

Bond Fixation in Polyene-Iron Tricarbonyl Complexes¹

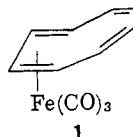
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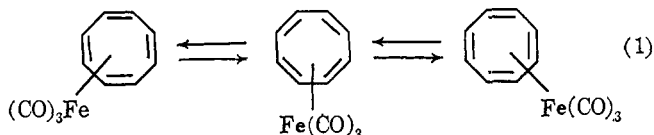
The two isomers of 1-phenyl-6-*p*-tolyl-1,3,5-hexatriene-iron tricarbonyl, differing in the position of attachment of the iron tricarbonyl residue, have been synthesized. They have been shown to interconvert by a first-order, presumably intramolecular, thermal process.

Introduction

Cyclooctatetraene-iron tricarbonyl (1)²⁻⁵ exhibits but a single peak in its n.m.r. spectrum, both at room temperature^{2,4} and at -60° .⁶



The structure of 1 has been determined via X-ray diffraction by Dickens and Lipscomb.⁷ With respect to the n.m.r. spectrum of 1, these authors have suggested that "a dynamical effect amounting to permutation of the C atoms of the ring relative to the Fe(CO)₃ group does, however, satisfy the experimental observations." This process may be summarized as in eq. 1.



Let us now ask ourselves whether, assuming the above explanation to be correct, shuffling of an iron tricarbonyl residue along a polyene chain is a unique feature of the structure of 1 or a general characteristic of polyene-iron tricarbonyl complexes. We wish to report here results of an investigation of this phenomenon in the 1,6-diarylhexatriene-iron tricarbonyl series which, together with other published data, suggests that mobility of an iron tricarbonyl residue is a general feature of polyene-iron tricarbonyl complexes. The effect is, however, greatly attenuated in complexes lacking the peculiar structural features of 1.

Results

As shown elsewhere,⁸ 1,6-diphenylhexatriene-iron tricarbonyl (2) is a chemically well-defined substance

(1) Preliminary communication: H. W. Whitlock, Jr., and Y. N. Chuah, *J. Am. Chem. Soc.*, **86**, 5030 (1964).

(2) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 336 (1960).

(3) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

(4) M. D. Rausch and G. N. Schrauzer, *Chem. Ind. (London)*, 957 (1959).

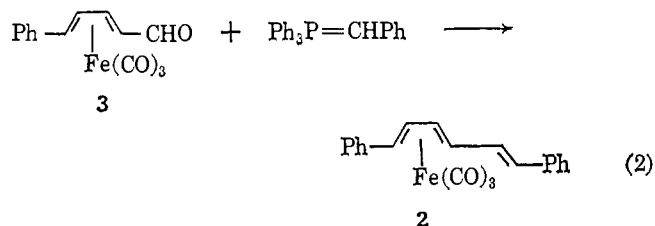
(5) G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *J. Am. Chem. Soc.*, **86**, 3590 (1964).

(6) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind. (London)*, 553 (1961).

(7) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

(8) H. W. Whitlock, Jr., and Y. N. Chuah, *Inorg. Chem.*, **4**, 424 (1965).

which may be prepared either by reaction of the triene with iron pentacarbonyl or by a Wittig condensation of 5-phenylpentadienal-iron tricarbonyl (3) and benzyldenetriphenylphosphorane (eq. 2). Application of the



Wittig condensation to 3, employing *p*-methylbenzyldenetriphenylphosphorane as the ylid, gave in high yield 1-phenyl-6-*p*-tolyl-1,3,5-hexatriene-(1,3)-iron tricarbonyl (5) (Figure 1), m.p. 125–126°. The structure of 5 was assigned by analogy with eq. 2 and on the basis of a suitable n.m.r. spectrum, the presence of a band at 962 cm.⁻¹ in its infrared spectrum assignable to the uncomplexed *trans*- $\Delta^{4,5}$ double bond of the hexatriene,⁹ elemental analysis, and smooth degradation by ferric chloride in acetonitrile to the parent triene 7. Condensation of 5-*p*-tolyl-2,4-pentadienal-iron tricarbonyl (4) with benzyldenetriphenylphosphorane in a similar manner gave in high yield 1-*p*-tolyl-6-phenyl-1,3,5-hexatriene-(1,3)-iron tricarbonyl (6), m.p. 143–144°. Complex 6 also afforded an elemental analysis and n.m.r. spectrum consistent with the assigned structure, possessed a 962-cm.⁻¹ band in its infrared spectrum, and was smoothly degraded by ferric chloride in acetonitrile to triene 7.

Complexes 6 and 7 are not identical. They not only have different melting points but afford a depressed mixture melting point. Their infrared spectra, although very similar, show small but distinct shifts in the out-of-plane deformation bands. The 747 cm.⁻¹ band in 7 ascribable⁹ to the phenyl group is almost unchanged in 6 (745 cm.⁻¹) but is shifted to 755 cm.⁻¹ in 5. The 796 cm.⁻¹ band in 7 ascribed to the 1,4-disubstituted benzene ring is almost unshifted in 5 (800 cm.⁻¹) but shifts to 812 cm.⁻¹ in 6.¹⁰ The n.m.r. spectra of 5 and 6 were very similar. Slight line broadening due to persistent traces of paramagnetic impurities thwarted use of the spectra for quantitative analysis of mixtures of the two complexes.

The ease with which 5 and 6 were handled and recrystallized from hot hexane-benzene mixtures placed an upper limit on their rate of interconversion as being orders of magnitude less than the rate of interconversion

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

(10) The shift to higher frequency of ca. 10 cm.⁻¹ of these aromatic, out-of-plane deformation bands on placing the aromatic rings adjacent to the butadiene-iron tricarbonyl moiety was also observed in the pentadienals and their iron tricarbonyl complexes 3 and 4, 1,4-diphenylbutadiene and its iron tricarbonyl complex, and 1,6-diphenylhexatriene and its complex 2. The 690 cm.⁻¹ band due to phenyl was not subject to this shift.

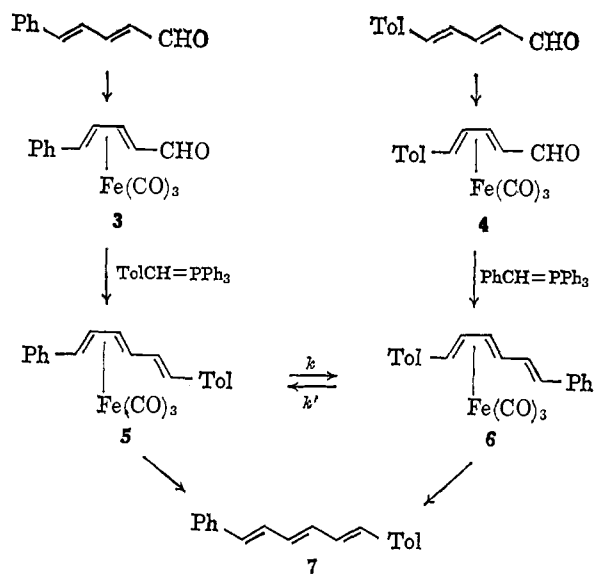


Figure 1.

of the isomers of 1. That 5 and 6 *did* interconvert was shown during a test of the thermal stability of 5. When 5 was heated *in vacuo* as a melt at 120° for 15 hr., a mixture of 5 and 6 (as determined by its infrared spectrum) was recovered in good yield. No degradation of the complexes occurred during the heating.¹¹ Extensive chromatography of the mixture led to ultimate isolation of small amounts of pure 6. That we were dealing with an equilibrium was established by converting 6 to a mixture (by infrared) of 5 and 6 on heating to 125°.

Rates of interconversion of 5 and 6 in dilute *n*-decane solution were determined by quantitative monitoring of the 755 and 745 cm^{-1} bands of 5 and 6, respectively (see Experimental section). The following data were obtained. The equilibrium constant *K* for interconversion of 5 and 6 was found to be 1 on approaching equilibrium from 6 ($K = 1.05$) or 5 ($K = 0.99$). Complex 5 undergoes a first-order approach to equilibrium, having $k = 9.2 \times 10^{-4} \text{ min}^{-1}$ at 99.6° in 0.032 *M n*-decane solution. The rate constant at 99.6° (one point) was unaffected by a tenfold decrease in concentration or in 0.029 *M n*-decane solution containing 0.11 *M* triphenylphosphine. The equilibration could be carried out through 7 half-lives at 99.6° in 0.032 *M n*-decane in the presence of 0.17 *M* triphenylphosphine without detectable degradation of the complexes to 7 and bis(triphenylphosphine)-iron tricarbonyl.²

Discussion

It appears from the above data that the first-order interconversion of 5 and 6 does not involve intermediates possessing "open" tetracoordinate iron.¹² The simplest mechanism that seems to fit the data is offered in Figure 2. The point of Figure 2 is that intermediate 8 would be expected to collapse intramolecularly with formation of 5 and 6 rather than be

(11) *I.e.*, no 993 cm^{-1} infrared band due to 7.

(12) An analogy between Figure 2 and allylic ester rearrangements might be drawn, *e.g.*, H. L. Goering, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 21, 109 (1960).

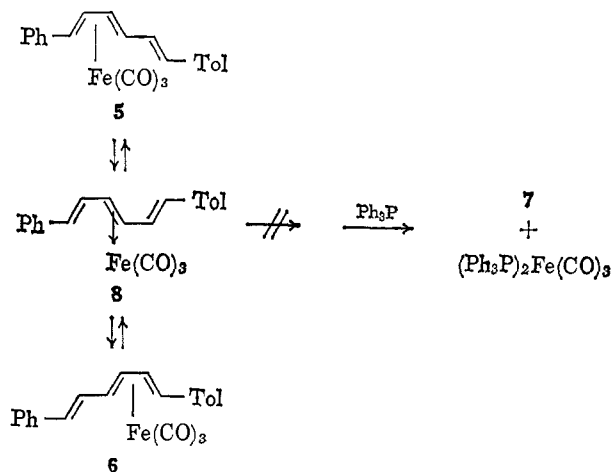
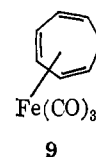


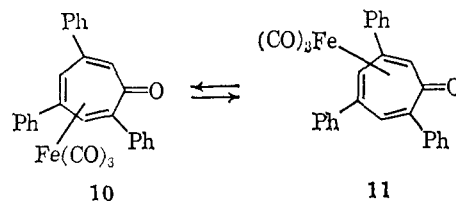
Figure 2.

captured by an exterior nucleophile such as triphenylphosphine.

A minimum rate constant for the time averaging of COT-iron tricarbonyl protons can be calculated as being¹³⁻¹⁵ *ca.* $2 \times 10^4 \text{ min}^{-1}$ at -60° . It is assumed that this process is mechanistically related to the equilibrium $5 \rightleftharpoons 6$. Making this assumption, two factors arise which may be responsible for the tremendous difference in rates, *ca.* 10^7 without correcting for the 160° temperature difference, of these two reactions. First, a feature of 1 but not of 2, 5, or 6 is a continuous cisoid arrangement of p-orbitals. Thus 1 and other cyclic polyene-iron tricarbonyls have available a possibility for continuous interaction of the iron with at least four carbon p-orbitals on movement of the $\text{Fe}(\text{CO})_3$ group around the ring. This must not be the main reason for the large rate difference, however, since cycloheptatriene-iron tricarbonyl (9) exhibits an n.m.r. spectrum interpretable in terms of



structure 9 with nonexistent (n.m.r. time scale) moving of the iron tricarbonyl group.¹⁶ Closer to home is the interconversion of the two 2,4,6-triphenyltropone-iron



(13) Assuming a chemical shift difference of 160 c.p.s.¹⁴ between the "internal" and "terminal" hydrogens of the butadiene-iron tricarbonyl moiety in 1.

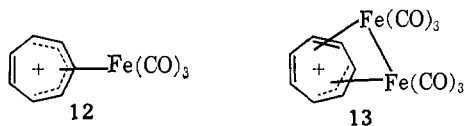
(14) G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, 29, 3620 (1964).

(15) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 61-79.

(16) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961).

tricarbonyl complexes¹⁷ **10** and **11**, a process which proceeds at an appreciable rate only at 80°. ¹⁸

The most important factor is felt to be cyclic through-conjugation present in the cyclooctatetraene ring in **1** and the cycloheptatrienyl rings in **12** and **13** which also exhibit rapid time averaging of the ring protons.^{5,19} As illustrated in eq. 1, **1**, **12**, and **13** may combine shifting of the iron tricarbonyl residues with a tautomerization of the ring. As a result, shifting of the iron tricarbonyl



residue past *one* carbon will result in reestablishment of the original structure. In **2**, **5**, **6**, **9**, **10**, and **11**, however, the iron must pass over at least two carbons before reestablishment of a butadiene-iron tricarbonyl part structure. The geometry of the ring in **1** would suggest that the tautomerization of the cyclooctatetraene ring should be considerably more facile than in the uncomplexed olefin²⁰ and its derivatives.²¹

We thus arrive at the conclusion that while equilibrium **5** \rightleftharpoons **6** represents a minimum residual "looseness" associated with iron tricarbonyl complexes of polyenes, incorporation of the polyene into a cyclic arrangement will not lead to a great speeding up of iron tricarbonyl residue shifting unless a completely through-conjugated system is present.

Experimental

trans,trans-5-Phenyl-2,4-pentadienal-Iron Tricarbonyl (**3**). A mixture of 3.0 g. of *trans,trans*-5-phenyl-2,4-pentadienal and 26 ml. of iron pentacarbonyl in 30 ml. of *n*-heptane was heated under reflux with stirring under nitrogen for 69 hr. The resulting black mixture was filtered, concentrated, and adsorbed on a column of 250 g. of acid-washed alumina. Elution with chloroform and recrystallization of the eluent from benzene-hexane (1:4) gave 4.05 g. (72% yield) of 5-phenyl-2,4-pentadienal-iron tricarbonyl as yellow plates, m.p. 163–164°. The analytical sample was prepared by repeated recrystallization from benzene-hexane as moderately air-stable yellow flakes, m.p. 166–166.5°. The n.m.r. spectrum showed aldehydic H as a doublet, $J = 5$ c.p.s. at δ 9.44; C₂H as an incompletely resolved quartet centered at 1.60; C₃H and C₄H as a multiplet centered at 6.07; C₅H as a doublet, $J = 10$ c.p.s., at 2.6; and phenyl as singlet at 7.34; all signals were of the correct intensity.

Anal. Calcd. for C₁₄H₁₀FeO₄: C, 56.37; H, 3.38. Found: C, 55.93; H, 3.11.

5-*p*-Tolyl-2,4-pentadienal-Iron Tricarbonyl (**4**). A mixture of 3.0 g. of 5-*p*-tolyl-2,4-pentadienal²² and 26.4 ml. of iron pentacarbonyl in 25 ml. of *n*-heptane was heated under reflux with stirring under nitrogen for

(17) E. H. Braye, C. Hoogzand, W. Hübel, V. Kruerke, R. Merenyi, and E. Weiss in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 190.

(18) E. H. Braye and W. Hübel, *J. Organometal. Chem.*, **3**, 25 (1965).

(19) M. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 3589 (1964).

(20) F. A. L. Anet, *ibid.*, **84**, 671 (1962).

(21) F. A. L. Anet, A. J. R. Bourne, and Y. S. Lin, *ibid.*, **86**, 3576 (1964).

(22) A. Lüttringhaus and G. Schill, *Chem. Ber.*, **93**, 3048 (1960).

64 hr. The black reaction mixture was filtered, concentrated, and adsorbed on a column of 100 g. of alumina. Elution with chloroform-hexane (2:3) and recrystallization of the eluent from benzene-hexane (1:3) gave 2.45 g. (42% yield) of 5-*p*-tolyl-2,4-pentadienal-iron tricarbonyl, m.p. 138–139.5°. The analytical sample was prepared by repeated recrystallization from benzene-hexane as yellow-orange needles, m.p. 140–140.5°. The n.m.r. spectrum showed aldehyde H as doublet, $J = 4$ c.p.s. at δ 9.42; C₂H as unresolved quartet centered at 1.52; C₃H and C₄H as multiplet centered at 6.0; C₅H as doublet, $J = 9$ c.p.s. at 2.64; ArCH₃ as singlet at 2.32; and ArH as a multiplet centered around 7.2; all peaks were in the correct intensity.

Anal. Calcd. for C₁₅H₁₂FeO₄: C, 57.69; H, 3.88; Fe, 17.89. Found: C, 57.85; H, 3.98; Fe, 17.46.

1-Phenyl-6-*p*-tolyl-1,3,5-hexatriene-(1,3)-Iron Tricarbonyl (**5**). To a stirred suspension of 5.0 g. (12.4 mmoles) of *p*-methylbenzyltriphenylphosphonium chloride in 100 ml. of dry tetrahydrofuran at 0° under nitrogen was injected 6.94 ml. of 1.44 *M* butyllithium in hexane. A deep orange color of the ylid appeared. After stirring at 0° for 20 min., a solution of 1.85 g. (6.2 mmoles) of 5-phenyl-2,4-pentadienal-iron tricarbonyl in 20 ml. of dry tetrahydrofuran was added in one portion. The deep orange color immediately changed to yellow. After stirring at 0° for 2 hr. and 25° for 1 hr. the reaction mixture was poured into an excess of water and the aqueous layer was repeatedly extracted with benzene. The combined benzene extracts were washed with water and saturated salt solution, dried over anhydrous sodium sulfate, filtered, concentrated, and adsorbed on a column of 100 g. of silica gel. Elution with benzene-hexane (1:9) gave 2.37 g. (98% yield) of crude 1-phenyl-6-*p*-tolyl-1,3,5-hexatriene-(1,3)-iron tricarbonyl, m.p. 114–120°. Two recrystallizations from benzene-hexane gave 1.73 g. (72% yield), m.p. 124.5–125.5°. The analytical sample was prepared by repeated recrystallization from benzene-hexane as sheaves of orange plates, m.p. 125–126°, or clumps of red rods (orange when crushed), m.p. 129–131°. Dimorphism was demonstrated by cross-seeding experiments. The low-melting form was used for succeeding experiments. The n.m.r. spectrum showed ArCH₃ as singlet, δ 2.32; C₁H and C₄H as multiplet centered around 2.34; C₂H, C₃H, C₅H, and C₆H as multiplets ranging from 5.1 to 6.8; and ArH as multiplet centered around 7.2. The infrared spectrum (out-of-plane deformation region) showed $\nu_{\text{max}}^{\text{C}=\text{C}}$ 962 (*trans*-CH=CH-), 800 (1,4-disubstituted phenyl), 755 and 690 cm.⁻¹ (phenyl).

Anal. Calcd. for C₂₂H₁₈FeO₃: C, 68.39; H, 4.70; Fe, 14.46. Found: C, 68.56; H, 4.76; Fe, 14.71.

1-*p*-Tolyl-6-phenyl-1,3,5-hexatriene-(1,3)-Iron Tricarbonyl (**6**). To a stirred suspension of 2.72 g. (7.0 mmoles) of benzyl triphenylphosphonium chloride in 20 ml. of dry tetrahydrofuran at 0° under nitrogen was injected 3.82 ml. of 1.44 *M* butyllithium in hexane. A deep orange color appeared. After stirring at 0° for 15 min., a solution of 1.39 g. (4.45 mmoles) of 5-*p*-tolyl-2,4-pentadienal-iron tricarbonyl in 10 ml. of dry tetrahydrofuran was added in one portion. The now yellow reaction mixture was stirred at 0° for 1 hr. and poured into 100 ml. of water. The aqueous layer was

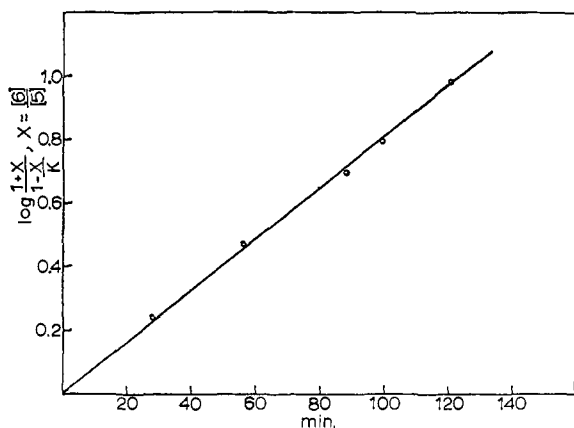


Figure 3.

repeatedly extracted with benzene and the combined benzene extracts were washed with water and saturated salt solution, dried over anhydrous sodium sulfate, concentrated, and adsorbed in 200 g. of silica gel. Elution with benzene-hexane (1:9) gave 1.13 g. (66% yield) of 1-*p*-tolyl-6-phenyl-1,3,5-hexatriene-(1,3)-iron tricarbonyl, as beautiful, golden orange rods, m.p. 142–144°. The analytical sample was prepared by repeated recrystallization from benzene-hexane as golden rods, m.p. 144–145°. The n.m.r. spectrum showed ArCH_3 as a singlet, δ 2.28; C_1H and C_4H as an unresolved multiplet centered around 2.25; C_2H , C_3H , C_5H , and C_6H as a complex multiplet stretching from 5.2 to 6.8; and ArH as a multiplet centered around 7.2. All peaks were present in approximately the correct ratio but were appreciably broadened by a persistent paramagnetic impurity. The infrared spectrum (out-of-plane deformation region) showed $\nu_{\text{max}}^{\text{C}=\text{C}}$ 962 (*trans*-CH=CH-), 812 (1,4-disubstituted phenyl), 745, and 690 cm^{-1} (phenyl).

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}\text{FeO}_3$: C, 68.39; H, 4.70; Fe, 14.46. Found: C, 68.32; H, 4.79; Fe, 13.94.

1-Phenyl-6-p-tolyl-1,3,5-hexatriene (7). To a stirred solution of 159 mg. of 1-phenyl-6-*p*-tolyl-1,3,5-hexatriene-(1,3)-iron tricarbonyl in 10 ml. of acetonitrile was added a solution of 390 ml. of anhydrous ferric chloride in 10 ml. of acetonitrile. The red color of the ferric chloride solution was discharged and 33.5 ml. (STP) of a gas was evolved over 15 min. The reaction mixture was poured into water and the aqueous phase

was extracted with chloroform. Evaporation of the washed and dried chloroform extracts and sublimation of the residue (100° at 0.03 mm.) gave 69 mg. (65% yield) of 1-phenyl-6-*p*-tolyl-1,3,5-hexatriene as light yellow flakes, m.p. 193–194.5°, m.m.p. with an authentic sample 192–194°. The infrared spectrum (out-of-plane deformation region) showed $\nu_{\text{max}}^{\text{C}=\text{C}}$ 993 (*trans*-CH=CH-), 795 (1,4-disubstituted phenyl), 745 and 689 cm^{-1} (phenyl). In a similar manner, the isomeric iron carbonyl complex 6 gave a 39% yield of the hexatriene, m.p. 195.5–196°, m.m.p. 195–196°.

Isomerization Experiment. Compound 5 (200 mg.) was sealed *in vacuo* in a small tube and immersed in an opaque oil bath at 130°. After 10 min. the bath temperature was lowered to 120–123° and maintained thusly for 17 hr. The tube was then opened and the dark pitch was dissolved in benzene and, after a preliminary chromatography on 50 g. of silica gel, adsorbed on a 2 cm. \times 2 m. column of silica gel. Elution with benzene-hexane (1:9) afforded 157 mg. of iron carbonyl complexes spread over six fractions. The first fraction, 11 mg., was recrystallized four times from hexane to afford 1.53 mg. of 6, m.p. 144–145°, the mixture melting point with authentic 6 as prepared above being 143–145°. Their infrared spectra (KBr) were identical. The remaining fractions were shown by infrared to be mixtures of 5 and 6, the former being concentrated in the later fractions.

Rate Data. The isomerization of 5 and 6 was followed by infrared monitoring of the 755 cm^{-1} band of 5 and the 745 cm^{-1} band of 6. A pair of 0.1-mm. NaCl cells were calibrated with known mixtures of the two complexes and a calibration curve of absorbancy ratios of the two peaks *vs.* concentration ratios was constructed. Kinetic runs were performed in dilute solution in degassed *n*-decane in the sealed tubes in the dark. For analysis a tube was opened, solvent was removed by lyophilization, and the residue was dissolved in carbon disulfide and subjected to infrared analysis. A plot of $\log(1+x)/(1-x/K)$ *vs.* time was constructed where $K = 1$ was the experimentally determined equilibrium constant and x was the concentration ratio $[\text{6}]/[\text{5}]$; the slope of the plot was $2k/2.3$ (Figure 3). A Perkin-Elmer Model 421 grating spectrophotometer was used.

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