coupling is significantly altered by the metal, decreasing in absolute value with decreasing electronegativity of the element with the $^1J(^{13}C-^1H)$ values in the order In > Ga > Al.

There is essentially no difference observed between the coupling constants for the bridging and terminal cyclopropyl groups in dimeric tricyclopropylaluminum. Thus, further supporting the proposed mode of stabilization of the bridge bond in these tricyclopropylmetal derivatives through the interaction of the nonbonding metal orbitals with the p orbitals of the α-carbon atom. These interactions would leave the s orbitals essentially unperturbed should not effect the $^{13}C-^1H$ coupling to any great extent.

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Registry No. tricyclopropylaluminum dimer, 21892-05-7; tricyclopropylgallium, 23719-82-6; tricyclopropylindium, 23719-81-5.

Metal Carbonyl Anion Generation Using Potassium Fluoride or Tetrabutylammonium Fluoride

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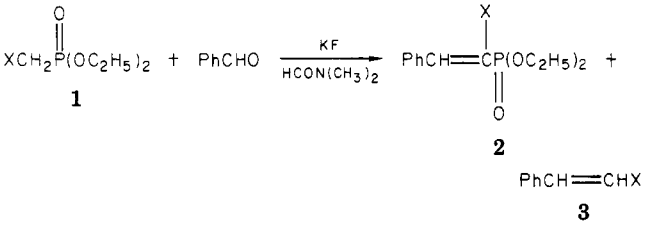
Triiron dodecacarbonyl reacts with dry potassium fluoride and commercial 18-crown-6, in tetrahydrofuran, to give the hydridoundecacarbonyltriferrate anion. The latter is also efficiently produced from $Fe_3(CO)_{12}$ and a 1 M solution of tetrabutylammonium fluoride. The quarternary ammonium fluoride can catalyze the reduction of nitrobenzenes to anilines by either $Fe_3(CO)_{12}$ or $Mn_2(CO)_{10}$. While $Co_2(CO)_8$ and $Co(CO)_3NO$ react with tetrabutylammonium fluoride, the resulting species are incapable of reducing nitrobenzene but can carbonylate 2-(bromomethyl)naphthalene.

Numerous publications have appeared in recent years on the utilization of fluoride ion as a base[2] and as a nucleophile[3] in organic synthesis. The fluoride used in these reactions is usually in the form of potassium fluoride or tetraalkylammonium fluorides.

There are many examples illustrating the ability of 18-crown-6 to solubilize potassium fluoride in relatively nonpolar solvents, thereby generating so-called "naked" fluoride ion. However, the exceedingly hygroscopic nature of potassium fluoride, tetraalkylammonium fluorides, and crown ethers cannot be overemphasized. The presence of water can have a major influence on the course of a variety of reactions involving fluoride ion. An example is the reaction of a phosphonate (1, X = CN, $COOC_2H_5$) with



benzaldehyde in *N,N*-dimethylformamide. In the presence of a small amount of "dry" potassium fluoride, the Knovenagel product (2) is the major product with little of the Wittig–Horner adduct (3) being obtained. Crown ether can accelerate this reaction. The proportion of 3 increases when some (but not too much) water is present, with the highest yield of 3 being attained with $KF{\cdot}2H_2O$.[4]

Liquid–liquid and solid–liquid phase-transfer catalysis is a useful technique in organometallic as well as in organic chemistry.[5] Crown ethers have been employed as catalysts for certain organometallic phase transfer processes, including the synthesis of ferrocenes[6] and bridging hydroxo complexes of platinum,[7] as well as the iron carbonyl induced reduction of nitroarenes to anilines.[8]

This paper describes the reactions of potassium fluoride and tetrabutylammonium fluoride with triiron dodecacarbonyl, dimanganese decacarbonyl, and several other metal carbonyls. Water plays a significant role in all of these reactions, with the facile generation of metal carbonyl hydrides being important in certain cases.

Results and Discussion

When triiron dodecacarbonyl was treated with an approximately equimolar amount of potassium fluoride and 0.25 equiv of "dry" 18-crown-6 in tetrahydrofuran, the solution remained intense green $[Fe_3(CO)_{12}]$ after being stirred at room temperature for 1 day. If, however, "wet" (i.e., commercial) 18-crown-6 was used instead, the reaction mixture turned deep red in less than 30 min. Under the latter conditions, the hydridoundecacarbonyltriferrate anion was generated and could be isolated as the bis(triphenylphosphin)iminium salt on addition of bis(triphenylphosphin)iminium chloride. The hydride was characterized on the basis of elemental analysis and the occurrence of an absorption maximum (methanol) at

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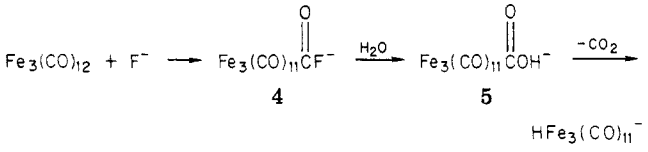
Table I. Yields of Anilines Obtained from the Reaction of Nitroarenes with $Fe_3(CO)_{12}$, $(C_4H_9)_4NF$, and Water

p-$RC_6H_4NO_2$(6), R, mmol	$Fe_3(CO)_{12}$, mmol	$(C_4H_9)_4NF$ (1 M), mmol	H_2O, mmol	p-$RC_6H_4NH_2$-(7),[a] %
CH_3, 9.92	5.95	0.18	28.0	37
CH_3, 10.2	6.12	0.60	6.5	21
CH_3, 10.3	6.15	0.60	27.0	45
CH_3, 10.2	6.10	0.60	32.0	48
CH_3, 9.91	5.94	0.80	23.0	66
CH_3O, 10.3	6.17	0.60	26.0	63
Cl, 10.2	6.09	0.60	27.0	71
COPh, 10.4	6.22	0.60	29.0	94

[a] Anilines were identified by comparison of physical data with those for authentic materials.

540–545 mm.[9] In addition, the red solution was capable of reducing p-nitrotoluene to p-toluidine. Such an H-$Fe_3(CO)_{11}^-$ mediated reduction of nitro compounds has previously been reported by using crown ether[8] and quaternary ammonium ion[10] catalysis, both under basic conditions.

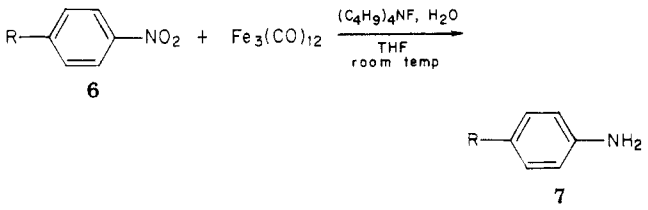
Being a solid, dibenzo-18-crown-6 proved easier to obtain in an anhydrous form than 18-crown-6. When the dry dibenzo derivative was used for the reaction of $Fe_3(CO)_{12}$ with potassium fluoride in anhydrous tetrahydrofuran, no reaction occurred after 18 h at room temperature. However, if the reaction mixture was heated to reflux for only 10 min, clean conversion to the hydride took place which, on addition of p-nitrotoluene, forms p-toluidine. What may be occurring at elevated temperatures is the attack of fluoride ion on $Fe_3(CO)_{12}$ to give **4**. Small amounts of



water (possibly from "dry" KF) can convert *4* to the hydroxycarbonyl anion **5** which, on subsequent elimination of carbon dioxide, would generate the trinuclear iron hydride. Alternatively, fluoride ion can convert water to hydroxide ion, the latter reacting with $Fe_3(CO)_{12}$ to give **5**.

The $HFe_3(CO)_{11}^-$ ion also is formed rapidly (less than 5 min) when $Fe_3(CO)_{12}$ in tetrahydrofuran was treated with a 1 M solution of tetrabutylammonium fluoride at room temperature. When the reaction was run in the presence of p-nitrotoluene (6.7/8.0/11.2 mmol ratio of $Fe_3(CO)_{12}$/$(C_4H_9)_4NF$/p-nitrotoluene), there was complete reduction to p-toluidine in 5 min. No reaction was observed when p-nitrotoluene was exposed to tetrabutylammonium fluoride (1 M) for 72 h.

Of greater potential was the finding that the reduction of nitro compounds (**6**) could be achieved by using a cat-



alytic amount of the tetraalkylammonium fluoride and a small quantity of added water. Good yields of amine (**7**) were realized by using the relative millimole quantities of $Fe_3(CO)_{12}$/**6**/H_2O/10% $(C_4H_9)_4NF$ (1 M) of 6/10/27/0.6 (approximate ratio-exact values are listed in Table I). The use of too little (6.5 mmol) or too much (99 mmol) water affords lower product yields, as does the use of less fluoride. In addition, allowing the solutions to stir overnight has little effect on the yield of the aromatic amine.

When dimanganese decacarbonyl was treated with either 1M $(C_4H_9)_4NF$ or the hydrated fluoride, $(C_4H_9)_4NF{\cdot}3H_2O$, in THF (under nitrogen or carbon monoxide), the manganese pentacarbonyl anion was formed. The reaction mixture displayed terminal metal carbonyl stretching bands at 1895 and 1860 cm^{-1} (THF) and addition of iodine/methylene chloride resulted in bleaching of the solution. Both of these observations are consistent with the presence of $Mn(CO)_5^-$.[11] *No* other metal carbonyl bands were observed in the infrared region. Interestingly, nitro compounds (**6**) were reduced to anilines (**7**) by $Mn_2(CO)_{10}$, added water, and a catalytic amount of tetrabutylammonium fluoride. Obviously, a catalytic quantity of a species which functions as a hydrogen source (e.g., metal carbonyl hydride) must be present, since $Mn(CO)_5^-$ will not convert **6** to **7** (Table II). The use of *cis*-$HMn(CO)_4PPh_3$ for the reduction of halides has been described in the literature.[12]

The reactions of several other metal carbonyls with tetrabutylammonium fluoride was also examined. Treatment of dicobalt octacarbonyl with hydrated tetrabutylammonium fluoride in THF afforded the cobalt tetracarbonyl anion (ν_{CO} = 1885 cm^{-1}).[11] However, these solutions do *not* reduce nitro compounds to amines. A nonreducing solution was also obtained from the reaction of cobalt tricarbonyl nitrosyl with $(C_4H_9)_4NF$. That solution, which also displayed a carbonyl stretching band at 1885 cm^{-1}, could be used for carbonylating 2-(bromomethyl)naphthalene to (2-naphthyl)acetic acid.[13] Cyclopentadienylcobalt dicarbonyl failed to react with fluoride ion. Iron pentacarbonyl affords the $HFe_3(CO)_{11}^-$ ion on exposure to 1 M $(C_4H_9)_4NF$.

In conclusion, potassium fluoride and tetrabutylammonium fluoride can induce the facile conversion of $Fe_3(CO)_{12}$ to $HFe_3(CO)_{11}^-$ and of $Mn_2(CO)_{10}$ to $Mn(CO)_5^-$. Tetrabutylammonium fluoride is an effective catalyst for reducing nitro compounds to amines by $Fe_3(CO)_{12}$ or $Mn_2(CO)_{10}$ under mild conditions.

Experimental Section

General Data. Infrared spectra were recorded on a Unicam SP-1100 spectrometer, equipped with a calibration standard. Nuclear magnetic resonance and mass spectral determinations were made by using Varian T60 and MS9 instruments, respectively.

Triiron dodecacarbonyl, dimanganese decacarbonyl, cobalt carbonyl, cobalt tricarbonyl nitrosyl, and cyclopentadienylcobalt

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Table II. Yields of Anilines Obtained from the Reaction of Nitroarenes with $Mn_2(CO)_{10}$, $(C_4H_9)_4NF$, and Water

p-$RC_6H_4NO_2$(6), R, mmol	$Mn_2(CO)_{10}$, mmol	$(C_4H_9)_4NF$ (1 M), mmol	H_2O, mmol	p-$RC_6H_4NH_2$ (7), %
CH_3, 9.96	5.94	0.60	33.5	52
CH_3, 5.54	2.85	7.40		58
OCH_3, 10.2	6.12	0.60	31.0	73
COPh, 10.6	6.20	0.60	29.5	88

dicarbonyl were purchased from Strem Chemicals, Inc., and were used as received. Iron pentacarbonyl was obtained from Pressure Chemical Co. The nitro compounds were purchased from Aldrich Chemical Co. or Fisher Scientific Co. The 1 M $(C_4H_9)_4NF$ solution and the crown ethers were obtained from Aldrich Chemical Co., while "dry" potassium fluoride was purchased from Alfa/Venton. 18-Crown-6 was dried by dissolving in methylene chloride, and the solution was left standing over magnesium sulfate (dry box). After filtration and removal of solvent, colorless powder was obtained.

Tetrahydrofuran was dried by distillation from sodium or potassium benzophenone ketyl. All reactions were run under a dry atmosphere of nitrogen (or carbon monoxide in isolated cases).

Reaction of $Fe_3(CO)_{12}$ with KF and Dry 18-Crown-6. Triiron dodecacarbonyl (0.91 g, 1.80 mmol) was dissolved in tetrahydrofuran (30–35 mL). The crown ether (0.12 g) was added, followed by potassium fluoride (0.10 g). The reaction mixture was stirred for 1 day at room temperature. The intense green-black color of $Fe_3(CO)_{12}$ remained, and thin-layer chromatography indicated no reaction. Addition of 0.10 g of p-nitrotoluene gave no reduction.

Reaction of $Fe_3(CO)_{12}$ with KF and Wet 18-Crown-6. To $Fe_3(CO)_{12}$ (2.09 g, 4.15 mmol) in THF or 1,2-dimethoxyethane (30 mL) was added 18-crown-6 (0.49 g) and then KF (0.24 g, 4.15 mmol). After the solution was stirred for 30 min at room temperature, bis(triphenylphosphin)iminium chloride was added to the deep red solution. When the mixture was left standing, $[(Ph_3P)_2N][HFe_3(CO)_{11}]$ precipitated: visible (CH_3OH) λ 545 nm;[9] yield 84%.

Anal. Calcd for $C_{47}H_{31}NO_{11}P_2$: C, 55.60; H, 3.08; N, 1.40. Found: C, 55.46; H, 3.21; N, 1.57.

Reaction of $Fe_3(CO)_{12}$ with KF and Dibenzo-18-crown-6. A mixture of $Fe_3(CO)_{12}$ (0.97 g, 1.93 mmol), KF (0.112 g, 1.93 mmol), and dibenzo-18-crown-6 (0.126 g) in THF (40 mL) was stirred for 18 h at room temperature. No reaction occurred. The reaction mixture was heated to reflux, p-nitrotoluene (0.091 g, 1.32 mmol) was added, and the solution was refluxed for 10 min. The solution was cooled to room temperature and filtered, and the filtrate was concentrated by rotary evaporation. Chromatograpy of the oily residue (silica gel) gave p-toluidine in 65% yield.

Reaction of $Fe_3(CO)_{12}$ with Tetrabutylammonium Fluoride. To $Fe_3(CO)_{12}$ (1.02 g, 2.03 mmol) in THF (30 mL) was added 2.0 mL of a 1 M THF solution of tetrabutylammonium fluoride. The solution turned deep red in 2–3 min and, after being concentrated, gave a UV absorption maximum at 540–545 mm, characteristic of $[(C_4H_9)_4N][HFe_3(CO)_{11}]$, yield 67%.

Reaction of $Fe_3(CO)_{12}$ with $(C_4H_9)_4NF$ and p-Nitrotoluene. p-Nitrotoluene (1.53 g, 11.1 mmol) was added to a THF (40 mL) solution containing $Fe_3(CO)_{12}$ (3.36 g, 6.68 mmol) and $(C_4H_9)_4NF$ (8.0 mL of a 1 M solution). A highly exothermic reaction took place, and after filtration and concentration of the filtrate, workup by column chromatography (1:1 ether–hexane) afforded pure p-toluidine in 95% yield.

Representative Procedure for the $(C_4H_9)_4NF$-Catalyzed Reaction of Nitroarenes (6) with $Fe_3(CO)_{12}$. To a mixture of $Fe_3(CO)_{12}$ (2.99 g, 5.94 mmol), $(C_4H_9)_4NF$ (0.80 mL), and p-nitrotoluene (1.36 g, 9.91 mmol) was added, after 20 min, water (0.408 g, 23 mmol). The reaction mixture was stirred overnight, filtered, and concentrated. Pure p-toluidine was isolated in 66% yield by chromatography on silica gel using 1:1 ether–hexane.

Reaction of $Mn_2(CO)_{10}$ with Hydrated $(C_4H_9)_4NF$. A mixture of $Mn_2(CO)_{10}$ (0.499 g, 1.28 mmol) and $(C_4H_9)_4NF{\cdot}3H_2O$ (0.816 g, 1.30 mmol) in THF (50 mL) was stirred overnight at room temperature. An infrared spectrum showed carbonyl stretching absorptions at 1895 and 1860 cm^{-1}. Then 0.088 g (1.28 mmol) of p-nitrotoluene was added, and the solution was stirred for 2 days at the end of which an IR spectrum revealed bands due to $Mn(CO)_5^-$ but not $Mn_2(CO)_{10}$.

Representative Procedure for the $[C_4H_9]_4NF$-Catalyzed Reaction of Nitroarenes (6) with $Mn_2(CO)_{10}$. To a mixture of dimanganese decacarbonyl (2.39 g, 6.12 mmol), $(C_4H_9)_4NF$ (0.6 mL of a 1 M THF solution) in THF (50 mL) was added p-nitroanisole (1.56 g, 10.2 mmol) followed by water (0.56 g). The reaction mixture was stirred for 3 days and then filtered. Rotary evaporation of the filtrate gave a semisolid which was chromatographed on silica gel. Elution with 5:1 hexane–ethyl acetate gave pure p-anisidine in 73% yield.

Reaction of $Co_2(CO)_8$ with Hydrated Tetrabutylammonium Fluoride. A mixture of $Co_2(CO)_8$ (0.493 g, 1.44 mmol) and $(C_4H_9)_4NF{\cdot}3H_2O$ (0.907 g, 1.44 mmol) in THF (50 mL) was stirred for 16 h at room temperature. The solution became much lighter in color, and a absorption maximum occurred in the infrared region at 1885 cm^{-1}. If p-nitrotoluene (0.100 g, 1.44 mmol) was added, no reduction of the nitro compound took place.

Reaction of $Co(CO)_3NO$ with $(C_4H_9)_4NF$. A mixture of $Co(CO)_3NO$ (0.93 g, 5.39 mmol) and $(C_4H_9)_4NF$ (6.6 mmol) in THF (50 mL) was stirred under a carbon monoxide atmosphere for 17 h. Addition of 2-(bromomethyl)naphthalene resulted in carbonylation to (2-naphthyl)acetic acid in 48% yield, mp 141–142 °C. The melting point was not depressed on admixture with authentic (2-naphthyl)acetic acid.

Reaction of Iron Pentacarbonyl with 1 M $(C_4H_9)_4NF$. To a THF (50 mL) solution containing iron pentacarbonyl (2.08 g, 10.6 mmol) was added 10.6 mL of a 1 M $(C_4H_9)_4NF$ solution. The solution turned deep red, and after 2–3 days, the $HFe_3(CO)_{11}^-$ ion could be isolated as the $(PPh_3)_2N^+$ salt as for $Fe_3(CO)_{12}$.

Acknowledgment. We are greatful to NSERC and NATO for support of this research.

Registry No. 6, R = CH_3, 99-99-0; 6, R = CH_3O, 100-17-4; 6, R = Cl, 100-00-5; 6, R = COPh, 1144-74-7; 7, R = CH_3, 106-49-0; 7, R = CH_3O, 104-94-9; 7, R = Cl, 106-47-8; 7, R = COPh, 1137-41-3; $[(Ph_3P)_2N][HFe_3(CO)_{11}]$, 23254-21-9; $[(C_4H_9)_4N][HFe_3(CO)_{11}]$, 80146-07-2; $[HFe_3(CO)_{11}]^-$, 55188-22-2; $[Mn(CO)_5]^-$, 14971-26-7; $Fe_3(CO)_{12}$, 17685-52-8; $Mn_2(CO)_{10}$, 10170-69-1; $Co_2(CO)_8$, 10210-68-1; $Co(CO)_3NO$, 14096-82-3; iron pentacarbonyl, 13463-40-6; fluoride, 16984-48-8; cobalt tetracarbonyl anion, 14971-27-8.