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Synthesis and Reaction Chemistry of an Iron/Pyrrolyl Reagent[1]

William K. Reagen and Lewis J. Radonovich*

Department of Chemistry, University of North Dakota
Grand Forks, North Dakota 58202

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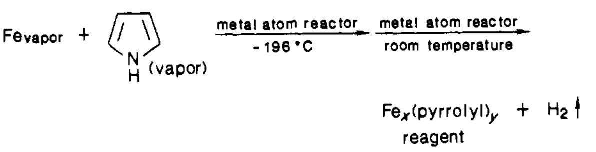
The formation of an Fe/pyrrolyl reagent has proved to be synthetically useful in expanding the number of iron pyrrolyl metal complexes available.[2-4] We communicate here two synthetic routes to a reactive Fe/pyrrolyl reagent and some of its interesting reaction chemistry including the synthesis of two new bis(η^1-pyrrolyl)iron(II) octahedral complexes.

In the metal atom reactor[5] synthesis outlined in reaction 1,



(1)

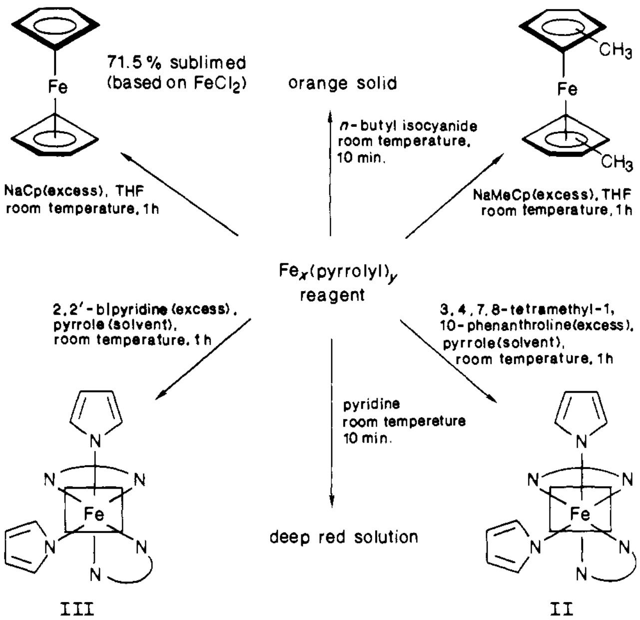
resistive heating of iron metal provides a source of reactive iron atoms which readily metalate pyrrole at the N-hydrogen, as evidenced from the lack of a N-H stretching frequency in the infrared spectrum of the resulting product. A frozen Fe/pyrrole matrix formed from the cocondensation (2 h) of iron (0.6 g) and pyrrole (100 mL) vapors at −196 °C is allowed to warm to room temperature. Observed upon melt down of the Fe/pyrrole matrix are the evolution of hydrogen gas, verified by GC analysis of the reactor head gas, and the formation of an insoluble dark brown solid, the reactive Fe/pyrrolyl reagent. The product is collected by filtration of the reactor slurry through a fine-porosity frit and is completely stable for months at room temperature under argon atmosphere. The dry solid is moderately pyrophoric when exposed to the atmosphere.

Following our discovery of the metal vapor synthesis in reaction 1, we explored the possibility of finding a solution route. Indeed, a second synthetic route to the Fe/pyrrolyl reagent is outlined in reaction 2. Anhydrous ferrous chloride (Aldrich) is added to

$$1\mathrm{FeCl_2} + 2\ \text{sodium pyrrolide} \xrightarrow[\text{nitrogen atm.}]{\substack{\text{THF}\\ \text{reflux, 12 h}}} \underset{\text{reagent}}{\mathrm{Fe}_x(\text{pyrrolyl})_y(\mathrm{s})} \qquad (2)$$

a tetrahydrofuran solution of sodium pyrrolide prepared by the addition of neat pyrrole to a stoichiometric amount of a 40% sodium dispersion (Aldrich, mineral spirits) in tetrahydrofuran. The reaction mixture is refluxed under nitrogen for 12 h and gradually darkens to a rich brown color. Stripping the solvent mixture under vacuum yields an insoluble light brown solid, a mixture of the Fe/pyrrolyl reagent and salt byproduct. Without further purification the rough solid can be used directly as a reagent. This reaction product is also completely stable at room temperature under inert atmosphere but rapidly turns black upon air exposure and is not pyrophoric. The difference in pyrophoricity between the two synthetic routes is attributed to excess metal incorporated into the product obtained via the metal atom reactor. One might expect the formation of (diazaferrocene)[Fe(η^5-pyrrolyl)$_2$] from reaction 2, but we were not able to isolate any of this product, consistent with the previous report by King and co-workers.[6] We do report, however, the isolation and synthesis of a very reactive and synthetically useful insoluble Fe/pyrrolyl reagent by reaction 2. Ease of reaction, high product yield, and the nonpyrophoric reaction product of reaction 2 make it the preferred route.

Scheme I



We have used the Fe/pyrrolyl reagent synthesized from reaction 2 to synthesize under mild conditions a variety of complexes including pyridine and *n*-butyl isocyanide products, ferrocene, methylferrocene, and the octahedral complexes II and III (Scheme I). The reactions occur in minutes (usually seconds) at room temperature. All reactions and manipulations are carried out under inert atmosphere conditions. Thus far, the metallocenes and the octahedral complexes II and III have also been synthesized by using the Fe/pyrrolyl reagent from the metal atom synthesis (reaction 1).

Bis(η^1-pyrrolyl)bis(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) (II) was synthesized as shown in Scheme I and was isolated as an air-sensitive dark blue crystalline solid from a pyrrole solution at room temperature. Preliminary results from our single-crystal X-ray structure determination have shown the complex to adopt an octahedral geometry as depicted in complex II. Elemental analysis suggests an analogous octahedral complex (III) is formed when 2,2'-bipyridine is used as the chelating ligand.

Anal. Calcd for $C_{36}H_{34}N_8Fe$ (includes 2 pyrroles of solvation): C, 68.17; H, 5.36; N, 17.67%. Found: C, 68.11; H, 5.31; N, 17.92%. The air-sensitive bipyridine complex was isolated as dark green crystals from a pyrrole solution. These new octahedral complexes provide us with a unique opportunity for direct comparisons of the pyrrolyl ligand (σ-bonding amido ligand) to a variety of ligands previously reported in octahedral phenanthroline and bipyridine complexes.[7]

While we have actively pursued the reaction chemistry of the Fe/pyrrolyl reagent, its complete characterization is still under investigation. Some difficulty arises due to its lack of solubility in many common solvents. The data accumulated to date lead us to propose a possible model for this Fe/pyrrolyl reagent. Accordingly, a model containing a π-pyrrolyl ligand that simultaneously functions as a σ-donor ligand seems likely to result in a coordination polymer (IV). Such a coordination polymer would account for the insolubility of the intermediate and its observed reaction chemistry. Indeed, as previously reported for a trinuclear manganese complex,[8] the pyrrolyl ring can simultaneously fullfill two functions, acting as a π-ligand to one transition metal and as a σ-ligand (through N) to another metal. Further, the high reactivity of intermediate I under mild conditions is

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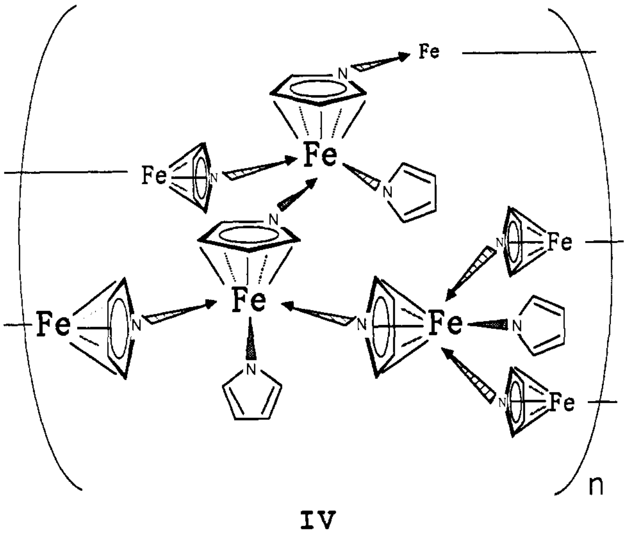

IV

analagous with the observed chemistry of azaferrocene[2,4,6] and supports the presence of a similar moiety in the polymer. Each pyrrolyl π-to-σ rearrangement opens two coordination sites, hence the addition of two bidentate π-acidic ligands to each iron site in IV might account for the breakdown of the polymeric structure and the formation of the octahedral complexes II and III reported in Scheme I.

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Complexes of Ir(III) Containing the Novel SF_3 Ligand

Russell W. Cockman, E. A. V. Ebsworth,* and
John H. Holloway†

Department of Chemistry, University of Edinburgh
Edinburgh EH9 3JJ, Scotland

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This paper describes the synthesis and characterization of the complexes $Ir(CO)FX(PEt_3)_2SF_3$, where X is Cl, Br, or I; we believe that these are the first complexes described that contain the SF_3 ligand, and they are formed by an unusual[1] oxidative addition of an SF bond to 4-coordinated Ir(I).

Reaction between *trans*-$Ir(CO)Cl(PEt_3)_2$ (A) and a small excess of SF_4 occurs rapidly in CD_2Cl_2 at 200 K. The single product has been identified from its ^{19}F- and $^{31}P\{H\}$ NMR spectra as $Ir(CO)ClF(PEt_3)_2SF_3$ (B). In the ^{19}F spectrum at 200 K we observed four resonances of equal intensity. One, at very low frequency (δ −337), was in the region associated[2] with Ir-*F* nuclei in phosphine fluorocomplexes of Ir(III). It appeared as a near triplet [$^2J(PF_{av})$ = 33 Hz] of narrower doublets of doublets of doublets. The other three resonances were in the region associated with F bound to a main-group element such as S (73.5, 45.2, −66.8 ppm). All appeared as complicated multiplets that could be analyzed as first-order patterns of overlapping doublets derived from coupling to five different spin-one-half nuclei. We assign these three resonances to the three S*F* nuclei in complex B, which must then be in different environments at this temperature in solution. The $^{31}P\{H\}$ spectrum at 190 K showed what was basically an AB pattern, with further splittings in both A and B sections of the spectrum; the further splittings could also be analyzed in simple first-order terms as derived from coupling to four different spin-one-half nuclei, which are clearly the three S*F* and one Ir*F* nuclei whose resonances were observed in the ^{19}F spectrum. The nonequivalance of the two phosphorus nuclei arises from the asymmetry at S, whose coordination positions are occupied by the metal, by three fluorine atoms (each chemically distinct), and by a lone pair (Table I).

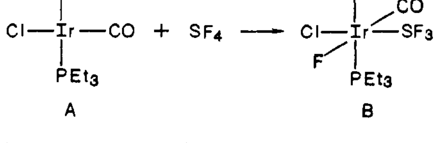

Table I. NMR Parameters for Ir–SF Complex $Ir(CO)XF(PEt_3)_2(SF_3)$

	chem shifts/ppm					
	SF			IrF	P	
X	F_1	F_2	F_3	F_4	P_A	P_B
Cl	75.53	45.22	−66.81	−336.9	7.56	0.28
Br	74.4	44.8	−66.11	−344.1	3.62	−3.58
I	72.8	41.7	−67.6	−356.2	−1.68	−8.72

	coupling constants/Hz		
	X = Cl	X = Br	X = I
$^2J(PP)$	340	336	331
$^2J(F_1F_2)$	179.7	182.2	183.2
$^2J(F_1F_3)$	58.8	58.0	60.0
$^3J(F_1F_4)$	3.6	3.5	3.5
$^2J(F_2F_3)$	80.6	78.9	80.3
$^3J(F_2F_4)$	9.6	10.0	10.0
$^3J(F_3F_4)$	nr	nr	nr
$^3J(F_1P_A)$	nr	nr	nr
$^3J(F_1P_B)$	11.2	10.4	9.1
$^3J(F_2P_A)$	22.9	20.7	18.4
$^3J(F_2P_B)$	13.0	14.3	13.4
$^3J(F_3P_A)$	nr	nr	nr
$^3J(F_3P_B)$	5.1	5.8	5.9
$^2J(F_4P_A)$	31.0	31.9	32.5
$^2J(F_4P_B)$	35.7	36.6	37.6

When the solution was allowed to warm, the spectra showed marked changes. The resonances assigned to the three S*F* nuclei broadened and collapsed, and at 298 K they gave a single very broad peak that could scarcely be distinguished from the base line. The Ir*F* resonance became a sharp triplet and lost the narrower doublet splittings. The $^{31}P\{H\}$ spectrum showed associated changes. At 220 K the detail in the A and B sections of the spectrum could no longer be resolved; at 298 K the P resonance appeared as a single very broad line ($w \sim 100$ Hz) which sharpened into a doublet at 325 K (see Figure 1). All these changes were reversible. Similar spectra were obtained from solutions in toluene; heating a solution of B in toluene to 345 K, however, resulted in irreversible decomposition. It is clear that the SF_3 group undergoes some fluxional or exchange process which is slow on the NMR time scale at 190 K but becomes fast on this time scale at temperatures above 300 K. We have no direct evidence to show whether the process is inter- or intramolecular. The apparent loss of $^3J(FF)$ from the Ir*F* resonance at 300 K is consistent with an intermolecular mechanism, though intramolecular interchange cannot be excluded. In SF_4 it appears that both inter- and intramolecular processes can be significant;[3] in $Ir(CO)Cl_2(PEt_3)_2(P'F_4)$, the fluxional interchange round P′ is intramolecular[4] at least up to 300 K and fast on the NMR time scale at 200 K,

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† Present address: Department of Chemistry, The University, Leicester.

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