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Preliminary communication

Novel products from reactions between allyliron tricarbonyl iodide and polypyrazolylborate salts: a new type of allyl–propenyl isomerization

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Within the last few years numerous coordination compounds have been prepared from the polypyrazolylborates and various transition metal complexes[1]. This communication reports the reactions of allyliron tricarbonyl iodide[2] with the polypyrazolylborate salts $K[H_2B(C_3H_3N_2)_2]$ and $K[HB(C_3H_3N_2)_3]$. In these reactions the following unusual features in polypyrazolylborate or related coordination chemistry are observed: (I) Isomerization of a π-allyl ligand to a σ-propenyl ligand; (2) Cleavage of a pyrazolyl ring from the polypyrazolylborate anion to give either a pyrazolylmetal carbonyl complex or an allylpyrazole metal carbonyl complex.

A mixture of 8.0 g (26 mmoles) of $C_3H_5Fe(CO)_3I$[2], 8.0 g (32 mmoles) of $K[HB(C_3H_3N_2)_3]$, 100 ml of tetrahydrofuran, and 100 ml of diethyl ether was stirred for 3 h at room temperature. After removal of solvent, the residue was extracted with diethyl ether. The residue from the diethyl ether extraction was extracted with dichloromethane. Evaporation of the filtered dichloromethane extracts gave purple crystals of the known[3] iron (II) compound $Fe[(C_3H_3N_2)_3BH]_2$ in 56% yield. The original diethyl ether extract combined a variety of novel iron carbonyl derivatives which were separated by chromatography on alumina in hexane solution. The following compounds were eluted from the chromatography column in the order indicated: (I) Orange $[C_3H_3N_2Fe(CO)_3]_2$, m.p. 103°, 2.6% yield; (2) Yellow $(C_3H_3N_2C_3H_5)Fe(CO)_3$, m.p. 61°, 1% yield; (3) Yellow $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$, m.p. 131°, ~1% yield; (4) Yellow $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$, m.p. 126°, 28% yield. The yellow compound $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$ could also be prepared in 94% yield by boiling a 0.5% cyclohexane solution of $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$ for 20 minutes. All of these compounds were characterized by correct elemental analyses.

The structures of these new iron carbonyl compounds are clearly indicated by their spectroscopic properties. The orange compound $[C_3H_3N_2Fe(CO)_3]_2$ exhibits three strong ν(CO) frequencies in its infrared spectrum (cyclohexane solution) at 2094 s, 2053 s, and 2017 s cm^{-1} similar to the infrared spectrum of other $[YFe(CO)_3]_2$ derivatives (*e.g.* ν(CO) reported[4] for $[C_6H_5SFe(CO)_3]_2$ in CS_2: 2073, 2036, 2003, and 1994 cm^{-1}). The

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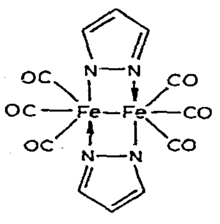
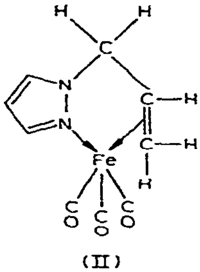


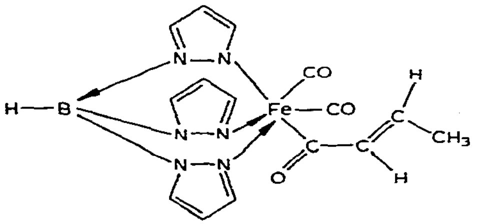
(I)



(II)

proton NMR spectrum of $[C_3H_3N_2Fe(CO)_3]_2$ in CS_2 solution exhibits only two apparent singlet resonances at τ 2.85 and 4.00 indicating equivalence of both pyrazolyl rings and of both ends of each pyrazolyl ring. These data indicate structure I for $[C_3H_3N_2Fe(CO)_3]_2$.

The yellow compound $(C_3H_3N_2C_3H_5)Fe(CO)_3$ in hexane solution exhibits ν(CO) frequencies at 2036, 1957, and 1951 cm^{-1} similar to those found in (diene)$Fe(CO)_3$ derivatives (*e.g.*, ν(CO) reported[5] for the butadiene complex $C_4H_6Fe(CO)_3$: 2051 and 1978 cm^{-1}). The proton NMR spectrum of $(C_3H_3N_2C_3H_5)Fe(CO)_3$ in CS_2 solution exhibits singlet resonance at τ 2.53, 2.86, and 3.88 arising from the non-equivalent protons of the pyrazolyl ring and resonances at τ 5.5 (complex multiplet), 6.29 (complex multiplet), 7.81 (doublet: J = 9 Hz), and 8.72 (doublet: J = 10 Hz) of relative intensities 2/1/1/1 corresponding to the protons of the allyl group. These data suggest that $(C_3H_3N_2C_3H_5)Fe(CO)_3$ is the *N*-allylpyrazole complex of structure II. Additional evidence favoring structure II for $(C_3H_3N_2C_3H_5)Fe(CO)_3$ comes from its synthesis in ~15% yield from equimolar quantities of $Fe_2(CO)_9$ and *N*-allylpyrazole[6] in hexane at room temperature.



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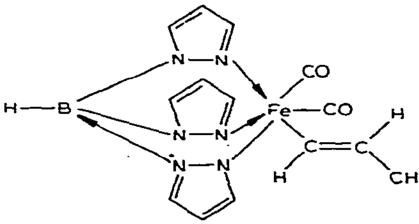

(IV)

The remaining two iron carbonyl products from this reaction, the yellow compounds $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$ and $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$, appear to be a pair of acyl and alkyl derivatives related by decarbonylation. The infrared spectrum of $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$ exhibits terminal metal ν(CO) frequencies at 2051 and 1988 cm^{-1} and a strong acyl ν(CO) frequency at 1615 cm^{-1} (KBr pellet). The infrared spectrum of $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$ exhibits terminal metal ν(CO) frequencies at 2038 and 1978 cm^{-1} but no acyl ν(CO) frequencies around 1600 cm^{-1}.

The proton NMR spectra of $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$ and

$C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$ are relatively complex. Most significantly, they indicate that the C_3H_5 portion of each compound is a propenyl rather than an allyl group. The proton NMR spectrum of $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$ in C_6D_6 solution* exhibits resonances at τ 3.91 (1/3/3/1 quartet; $J = 6.0$ Hz), 4.06 (multiplet; $J = 1.2$ Hz), and 8.80 (double doublet; $J_1 = 6.0$ Hz; $J_2 = 1.2$ Hz) of approximate relative intensities 1/1/3 arising from the two non-equivalent olefinic protons and the three methyl protons, respectively, of the propenyl group and resonances at τ 2.47 (doublet; $J = 2$ Hz), 2.70 (doublet; $J = 2$ Hz), 2.74 (doublet; $J = 2$ Hz) and 4.22 (triplet; $J = 2$ Hz) of approximate relative intensities 2/3/1/3, respectively, from the three pyrazolyl rings. The proton NMR spectrum of $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$ in CS_2 solution* exhibits resonances at τ 3.91 (doublet of 1/3/3/1 quartets; $J_D = 15.4$ Hz; $J_Q = 1.3$ Hz), 4.45 (doublet of 1/3/3/1 quartets; $J_D = 15.4$ Hz; $J_Q = 6.0$ Hz), and 8.16 (double doublet; $J_1 = 6.0$ Hz; $J_2 = 1.3$ Hz) of approximate relative intensities 1/1/3 arising from the two non-equivalent olefinic protons and the three methyl protons, respectively, of the propenyl group and resonances at τ 2.38 (doublet; $J = 2$ Hz), 2.43 (doublet; $J = 2$ Hz), 2.49 (doublet; $J = 2$ Hz), and 3.90 (triplet; $J = 2$ Hz) of approximate relative intensities 2/1/3/3, respectively, from the three pyrazolyl rings. The resonances of the pyrazolyl ring protons in both $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$ and $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$ indicate two of the three pyrazolyl rings to be equivalent and the third pyrazolyl ring to be slightly different. All of these infrared and NMR spectroscopic data are consistent with formulation of $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$ as the acyl derivative III and $C_3H_5Fe(CO)_2(C_3H_3N_2)_3BH$ as the propenyl derivative IV. The observed vicinal olefinic coupling constant of 15.4 Hz in the propenyl derivative falls into the 12 to 19 Hz range expected for the indicated *trans* isomer IV rather than the smaller 4 to 12 Hz range expected for the corresponding *cis* isomer[7].

Figure 1 suggests a scheme for the reaction between $C_3H_5Fe(CO)_3I$ and $K[HB(C_3H_3N_2)_3]$ which is consistent with the experimental observations. In the first step the tripyrazolylborate anion replaces the iodide in $C_3H_5Fe(CO)_3I$ to give the monodentate product A. A second nitrogen of the tripyrazolylborate ligand then partially displaces the allyl group converting the *trihapto*[8] allyl group into a *monohapto*[8] allyl group to give the bidentate product B. The third nitrogen then displaces the *monohapto*-allyl group in B. However, this allyl group is not lost completely but instead migrates to an adjacent carbonyl group to form an acyl derivative C. However, during this allyl migration a 1,3-hydrogen shift occurs thereby converting the allyl group to a propenyl group. The acyl derivative C corresponds to the first isolated compound $C_3H_5COFe(CO)_2(C_3H_3N_2)_3BH$ (III) of this sequence. This acyl derivative can then undergo decarbonylation by the usual migration of an alkyl from a carbonyl group to the metal atom to give the propenyl derivative D (*i.e.* IV)[9].

The reaction between $C_3H_5Fe(CO)_3I$ and the dipyrazolylborate $K[H_2B(C_3H_3N_2)_2]$ in 1/1 tetrahydrofuran–diethyl ether at room temperature results in complete displacement

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*These NMR spectra were also taken in other solvents such as $CDCl_3$ but the indicated solvents gave spectra in which the chemical shifts and fine structures of the closely spaced peaks could be most readily determined.

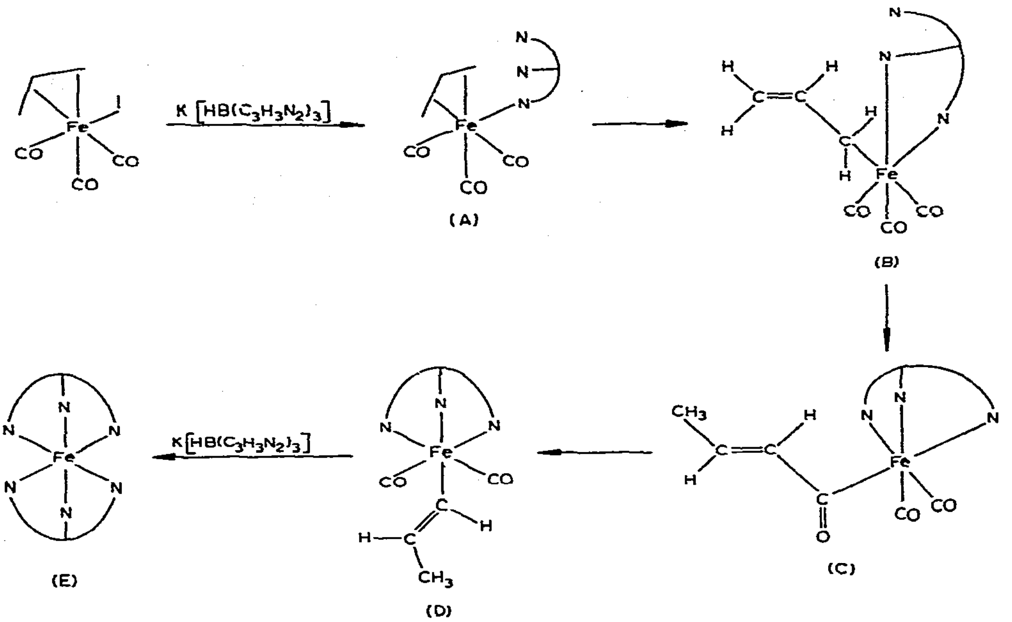
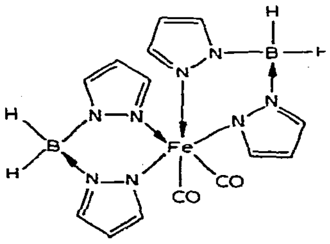


Fig. 1. Proposed scheme for the reaction between allyliron tricarbonyl iodide and potassium tripyrazolylborate.

of the allyl group to give a 44% yield of the yellow-orange iron carbonyl derivative $[H_2B(C_3H_3N_2)_2]_2Fe(CO)_2$ (V) identified by elemental analyses (C, H, N), infrared ν(CO) frequencies at 2088 and 2042 cm^{-1}, and proton NMR resonances ($CDCl_3$ solution) at τ 2.32, 2.70, 3.80, 4.04, and 4.50 of approximate relative intensities 2/1/1/1/1 indicative of two pyrazolyl rings of one type and two pyrazolyl rings of a second type. The reaction between $C_3H_5Fe(CO)_3I$ and $K[H_2B(C_3H_3N_2)_2]$ can follow the scheme in Fig. 1 only as far as product B. Further reaction in this system then must involve displacement of the allyl group in B with a second dipyrazolylborate anion which after replacement of a carbonyl group by the remaining pyrazolyl nitrogen on the second dipyrazolylborate anion leads to the observed product V.



(V)

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