63625-70-7; $Fe(CO)_2(\eta^4\text{-}4\text{-}NMe_2\text{-}C_6H_4CH{=}CHCHO)CO$, 63625-71-8; $Fe(CO)_2(\eta^4\text{-}4\text{-}NMe_2\text{-}C_6H_4CH{=}CHCHO)PPh_3$, 63625-72-9; $Fe(CO)_2(\eta^4\text{-}3\text{-}OMe\text{-}C_6H_4CH{=}CHCHO)CO$, 63625-73-0; $Fe(CO)_2(\eta^4\text{-}3\text{-}OMe\text{-}C_6H_4CH{=}CHCHO)PPh_3$, 63625-74-1; $Fe(CO)_2(\eta^4\text{-}3\text{-}OMe\text{-}C_6H_4CH{=}CHCHO)P(n\text{-}Bu)_3$, 63625-75-2; $Fe(CO)_2(\eta^4\text{-}4\text{-}OMe\text{-}C_6H_4CH{=}CHCHO)CO$, 63625-76-3; $Fe(CO)_2(\eta^4\text{-}4\text{-}OMe\text{-}C_6H_4CH{=}CHCHO)PPh_3$, 63625-77-4; $Fe(CO)_2(\eta^4\text{-}4\text{-}Cl\text{-}C_6H_4CH{=}CHCHO)CO$, 63641-40-7; $Fe(CO)_2(\eta^4\text{-}4\text{-}Cl\text{-}C_6H_4CH{=}CHCHO)PPh_3$, 63625-78-5; $Fe(CO)_2(\eta^4\text{-}4\text{-}Me\text{-}C_6H_4CH{=}CHCHO)CO$, 63625-79-6; $Fe(CO)_2(\eta^4\text{-}4\text{-}Me\text{-}C_6H_4CH{=}CHCHO)PPh_3$, 63625-61-6; $Fe(CO)_2(\eta^4\text{-}3\text{-}NO_2\text{-}C_6H_4CH{=}CHCHO)CO$, 63625-62-7; $Fe(CO)_2(\eta^4\text{-}2\text{-}NO_2\text{-}C_6H_4CH{=}CHCHO)CO$, 63625-63-8; $Fe_2(CO)_9$, 15321-51-4; PPh_3, 603-35-0; $SbPh_3$, 603-36-1.

Supplementary Material Available: Tables of elemental analyses and melting points of the new compounds and kinetic data at various concentrations and temperatures for the reactions studied (three tables) (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, **13**, 627, 632 (1974).
(2) B. J. McKerley, G. C. Faber, and G. R. Dobson, *Inorg. Chem.*, **14**, 2275 (1975); R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586, 5590 (1965).
(3) G. R. Dobson, *Acc. Chem. Res.*, **8**, 300 (1976).
(4) G. R. Dobson and L. D. Schultz, *J. Organomet. Chem.*, **131**, 285 (1977).
(5) J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes", Springer-Verlag, Berlin, 1975.
(6) B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 2546 (1974).
(7) G. Cardaci and G. Concetti, *J. Organomet. Chem.*, **90**, 49 (1975).
(8) A. Vessieres and P. Dixneuf, *Tetrahedron Lett.*, 1499 (1974).
(9) G. Cardaci and S. Sorriso, *Inorg. Chem.*,**15**, 1242 (1976).
(10) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).
(11) R. B. Moffett, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 834.
(12) C. C. Price, *Org. Synth.*, **52**, 5 (1972).
(13) J. J. Eisch and R. B. King "Organometallic Synthesis", Vol. 1, Academic Press, New York, N.Y., p 93.
(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, N.Y., 1965, p 186.
(15) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **53**, 288 (1963).
(16) K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch., B*, **19**, 284 (1963).
(17) A. M. Brodie, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 2031 (1972).
(18) S. Sorriso and G. Cardaci, *J. Chem. Soc., Dalton Trans.*, 1041 (1975).
(19) A. R. Luxmore and M. R. Trutter, *Acta Crystallogr.*, **15**, 1117 (1962).
(20) A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975).
(21) M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **7**, 222 (1968); E. H. Schubert and R. K. Sheline, *Inorg. Chem.*, **5**, 1071 (1966).
(22) A. De Cian and R. Weiss, *Acta Crystallogr., Sect. B*, **28**, 3264 (1972).
(23) M. I. Davis and C. S. Speed, *J. Organomet. Chem.*, **21**, 401 (1970).
(24) G. Cardaci, *Int. J. Chem. Kinet.*, **5**, 805 (1973).
(25) T. H. Whitesides and J. P. Neilan, *J. Am. Chem. Soc.*, **98**, 63 (1976).

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Isomerization of the Alkyl Group in $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(alkyl)$ Complexes

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The *sec*-butyl group in $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(*sec*-butyl) isomerizes to a *n*-butyl group when heated for 4 h at 63 °C in xylene. Some $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ is also isolated from this isomerization reaction as well as butenes due to a competitive thermal decomposition reaction. The deuterium label in $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(isobutyl-*1,1*-$d_2$) is scrambled when this complex is heated for 2.5 h at 65 °C in xylene solution in reisolated alkyl and in the 2-methylpropene produced from the thermal decomposition reaction. This shows that transition metal to tertiary carbon intermediates are accessible in these isomerization reactions. In addition, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(2-methylbutyl) isomerizes to a 5.7 to 1 mixture of the 3-methylbutyl to 2-methylbutyl derivative over a 4-h period at 64 °C demonstrating that the iron has a fairly strong preference for a primary carbon β to a secondary carbon over a primary carbon β to a tertiary carbon.

Introduction

The preference of transition metals for different types of carbon atoms during a catalytic process such as olefin isomerization or hydroformylation reactions strongly influences the product ratios.[1] Investigations into the criteria for the stability of varying types of metal alkyls are thus important. In a study by Bennett and Charles[2] on the oxidative addition of acyl halides to $IrCl(N_2)(PPh_3)_2$ which yields the alkyliridium compounds $Ir(Cl)_2R(CO)(PPh_3)_2$, it was shown that if the acyl halide is branched at the α-carbon atom, the resulting alkyliridium complex is exclusively the straight-chain compound. It was proposed that the instability of the *sec*-alkyls was due to steric interactions of the branched alkyls with the phenyl rings of the triphenylphosphine ligands. Kumada and co-workers[3] have reported on the catalytic activity of nickel diphosphine complexes in the cross coupling of Grignard reagents with olefinic and aromatic halides and have shown that the coupling reaction was accompanied by alkyl group isomerizations from secondary to primary carbons. The extent of the isomerization was dependent on the electronic nature of the phosphine ligand of the catalyst. They invoked a mechanism that involved the formation of σ-alkyl intermediates followed by hydridoolefinnickel intermediates to account for the product distributions received. Kochi has shown that an isopropylgold(III) complex can isomerize to the *n*-propyl derivative.[4] In addition, the alkylzirconium complexes produced from the reaction of $(\eta^5\text{-}C_5H_5)_2Zr(Cl)H$ with internal olefins rearrange rapidly to the primary alkyls although this isomerization cannot proceed past a tertiary carbon.[5] In a study by Casey et al.[6] on the thermal decomposition of the erythro and threo isomers of (2,3-dimethylpentanoyl)manganese pentacarbonyl, (4-methylhexanoyl)manganese pentacarbonyl, and (3-ethylpentanoyl)manganese pentacarbonyl, it is shown that a tertiary carbon intermediate (a 3-methyl-3-pentylmanganese species) was high in energy and acted "as a roadblock along the alkene isomerization pathway".

Reported in this paper are results for a system, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(alkyl), that is well suited for a study of metal–alkyl isomerizations. Using this system, it has been shown that isomerization reactions can readily take place through tertiary carbon atoms and that slight changes in substitution at the carbon β to the metal center also have an important influence on the isomerization if alkyls. We have previously determined the mechanism of thermal decomposition of these metal alkyls decomposing to $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ and olefin.[7]

Experimental Section

General Data. All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen using solvents that were purified and degassed before use. Carbon-13 NMR spectra were recorded using CH_2Cl_2 as solvent and internal standard; $\delta_c(CH_2Cl_2)$ 54.0 ppm. All Raman samples were run as neat liquids in capillary tubes. The alkyllithium reagents were produced by reacting lithium dispersion (30%-high Na content) with the appropriate alkyl chloride or bromide in refluxing pentane for 6 h. The preparation of the *sec*-butyliron complex has previously been described[8] and the isobutyl-*1,1*-d_2-iron complex was prepared as described previously[7] for the analogous *n*-butyl-*1,1*-d_2 derivative with isobutyric acid being substituted for butyric acid.

(2-Methylbutyl)(carbonyl)(η^5-cyclopentadienyl)triphenylphosphineiron(II). A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ (5.0 g, 9.3 mmol) in THF (400 mL) was cooled to −78 °C and treated with a 10% excess of 2-methylbutyllithium. The solution was warmed to room temperature, the solvent evaporated, the residue extracted with a benzene–hexane mixture (5:1 v/v, 150 mL), and this solution filtered. This solution was reduced to ca. 10 mL by evaporation and chromatographed (3 × 30 cm alumina column). Elution with hexane developed a red band which was collected and the solvent reduced to 15 mL. This solution was cooled overnight to yield red crystals. These crystals were collected and dried in vacuo (2.33 g, 52%), mp 112–113 °C.

Anal. Calcd for $C_{29}H_{31}FeOP$: C, 72.20; H, 6.43. Found: C, 72.08; H, 6.33. ^1H NMR spectrum at 90 MHz (δ in toluene-d_8): multiplet centered at 1.18 (11, alkyl protons), 4.18 (5, doublet, $J = 1.2$ Hz, $\eta^5\text{-}C_5H_5$), 7.00 and 7.48 (15, PPh_3). IR spectrum (cm^{-1}): ν(CO) 1890 (vs) (Fluorolube mull), 1895 (CH_2Cl_2). ^{13}C NMR spectrum (δ vs. TMS): 226.06, 225.68 (pair of doublets, $J = 34.8$ Hz, CO), 137.13 (doublet, $J = 39.6$ Hz, P-bound phenyl carbons), 133.37 (doublet, $J = 10.0$ Hz, ortho phenyl carbons), 129.53 (singlet, para phenyl carbons), 129.11 (doublet, $J = 8.9$ Hz, meta phenyl carbons), 85.08, 84.88 (singlets, $\eta^5\text{-}C_5H_5$), 42.90, 42.32 (doublet, singlet, $J = 2.7$ Hz, $Fe{-}CH_2\mathit{CH}(CH_3)CH_2CH_3$), 34.08, 33.26 (singlets, $Fe{-}CH_2CH(CH_3)\mathit{CH}_2CH_3$), 23.17, 22.31 (singlets, $Fe{-}CH_2CH(\mathit{CH}_3)CH_2CH_3$), 11.79 (complex, $Fe{-}\mathit{CH}_2CH(CH_3)CH_2\mathit{CH}_3$).

(3-Methylbutyl)(carbonyl)(η^5-cyclopentadienyl)triphenylphosphineiron(II). This compound was prepared by the method described for the 2-methylbutyl derivative starting with 3-methylbutyllithium in 50% yield, mp 111–112.5 °C.

Anal. Calcd for $C_{29}H_{31}FeOP$: C, 72.20; H, 6.43. Found: C, 72.47; H, 6.19. ^1H NMR spectrum at 90 MHz (δ in toluene-d_8): multiplet centered at 1.20 (11, alkyl protons), 4.17 (5, doublet, $J = 1.2$ Hz, $\eta^5\text{-}C_5H_5$), 7.08, 7.50 (15, PPh_3). IR spectrum (cm^{-1}): ν(CO) 1865 (vs) (Fluorolube mull), 1905 (hexane). ^{13}C NMR spectrum (δ vs. TMS): 223.51 (doublet, $J = 33.3$ Hz, CO), 137.33 (doublet, $J = 39.6$ Hz, P-bound phenyl carbons), 133.43 (doublet, $J = 9.8$ Hz, ortho phenyl carbons), 129.55 (singlet, para phenyl carbons), 128.17 (doublet, $J = 9.1$ Hz, meta phenyl carbons), 84.95 (singlet, $\eta^5\text{-}C_5H_5$), 49.35 (doublet, $J = 2.9$ Hz, $Fe{-}CH_2\mathit{CH}_2CH(CH_3)_2$), 33.09 (singlet, $Fe{-}CH_2CH_2\mathit{CH}(CH_3)_2$), 22.66, 22.37 (singlets, $Fe{-}CH_2CH_2CH(\mathit{CH}_3)_2$), 1.79 (doublet, $J = 17.9$ Hz, $Fe{-}\mathit{CH}_2CH_2CH(CH_3)_2$).

Isomerization Reactions. (a) The *sec*-butyl- and isobutyl-*1,1*-d_2-iron compounds (0.5 g) were decomposed at ca. 63 °C under an atmosphere of N_2 in 25 mL of xylene in a 100-mL flask connected through a water condenser to two cold traps immersed in liquid nitrogen. After 4 h the solution was freeze–thawed twice to remove any dissolved gases. The volatile products were separated from trace amounts of solvent by standard vacuum line techniques and were stored in a gas bulb for future analysis. The volume of the remaining xylene solution was reduced to 5 mL and chromatographed (8 × 1.5 cm column of alumina). Elution with hexane developed two bands that were removed from the column by hexane–ether (2:1, v/v) after initial separation had occurred. The first band was shown to be $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ by comparison with an authentic sample. The second band was metal alkyl. The solvent was removed by vacuum evaporation from this solution and the crystalline material stored for analysis. Recovered yields of metal alkyl were ca. 50%.

(b) The 2-methylbutyl- and 3-methylbutyliron complexes were decomposed in 10 mL of xylene in the same manner as above. The volatile products were isolated by vacuum evaporation of the first 3 mL of the reaction solution into a cold trap immersed in liquid nitrogen. This solution was then stored in a sealed vial for analysis. (Control experiments showed that this evaporation method removed the volatile products from the reaction solution.) The metal alkyl was isolated as described above.

Analysis of Volatile Products. (a) The butenes from the *sec*-butyliron decomposition were analyzed by Raman spectroscopy of the carbon–carbon double bond stretching region. The spectrum showed three peaks indicative of 1-butene (1641 cm^{-1}), *cis*-2-butene (1699 cm^{-1}), and *trans*-2-butene (1681 cm^{-1}) in a ratio of 10.4:1.2:1, respectively.

(b) The 2-methylpropene-d_2 from the decomposition of the isobutyl-*1,1*-d_2-iron complex was analyzed by ^2H NMR.[7] The ^2H NMR gave two resonances corresponding to the methylene and the methyl group. Integration of these resonances demonstrated complete scrambling of the deuteriums. The Raman spectrum of carbon–carbon double bond stretching region confirmed the scrambling of the deuteriums.

(c) The volatile products from the 2-methylbutyl- and 3-methylbutyliron compounds were identified by gas chromatographic analysis (15 ft × 0.25 in., 10% silicon UC W-982, Chrom P AW 80/100, 30 °C). The volatile products, 2-methyl-1-butene and 3-methyl-1-butene, were conclusively identified by comparison with authentic samples. There was no detectable amount of 2-methyl-2-butene found. The ratio of the 3-methyl-1-butene to 2-methyl-1-butene was 1.3:1. The ratio of volatile products is the same from either the 2-methylbutyliron or the 3-methylbutyliron decomposition.

Analysis of Recovered Metal Alkyl. (a) The recovered metal alkyl from the *sec*-butyliron complex decomposed for 1 half-life was analyzed by ^{13}C NMR and was shown to be exclusively the *n*-butyliron complex as compared with an authentic sample. The *n*-butyliron complex did not isomerize under the same conditions.

(b) The metal alkyl recovered from the decomposition of the isobutyl-*1,1*-d_2-iron complex was shown to be the isobutyl-d_2-iron complex from mass spectral and ^1H NMR studies. The deuteriums were found to be completely scrambled by ^2H NMR.

(c) The recovered metal alkyl from the 2-methylbutyliron complex (and also the 3-methylbutyliron complex) was shown to be a mixture of the 2- and 3-methylbutyliron complexes by comparison with the ^{13}C NMR and ^1H NMR of authentic samples. The ratio of the 3-methyl- to 2-methylbutyliron complex is 5.7:1, respectively, as determined by integration of the $\eta^5\text{-}C_5H_5$ resonances in the ^1H NMR spectrum.

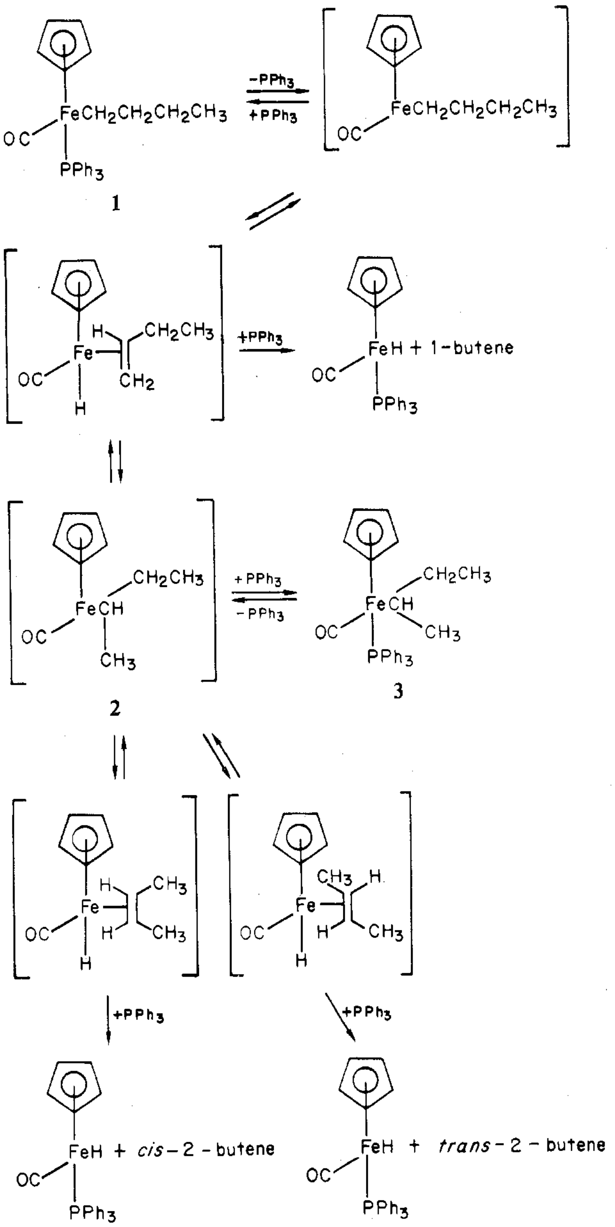
Results and Discussion

We have recently described a direct preparation[8] of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(*n*-butyl) (**1**) and determined the mechanism for its thermal decomposition into $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ and butenes as shown in Scheme I.[7] The rate-determining steps in this mechanism are collapse of the proposed $(\eta^5\text{-}C_5H_5)Fe(CO)$(butene)H intermediates. The complete scrambling in butene products of specific deuterium labels in starting materials demonstrated that all the equilibria shown are fast and take place many times on the average before the olefin is liberated to yield products.

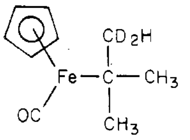
Another entrance point into this mechanistic scheme is the dissociation of phosphine from $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(*sec*-butyl) (**3**) as shown in Scheme I to form intermediate **2**. In fact, the ratio of butenes produced from the decomposition at 61.2 °C in xylene solution of both **1** or **3** is the same. Thus, the isomerization of **3** to **1** or possibly the establishment of an equilibrium mixture seemed feasible to observe. Heating either compound **1** or **3** for 4 h at 63 °C (ca. 1 half-life of the thermal decomposition reaction) in xylene solution led to the reisolation of compound **1** as the only iron alkyl (some metal hydride is also isolated) as shown by ^{13}C NMR studies. Thus, the *sec*-butyl compound has isomerized to the *n*-butyl compound demonstrating the preference of the iron for primary over secondary carbon, as has been observed for other systems.[2,3]

Having demonstrated that this system was convenient for the study of alkyl isomerization reactions (the ability to prepare directly and isolate metal alkyls prior to isomerization is

Scheme I



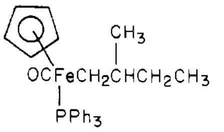
critical), it is important to determine if isomerization reactions could take place through tertiary carbon intermediates. To determine this point, (η^5-C_5H_5)Fe(CO)(PPh_3)(isobutyl-*1,1*-d_2) (**4**) was prepared. The only alkene that can be produced from **4** is 2-methylpropene, but in order to scramble the deuterium label the intermediate **5** as pictured below (and many other



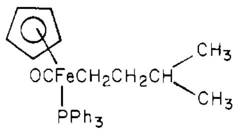
5

analogous intermediates with the deuteriums scrambled) must be accessible in the reaction. Analysis of the volatile products produced from heating **4** for 2.5 h at 65 °C in xylene using both Raman and ^2H NMR shows conclusively that the deuteriums are scrambled in the 2-methylpropene product. In addition, ^1H and ^2H NMR studies on the iron–isobutyl complex reisolated in the above experiment establish that the deuterium label has been scrambled. This demonstrated that the isomerization reaction could readily take place through tertiary carbon intermediates.

Having shown that the iron prefers a primary carbon over a secondary carbon and that tertiary intermediates are accessible for this system, it was decided to determine the effect of substitution at the β carbon. Compound **6** pictured below



6



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was thus prepared (both diastereomers form in approximately equal amounts). Analysis of reisolated metal alkyl using ^{13}C and ^1H NMR demonstrated that an equilibrium mixture of **6** and **7** is established at 64 °C over a 4-h period that does not change with further heating. Isomer **7** is predominant in this mixture with the ratio of **7** to **6** being 5.7:1. Analysis of the volatile products via gas chromatography showed that both 3-methyl- and 2-methyl-1-butene are produced in a ratio of 1.3:1. No detectable amount of 2-methyl-2-butene was observed. The isomerization of **7** yields a mixture with the ratio of **7** to **6** identical with that mentioned above. The volatile product ratio is also the same. This study thus shows that a transition metal has a fairly strong preference for particular carbon atoms in an alkyl chain even when the difference of one carbon over the other is the simple substitution of a methyl group for a hydrogen at the carbon β to the metal. Note that this isomerization passes through a tertiary intermediate.

An isomeric mixture of olefins is produced (when more than one isomer is possible) from the thermal decomposition reactions which accompany the isomerization reactions discussed above. In all cases, the olefin isomer which would be formed directly from the preferred metal alkyl is formed in greatest abundance. Thus the *n*-butyl and *sec*-butyl compounds produce mainly 1-butene and the 2- and 3-methylbutyl compounds produce 3-methyl-1-butene in preference to 2-methyl-1-butene and no 2-methyl-2-butene. These preferred olefins would also presumably form the most stable (η^5-C_5H_5)Fe(CO)(olefin)H intermediates.[9] The olefins produced are, of course, not the thermodynamically most stable. In contrast to these results, transition metal complexes that promote double bond isomerization "give invariably the thermodynamically most stable isomeric mixture".[10] Two competing factors decide which olefins are produced. The first is the relative stability of the (η^5-C_5H_5)Fe(CO)(olefin)H intermediates which decides their relative abundance in these rapidly equilibrating systems such as outlined in Scheme I. The second is the rate that each of these intermediates decomposes to yield olefin and metal hydride (the reactions have been shown to be irreversible[7]). Apparently the rate that the intermediates decompose must be fairly similar because the first factor dominates the product ratios.

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Registry No. 3, 59308-08-6; 4, 64345-50-2; 6, 64345-51-3; 7, 64345-52-4; (η^5-C_5H_5)Fe(CO)(PPh_3)I, 12099-18-2; ^{13}C, 14762-74-4.

References and Notes

(1) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, N.Y., 1972, pp 785–793; (b) C. P. Casey and C. P. Cyr, *J. Am. Chem. Soc.*, **95**, 2240, 2248 (1973), and references

therein; (c) D. E. James and J. K. Stille, *ibid.*, **98**, 1810 (1976).
(2) M. A. Bennett and R. Charles, *J. Am. Chem. Soc.*, **94**, 666 (1972).
(3) (a) K. Tamao, Y. Kiso, K. Sumitani, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 9268 (1972); (b) Y. Kiso, K. Tamao, and M. Kumada, *J. Organomet. Chem.*, **50**, C12 (1973).
(4) (a) A. Tamaki and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 423 (1973); (b) A. Tamaki, S. A. Magennis and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 6140 (1974).
(5) J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, **15**, 333 (1976).
(6) C. P. Casey, C. R. Cyr, and J. A. Grant, *Inorg. Chem.*, **13**, 910 (1974).
(7) D. L. Reger and E. C. Culbertson, *J. Am. Chem. Soc.*, **98**, 2789 (1976).
(8) D. L. Reger and E. C. Culbertson, *Synth. React. Inorg. Met.-Org. Chem.*, **6**, 1 (1976).
(9) F. R. Hartley, *Chem. Rev.*, **73**, 163 (1973).
(10) Reference 1a, p 785.

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(Diorganodithiocarbamato)iron Complexes. Effect of Organic Substituents

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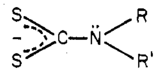
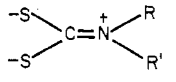
A series of $Fe(CO)_2(S_2CNRR')_2$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNRR')$ complexes have been prepared, where R and R′ are organic substituents, both aliphatic and aromatic. The Mössbauer, infrared, and (for the second series) proton NMR spectra have been determined. For each series the ^{57}Fe Mössbauer parameters are essentially constant when R and R′ are varied. In contrast, the CO force constants (k_{CO}) in each series exhibit a linear dependence on the aqueous pK_a values of $H_2NRR'^+$ for the separate cases of R = R′ = alkyl, R = alkyl, R′ = aryl, and R = R′ = aryl. This separation into three groups is explained by the resonance, base-weakening effect of phenyl substituents in aqueous solutions of amines. Examination of the ^1H NMR of $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNRR')$ and the literature x-ray structure of $Fe(S_2CN(C_2H_5)(C_6H_5))_3$ suggest that this resonance base-weakening effect does not take place in coordinated dithiocarbamates. When the resonance base-weakening effect of the phenyl substituents is taken into account, a single linear dependence of k_{CO} on pK_a is observed. These results indicate that inductive effects of R and R′ play a major role in the bonding of these carbonyls of iron dithiocarbamates. Furthermore, the aryl resonance base-weakening effect considerations allow a reinterpretation of the solution magnetic moment vs. pK_a data in the $Fe(S_2CNRR')_3$ series.

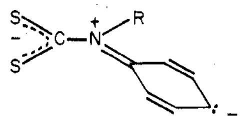
Introduction

Since the early 1930s it has been known[1] that the dithiocarbamates of iron(III) [$Fe(dtc)_3$, dtc = $S_2CNRR'^-$, where R and R′ are organic substituents] exhibit magnetic moments (μ_{eff}) intermediate between the high-spin (μ_{eff} = 5.9 μ_B) and low-spin ($\mu_{eff} \simeq 2\ \mu_B$) states for d^5 complexes in octahedral symmetry. The exact value of the magnetic moment depends, in part, on the identity of R and R′. The intermediate magnetic moments, both in the solid state and in solution, are believed to arise from an equilibrium involving iron atoms in these two different electronic configurations.[2-4] The ligand itself may be described as a resonance hybrid with two limiting resonance structures (A and B) being the major contributors


A


B

to the description of the bonding. The variation of the intermediate magnetic moment value with changing R and R′ is taken to indicate that the relative contribution of structures A and B to the resonance hybrid depends on the identity of R and R′. One explanation[5] has proposed that R and R′ affect the ligand field strength according to the steric requirements of the substituents and has assigned form A above as the low ligand field form of the ligand. A second explanation has proposed that the effect of the organic groups is inductive.[6] An extension of this explanation by Eley, Myers, and Duffy[7] proposed that the inductive effect may be quantified by use of the aqueous pK_a of the protonated form of the parent secondary amine (pK_a of $H_2NRR'^+$). Eley et al. assigned form A above as the high ligand field form. This assignment was shown to be incorrect by a temperature-dependent structure determination of $Fe(S_2CN(C_2H_5)_2)_3$.[8] The data of Eley et al.[7] were reinterpreted by Chant et al.[9] who reported that the incorporation of an aryl group displaces the pK_a of the free amine to lower values and proposed that such dithiocarbamates of iron(III) are subject to the "exceptional π-mesomeric effects", such as limiting resonance form C.


C

This study concentrates on the nature of these "exceptional π-mesomeric effects" when R and/or R′ are aryl. Two series of complexes, *cis*-$Fe(CO)_2(dtc)_2$ (hereafter called the dicarbonyls) and $(\eta^5\text{-}C_5H_5)Fe(CO)dtc$ (hereafter the monocarbonyls), were prepared and studied by various spectroscopic techniques. In addition $Fe(S_2CNCH_3(OCH_3))_3$ was prepared and its measured properties support a reinterpretation of the $Fe(dtc)_3$ data suggested by measurements presented herein for the dicarbonyls and monocarbonyls.

Experimental Section

The dicarbonyl complexes were prepared by two different routes (A and B). Synthesis A was the previously published synthetic method of Büttner and Feltham.[10] In this method the sodium salt of the dithiocarbamate ligand was prepared by the method of Delepine[11] and von Braun[12] (updated by Akerström)[13] if both substituents were aliphatic or by the method of Semon[14] if one or more substituents were aromatic. This sodium dithiocarbamate was then added to an acetone solution of ferrous sulfate, and carbon monoxide was bubbled through to form the desired product.

Synthetic route B involved first the preparation of the desired bis(diorganothiocarbamoyl) disulfide ($[RR'NC(S)S-]_2$) by published methods.[14] This compound was then added to stoichiometric amounts of triiron dodecacarbonyl ($Fe_3(CO)_{12}$) (3:1 ratio) also prepared according to a published method.[15] The mixture was refluxed in absolute ethanol for about 20 min until the solution was observed to change color from the green of the reactants to the brown or black of the products. The solution was cooled and the product isolated as a solid (sometimes partial removal of solvent was necessary). Table I shows in part the method used to prepare each of these compounds.