) in 120 ml of H_2O was added; the mixture was filtered, and then evaporated on a rotary evaporator until a dark precipitate of the azide complex had formed. This was collected and combined with dichloromethane extracts of the aqueous solution. The CH_2Cl_2 solution was dried over $MgSO_4$, filtered and concentrated under vacuum. The product crystallized on addition of pentane followed by cooling at –20°C. Large, dark purple crystals of $(C_5H_5)Fe(CO)_2N_3$ (3.70g, 43%) were obtained.

Anal. Calcd for $(C_5H_5)Fe(CO)_2N_3$; C, 38.4; H, 2.3; N, 19.2. Found: C, 38.6; H, 2.8; N, 19.3. (g) *$(C_5H_5)Fe(CO)_2O_2CH$*. $[(C_5H_5)Fe(CO)_2]_2$ (4.95g, 1.40 mmol) was oxidized with oxygen in acetone and HBF_4. Sodium formate (2.9g, 4.25 mmol) in 60 ml of water was added. The mixture was evaporated to remove the acetone and filtered. The aqueous solution was alternately heated under hot tap water and extracted with CH_2Cl_2. This procedure was repeated until no more red color was taken into the CH_2Cl_2. The combined extracts were dried over $MgSO_4$, filtered, concentrated, and poured onto a 1.5 × 25 cm column packed with florisil in CH_2Cl_2. After elution with CH_2Cl_2 and finally acetone, the red solution was concentrated under vacuum. Addition of hexane to the solution and cooling gave red crystals of $(C_5H_5)Fe(CO)_2O_2CH$ (1.1g, 17.5%).

Anal. Calcd for $(C_5H_5)Fe(CO)_2O_2CH$: C, 43.3; H, 2.7. Found: C, 43.0; H, 2.9. (h) *$(C_5H_5)Fe(CO)_2O_2CCCl_3$*. This compound was conveniently prepared by bubbling oxygen into a solution of $[(C_5H_5)Fe(CO)_2]_2$ (6.40g, 1.81 mmol) and trichloroacetic acid (6.4g, 3.65 mmol) in 150 ml of $CHCl_3$ for 30 min. The solution was dried over $MgSO_4$, filtered and concentrated. Crystallization from $CHCl_3$-hexane-pentane gave dark red $(C_5H_5)Fe(CO)_2O_2CCCl_3$ (6.00g, 49%).

Anal. Calcd for $(C_5H_5)Fe(CO)_2O_2CCCl_3$: C, 31.9; H, 1.5. Found: C, 32.3; H, 1.9. (i) $[(C_5H_5)Fe(CO)_2NC_5H_5]BF_4$. $[(C_5H_5)Fe(CO)_2]_2$ (2.15g, 0.60 mmol) was oxidized in 80 ml of acetone, and pyridine (1.44g, 2.0 mmol) was added. The mixture was filtered and evaporated nearly to dryness. An additional 1.0g of pyridine was added in 80 ml of $CHCl_3$, and evaporation was continued until the solid was dry. It was then crushed, washed repeatedly with $CHCl_3$, dissolved in CH_2Cl_2 and crystallized with pentane. Yellow crystals of $[(C_5H_5)Fe(CO)_2NC_5H_5]BF_4$ (2.20g, 53%) were collected. (j) *$[(C_5H_5)Fe(CO)_2P(C_6H_5)_3]BF_4$*. $[(C_5H_5)Fe(CO)_2]_2$ (2.55g, 0.72 mmol) was oxidized in 80 ml of acetone, and triphenylphosphine (4.3g, 1.64 mmol) was added. The mixture was evaporated to an oil under water aspirator vacuum and 100 ml of $CHCl_3$ was added. After evaporation to dryness, the solid was washed repeatedly with $CHCl_3$ and recrystallized from CH_2Cl_2-hexane (3.93g, 52%). (k) $[(C_5H_5)Fe(CO)_2H_2NNH_2]PF_6$. $[(C_5H_5)Fe(CO)_2]_2$ (1.83g, 0.53 mmol) was oxidized in acetone (75 ml). Then 95% hydrazine (2.0g, 5.63 mmol) in 15 ml of acetone was added, and the resulting mixture was filtered and evaporated until dry. Extraction of the solid with six 20 ml portions of warm H_2O and addition of excess aqueous NH_4PF_6 gave a yellow precipitate. Recrystallization from CH_2Cl_2-pentane yielded $[(C_5H_5)Fe(CO)_2H_2NNH_2]PF_6$ (1.98g, 53%). (l) *$[(C_5H_5)Fe(CO)_2S(C_4H_9)_2]PF_6$*. $[(C_5H_5)Fe(CO)_2]_2$ (1.85g, 0.52 mmol) was oxidized in 75 ml of acetone, and dibutyl sulfide (2.5g, 1.71 mmol) in 15 ml of acetone was added. The mixture was evaporated to an oil, washed several times with hexane, and evaporated further for one hour under high vacuum. The oil was extracted repeatedly with warm water, and addition of aqueous NH_4PF_6 yielded a yellow precipitate. Recrystallization from $CHCl_3$-hexane gave the product (2.20g, 45%).

Anal. Calcd for $[(C_5H_5)Fe(CO)_2S(C_4H_9)_2]PF_6$: C, 41.2; H, 5.3. Found: C, 42.9; H, 5.4.

Results and Discussion

Syntheses of the $(C_5H_5)Fe(CO)_2X$ and $(C_5H_5)Fe(CO)_2L^+$ complexes reported here involve two steps: first, the oxidation of $[(C_5H_5)Fe(CO)_2]_2$ by O_2 in the presence of a stoichiometric amount of acid according to equation 1; and second, reaction of the resulting $(C_5H_5)Fe(CO)_2(OH_2)^+$ complex with X^- or L to give the desired products (equation 2). The intermediate $(C_5H_5)Fe(CO)_2(OH_2)^+$ was previously[2] prepared by the reaction of $C_5H_5Fe(CO)_2Cl$ with $AgNO_3$ in aqueous solution. Subsequently the aquo complex has been reported in several other reactions.[4-6]

To establish that the reaction does indeed proceed in this manner, it was followed by proton nmr spectrometry. An acetone solution of $[(C_5H_5)Fe(CO)_2]_2$ containing aqueous HBF_4 shows a single resonance at $\tau 5.05$ due to the C_5H_5 group of the dimer and a water resonance at $\sim\tau 2.5$. When air is introduced into the solution, a peak at $\tau 4.48$ assigned to the C_5H_5 group of $(C_5H_5)Fe(CO)_2(OH_2)^+$ begins to grow and the water peak broadens and shifts downfield. Saturation with O_2 causes $[(C_5H_5)Fe(CO)_2]_2$ to disappear, the $\tau 4.48$ peak to increase and the water peak to broaden and shift downfield further. Rapid proton exchange between coordinated and uncoordinated water molecules is most probably the reason for the observed broading and shifting of the water peak. An infrared spectrum of acetone solutions showed terminal C=O stretching absorptions at 2066(s) and 2018(s) cm^{-1}, which are attributed to the $(C_5H_5)Fe(CO)_2(OH_2)^+$ complex.

In addition to the peaks assigned to $(C_5H_5)Fe(CO)_2(OH_2)^+$, the nmr spectrum showed one small absorption (about 20% as large as the $\tau 4.48$ absorption) at $\tau 3.92$. This is an unidentified side-product which did not diminish when ligands were added. However, addition of pyridine, $P(C_6H_5)_3$, or KI caused the disappearance of the $\tau 4.48$ band and the appearance of product bands (Table I). The reactions with ligands are rapid but not instantaneous. This latter reaction is apparently not reversible under these conditions since addition of aqueous HBF_4 to acetone-d_6 solutions

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Table I. Infrared and Proton Nmr Results.

Compound	ν_{CO},[a] cm^{-1}	C_5H_5,τ [b]	Other Resonances, τ[c]
$(C_5H_5)Fe(CO)_2Cl$	2057, 2011	4.91 [d]	
$(C_5H_5)Fe(CO)_2Br$	2052, 2007	4.93 [d]	
$(C_5H_5)Fe(CO)_2CN$	2061, 2018	4.80 [d]	
$(C_5H_5)Fe(CO)_2NCO$	2062, 2017	4.91 [d]	
$(C_5H_5)Fe(CO)_2NO_3$	2069, 2025	4.86 [d]	
$(C_5H_5)Fe(CO)_2N_3$	2064, 2024, 2010 [e]	4.90 [d]	
$(C_5H_5)Fe(CO)_2O_2CH$	2054, 2008	4.90 [d]	2.38 [b]
$(C_5H_5)Fe(CO)_2O_2CCCl_3$	2063, 2019	4.86 [d]	
$[(C_5H_5)Fe(CO)_2NC_5H_5]BF_4$	2065, 2022	4.34 [f]	1.05(m), 1.90(m), 2.45(m)
$[(C_5H_5)Fe(CO)_2P(C_6H_5)_3]BF_4$	2057, 2014	4.35 [f,g]	2.30(m)
$[(C_5H_5)Fe(CO)_2H_2NNH_2]PF_6$	2067, 2017	4.38 [f]	7.28,[b] 7.69 [b]
$[(C_5H_5)Fe(CO)_2S(C_4H_9)_2]PF_6$	2061, 2016	4.26 [f]	7.05(m), 8.37(m). 9.04(m)

[a] $CHCl_3$ solvent. All absorptions are very strong. [b] Singlets except as noted. [c] m = multiplet. [d] Chloroform-d_1 solvent. [e] One of the two lower frequency absorptions is the asymmetric N_3 stretch. [f] Acetone-d_6 solvent. [g] Doublet due to coupling with ^{31}P; J = 1.5 Hz.

of several $(C_5H_5)Fe(CO)_2X$ and $(C_5H_5)Fe(CO)_2L^+$ complexes in air showed no evidence for the formation of $(C_5H_5)Fe(CO)_2(OH_2)^+$.

Coordinated acetone was not observed in nmr spectra of any of these solutions, and the chemical shift of the C_5H_5 protons assigned to $(C_5H_5)Fe(CO)_2(OH_2)^+$ differs from that assigned* to $(C_5H_5)Fe(CO)_2(acetone)^{+,1}$. Thus $(C_5H_5)Fe(CO)_2(acetone)^+$ is not present in these preparations.

Syntheses of sizeable quantities of $(C_5H_5)Fe(CO)_2X$ (X = Cl, Br, CN, NCO, N_3, NO_3, O_2CH, O_2CCCl_3), and $(C_5H_5)Fe(CO)_2L^+$ (L = pyridine, $P(C_6H_5)_3$, NH_2NH_2, and $S(n\text{-}C_4H_9)_2$) were carried out using this general method. Although complexes where X = Cl,[2] Br,[4] CN,[2] NCO,[7] NO_3,[1] and L = pyridine[8] $P(C_6H_5)_3$,[9] NH_2NH_2,[10] had previously been prepared, this method offers considerable advantages in timesavings and convenience. The complexes, $(C_5H_5)Fe(CO)_2N_3$, $(C_5H_5)Fe(CO)_2O_2CH$, $(C_5H_5)Fe(CO)_2O_2CCCl_3$, and $(C_5H_5)Fe(CO)_2S(n\text{-}C_4H_9)_2^{+,11}$ had not been reported previously. Infrared and nmr data for all of the derivatives are given in Table I.

Attempts to prepare certain other $(C_5H_5)Fe(CO)_2X$ and $(C_5H_5)Fe(CO)_2L^+$ complexes were unsuccessful. Reactions in acetone of $(C_5H_5)Fe(CO)_2(OH_2)^+$ with F^- did not give a stable product. With $NaNO_2$, golden crystals of a product believed to be $(C_5H_5)Fe(CO)_2NO_2$ were isolated but they decomposed even under vacuum at room temperature within a few hours. The compound had C-O stretching bands at 2067 and 2023 cm^{-1} and a single resonance in the nmr at τ4.83.

No reaction was observed when H_2S was added to a solution of $(C_5H_5)Fe(CO)_2(OH_2)^+$. With CH_3NH_2, a rapid reaction occurred which yielded primarily $[(C_5H_5)Fe(CO)_2]_2$. Low yields of $(C_5H_5)Fe(CO)_3^{+,12}$ were obtained by bubbling CO into a warmed aqueous solution of $(C_5H_5)Fe(CO)_2(OH_2)^+$.

In acetone and $CHCl_3$, $[(C_5H_5)Fe(CO)_2]_2$ reacts with HCl and O_2 to give $(C_5H_5)Fe(CO)_2Cl$ almost instantaneously. Under the same conditions, neither $[(C_5H_5)W(CO)_3]_2$ nor $Mn_2(CO)_{10}$ showed any reaction even after many hours.

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(*) The reported[1] chemical shift of $(C_5H_5)Fe(CO)_2(acetone)^+$ may be in error as indicated by the incorrect assignment of uncoordinated acetone at τ8.58. Reassignment to τ7.90 changes the chemical shift of the (C_5H_5) group in $(C_5H_5)Fe(CO)_2(acetone)^+$ to τ4.36 (rather than τ5.04). The adjusted value is more consistent with values of other cationc $(C_5H_5)Fe(CO)_2L^+$ complexes (Table (I).

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