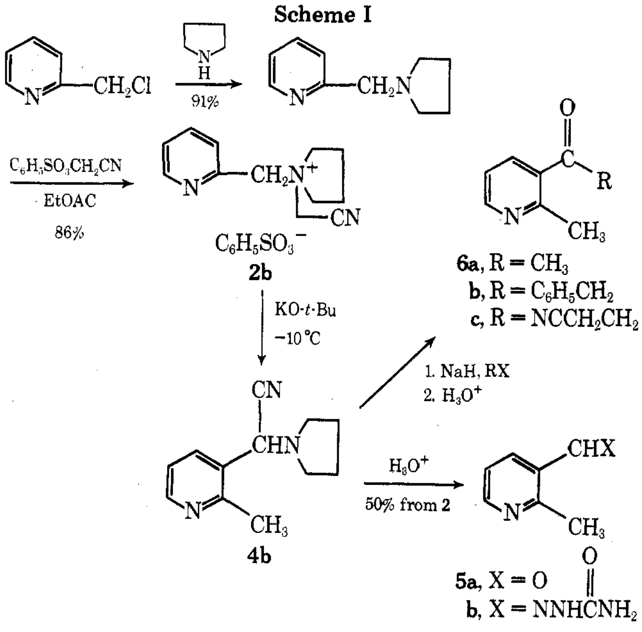
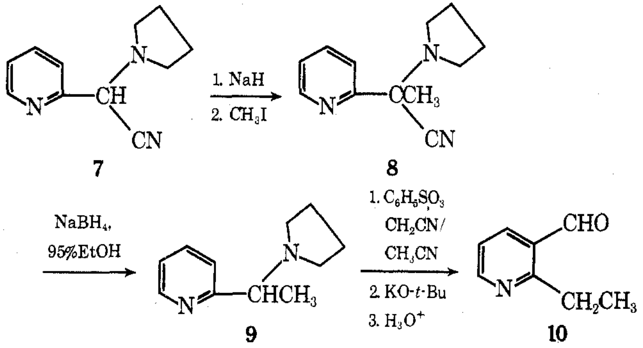
Scheme I



Scheme II



Having successfully ortho-formylated 2-picoline, we turned our attention to alkylation of intermediate **4b** to achieve ortho-acylation of 2-picoline. Rearrangement of **2b** (R = H) was carried out as above. After the reaction was complete, as judged by TLC and NMR, 1 equiv of sodium hydride was added followed by 1 equiv of methyl iodide. Acid hydrolysis of the crude product gave 3-acetyl-2-picoline[11] (**6a**, 78%). The corresponding benzyl ketone **6b**[11] was obtained in a similar fashion by alkylation with benzyl bromide (87%). Further investigation showed that this procedure could be simplified by using sodium hydride to effect both rearrangement and alkylation. Thus, the salt **2b** (R = H) was treated with 2 equiv of sodium hydride; after the rearrangement and second anion formation were complete, 3-bromopropionitrile was added followed by acid hydrolysis to give **6c** (48%).

The demonstration that these α-cyanoamines are alkylated with relative ease allows further generalization of this procedure for the preparation of 2-alkyl-3-acylpyridines. Since α-halo-2-alkylpyridines are not readily obtained by direct halogenation of the respective 2-alkylpyridines, the alkylation reaction described above was utilized. The α-cyanoamine **7**, prepared from 2-pyridinecarboxaldehyde, pyrrolidine, and KCN (58%), was treated with sodium hydride and methyl iodide giving **8** which, upon treatment with sodium borohydride in 95% ethanol, underwent reductive cleavage[12,13] to **9** (70% from **7**). Alkylation (Scheme II), rearrangement, and hydrolysis to **10**, isolated as its semicarbazone (10%), were achieved as described above.[14]

The preparation of 2-alkyl-3-acylpyridines using these procedures appears limited only by the nature of those alkyl halides capable of being alkylated by the α-cyanoamine anions.[14] We are currently investigating the scope of these alkylations as well as exploring other transformations of α-cyanoamines which could extend the use of these procedures for the synthesis of more complex heterocyclic systems.

Acknowledgment. We thank Dr. Jerry F. Whidby and Mr. Ron Bassfield for technical assistance.

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(13) In the sequence **7** → **9**, cyanoamine **7** can be regarded as an α-amino carbanion equivalent.
(14) Thorough investigation of the product mixture from the alkylation–rearrangement and hydrolysis of **9** indicates that a significant portion of the quaternary salt rearranges via a 1,2 shift; i.e., Stevens rearrangement. We are presently studying the effect of reaction conditions on product composition.

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Protonated Cyclobutadieneiron Tricarbonyl, a σ–π Bonded Cyclobutadiene Hydridoiron Tricarbonyl Cation[1]

Summary: ^{1}H and ^{13}C NMR spectroscopic study of cyclobutadieneiron tricarbonyl in fluorosulfuric acid solution at low temperature shows iron protonation with formation of a static σ–π complex resulting from an unusual π to σ change in the metal–ligand bonding; the observation of the geminal $^{1}H_4$–Fe–$^{1}H_x$ (29 Hz) and ^{13}C–Fe–H_x (81.2 Hz) coupling substantiates the proposed structure; evidence of σ–π complex formation was further provided by studies in deuterated fluorosulfuric acid solution.

Sir: The enhanced stability of organometallic carbonyl cations has been well recognized and the nature of metal–ligand bonding in these ions has also been extensively investigated using both spectroscopic methods and quantum mechanical calculations.[2] Brookhart and Harris[3] first reported the π to σ change in metal–ligand bonding yielding stable σ–π complex when bicyclo[6.1.0]nonatrienemolybdenum tricarbonyl was protonated by excess fluorosulfuric acid in SO_2F_2 solution. Evidence for it was also found by Whitesides and Arhart[4] in the case of butadieneiron tricarbonyl complexes. Using ^{13}C

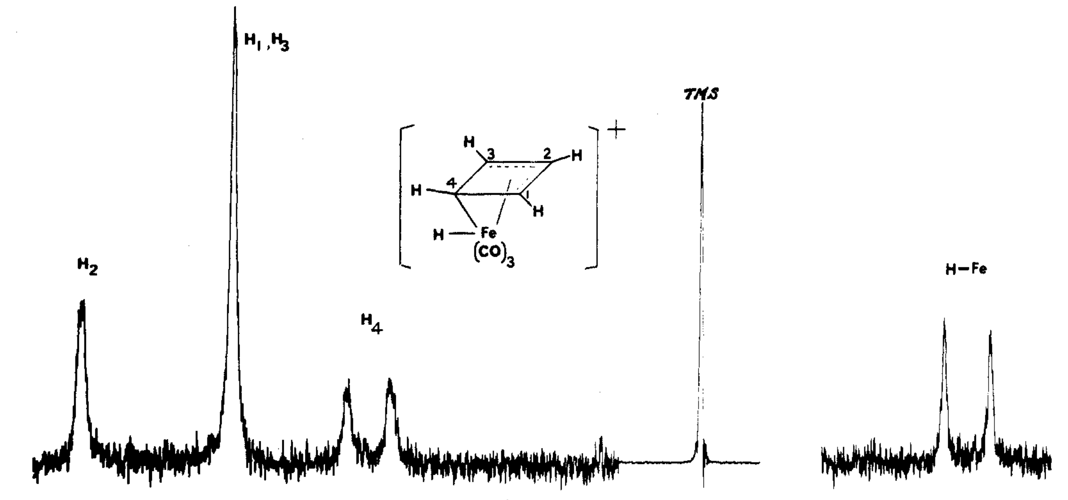
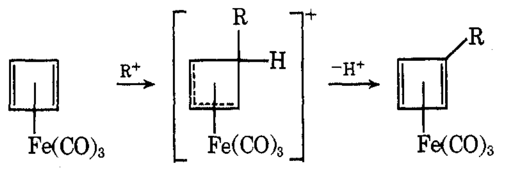


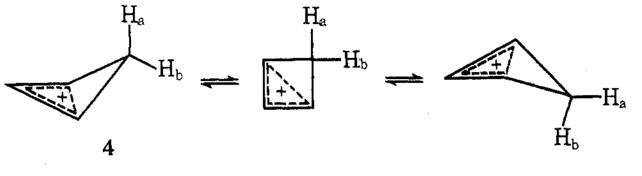
Figure 1. 60-MHz ^{1}H NMR spectrum of the protonated cyclobutadieneiron tricarbonyl in FSO_3H-SO_2 at −85 °C.

NMR spectroscopy, we have recently investigated the protonation of butadieneiron tricarbonyl[5] and its nonconjugated analog, norbornadieneiron tricarbonyl,[5] in fluorosulfuric acid–sulfur dioxide solution at low temperatures. The direct observation of geminal ^{13}C–Fe–^{1}H coupling in the protonated butadieneiron tricarbonyl (73.7 Hz) and norbornadieneiron tricarbonyl (38.2 Hz) complexes can indeed be explained only in term of σ–π-type complex formation.

Cyclobutadieneiron tricarbonyl (1), which was originally prepared and studied by Pettit and coworkers[6] has been regarded as aromatic in the sense that it underwent electrophilic substitution reactions via the assumed π-cyclobutenyliron tricarbonyl cation (2) to give substituted cyclobutadieneiron tricarbonyl complexes 3. Cation 2 should be closely related to the cyclobutenyl (homocyclopropenyl) cation 4 which we recently reported, a homoaromatic 2-π system adoping nonplanar geometry undergoing rapid ring flipping process.[7] We wish to report now that 1 upon protonation undergoes π to σ isomerization and gives the σ–π complex 5 which was directly observed and studied by both ^{1}H and ^{13}C NMR spectroscopy.[8]



1 2 3



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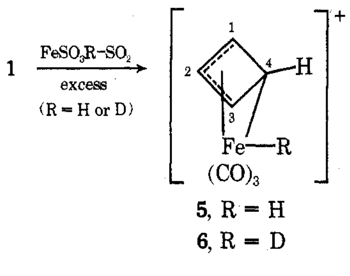
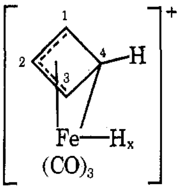


5, R = H
6, R = D

Careful addition (with good stirring) of a solution of 1 in sulfur dioxide to excess FSO_3H-SO_2 at −78 °C gave a dark reddish brown solution. The 60-MHz ^{1}H NMR spectrum (Figure 1) of this solution taken at −85 °C exhibited three-proton absorptions centered at δ 6.44 (broad singlet, H_2), 4.86 (broad singlet, H_1 and H_3), 3.45 (broad doublet, J = 29.0 Hz, H_4), and −11.16 (doublet, J = 29.0 Hz, H–Fe). The species did not show temperature dependent NMR spectra and slowly decomposed above −50 °C. When deuterated fluorosulfuric acid–sulfur dioxide was used, the 60-MHz ^{1}H NMR spectrum of the species also showed three-proton absorptions centered at δ 6.44 (broad singlet, H_2), 4.86 (broad singlet, H_1 and H_3), and 3.42 (broad singlet, H_4). The upfield broad doublet at δ 3.42 originally found in the species derived from 1 in excess FSO_3H-SO_2 solution collapsed into a broad singlet, when FSO_3D-SO_2 was used, while the doublet at δ −11.16 was absent, indicating the disappearance of the internal proton–proton coupling.

The Fourier transform ^{13}C (proton coupled) NMR spectrum of the species obtained in FSO_3H-SO_2 at −90 °C showed three-carbon resonances centered at $\delta_{^{13}C}$ 117.3 (doublet, $J_{^{13}C-H}$ = 191.2 Hz, 1 C), 65.8 (doublet, $J_{^{13}C-H}$ = 202.9 Hz, 2 C), and 9.0 (doublet of doublets, $J_{^{13}C-H}$ = 191.4 and 81.2 Hz) which were assigned to C_2, C_1 and C_3, and C_4, respectively. In addition, there were two-carbon absorptions at $\delta_{^{13}C}$ 202.7 (singlet, 1 C) and 200.0 (singlet, 2 C) in the carbonyl region. In FSO_3D-SO_2 solution, the species showed the same two low field doublets at $\delta_{^{13}C}$ 117.7 ($J_{^{13}C-H}$ = 191.2 Hz) and 65.8 ($J_{^{13}C-H}$ = 202.7 Hz), while the upfield signal at $\delta_{^{13}C}$ 9.0 became a broadened doublet ($J_{^{13}C-H} \simeq$ 190 Hz).

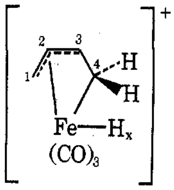
The ^{1}H and ^{13}C NMR spectra of the observed species from cyclobutadieneiron tricarbonyl (1) in excess acid are in good agreement with the formation of σ–π complexes 5 and 6. Since C_4 is σ bonded to the iron atom, the large coupling constants $J_{H_4-Fe-H_x}$ (29.0 Hz) and $J_{^{13}C_4-Fe-H_x}$ (81.2 Hz) are as expected. In addition, both H_4 and C_4 are highly *shielded* indicating the formation of C_4–Fe σ bond. Chemical shifts and coupling constants for the C_1–C_3 moiety are consistent with that for a π-allyl system. We have previously reported that large geminate coupling constants are found in both protonated butadieneiron tricarbonyl (7)[5] (static) and norbornadieneiron tricarbonyl (8)[5] (rapidly equilibrating). The protonated cyclobutadieneiron tricarbonyl complex should also be described as static σ–π complex 5. Cyclobutadieneiron tricarbonyl (1) thus undergoes protonation (or deuteration) on iron and the present NMR spectroscopic data are inconsistent with the originally suggested C-protonated cyclobutenyliron tricarbonyl cation (2, R = H),[6] although this ion still could be formed under kinetically controlled conditions, but is not the thermodynamically favored species.



5

$J_{\mathrm{H_4\text{-}Fe\text{-}H_x}} = 29.0$ Hz

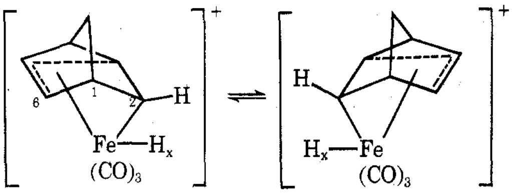
$J_{\mathrm{^{13}C_4\text{-}Fe\text{-}H_x}} = 81.2$ Hz



7

$J_{\mathrm{H_4\text{-}Fe\text{-}H_x}} = 22$ Hz

$J_{\mathrm{^{13}C_4\text{-}Fe\text{-}H_x}} = 73.7$ Hz



8

$J_{\mathrm{H_{2(6)}\text{-}Fe\text{-}H_x}} = 13$ Hz (av)

$J_{\mathrm{^{13}C_{2(6)}\text{-}Fe\text{-}H_x}} = 37.8$ Hz (av)

Both experimental data and theoretical calculations have shown the homoaromatic nature of the parent cyclobutenyl cation 4 and its puckered structure.[7] Nonplanar structures are also indicated in a number of cyclobutenylmetal complexes,[9] such as the σ complex of tetramethylcyclobutadiene with aluminum trichloride.[10] Although the present NMR spectra obtained for the protonated (deuterated) cyclobutadieneiron tricarbonyl **5** (**6**) indicate that **5** should possess a plane of symmetry, they do not allow clear differentiation as to whether the ion is planar or puckered. They indicate, however, clearly, the formation of a new carbon–iron σ bond, and the transformation of the original nonconjugated cyclobutadiene system into an allylic cyclobutenyl system.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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(11) A comprehensive report on our continued study concerning protonation and oxidation of cyclobutadieneiron tricarbonyl complexes will be published in a forthcoming full paper.

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Organomercury Compounds as Synthetic Intermediates. Coupling of Arylmercuric Salts

Summary: Arylmercuric salts are converted to biaryls in high yield upon treatment with copper and a catalytic amount of palladium chloride in pyridine.

Sir: The preparation of biaryls is ordinarily accomplished by the metal promoted decomposition of aryl halides, which includes the Ullmann reaction[1] and the use of zerovalent nickel complexes.[2] In addition, the reaction of an arylmagnesium halide[3] or aryllithium reagent[3e–g,4] with a salt such as a thallium, uranium, or first group transition metal salt has also been found to be preparatively useful for the generation of biaryls. The Ullmann reaction, however, is often unsatisfactory since (1) temperatures in excess of 200 °C are frequently required; (2) the reaction fails when the aromatic nucleus carries functional groups such as $-NH_2$, $-NHCOCH_3$, and $-NHCH_3$; and (3) a satisfactory result may require the use of relatively inaccessible aryl iodides when an activating substituent is not present. The alternative coupling of aryl halides with a zerovalent nickel complex suffers from one or more operational disadvantages which include air[2] and thermal sensitivity[2a] of the complex and the generation of difficulty separable by-products.[2b,c] Finally, the generation of biaryls from arylmagnesium halides or aryllithium reagents is suitable only in the absence of reactive functional groups.

We wish to report that arylmercuric salts are converted to biaryls in high yield (Table I) and under mild reaction conditions by treatment with copper metal and a catalytic amount of palladium chloride in the presence of pyridine according to eq 1. The reaction is compatible with most functional groups, and the arylmercuric salts required as starting materials are readily available[5] and are easily purified by crystallization. Ordinarily, the reaction is complete within 1 or 2 h at reflux temperature, but longer reaction times are not ordinarily harmful and serve to ensure completion of the reaction.

$$2\mathrm{ArHgX} + \mathrm{Cu} \xrightarrow[\mathrm{PdCl_2,\ 115\ ^\circ C}]{\text{pyridine}} \mathrm{Ar{-}Ar} + \mathrm{Hg} + \mathrm{CuX_2} \tag{1}$$

The experimental procedure is illustrated by the conversion of 4-chlorophenylmercuric acetate to 4,4′-dichlorobiphenyl.

A mixture of 4-chlorophenylmercuric acetate (2.001 g, 5.48 mmol), copper powder (1.501 g, 23.62 g-atoms), and palladium chloride (0.101 g, 0.57 mmol) in 20 ml of pyridine was heated under reflux in a nitrogen atmosphere with stirring for 5 h. The resulting mixture was filtered while hot through Celite, and the inorganic residues were washed with 75 ml of benzene. The combined filtrates were washed three times with 50-ml portions of 15% ammonium hydroxide, three times with 50-ml portions of 3 M HCl, and once with 50 ml of saturated brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give 0.515 g of tan needles. Recrystallization from ethanol afforded pure 4,4′-dichlorobiphenyl (0.377 g, 62%), mp 145–148 °C (lit.[6] mp 147–148 °C).

It is known that exposure of diarylmercury compounds to temperatures of 200–400 °C either in the absence[7] or presence[8]