Acid- and Base-Catalyzed Anti to Syn Isomerization of (Dienone)tricarbonyliron Compounds[1]

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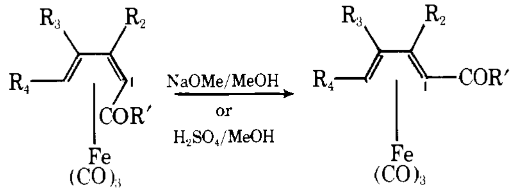
Abstract: (Dienone)tricarbonyliron compounds which have anti acyl groups rearrange quantitatively to their syn isomers in the presence of strong acids or bases. In methanol the reactions are first order in methoxide or methyloxonium ion. Introduction of substituents on diene carbons causes only small rate changes, but substitution of triphenylphosphine for CO slows isomerization drastically. Isomerization in methanol-*O-d* proceeds with ca. 40% deuterium incorporation α to the carbonyl group. These observations lead to the conclusion that rate-determining nucleophilic attack of methoxide (or methanol) at iron produces an intermediate which is capable of rapid isomerization and deuterium incorporation. Dienonitrile complexes undergo H–D exchange at C_α with retention of configuration by a different mechanism.

Isomerization of anti (dienone)tricarbonyliron complexes to their syn isomers in the presence of acid or base, eq 1, was first reported by Greaves, Knox, and Pauson in connection with a study of Friedel–Crafts acylation of (diene)tricarbonyliron complexes.[2] Graf and Lillya elucidated the role this isomerization plays during the quenching phase of acylation and used this knowledge to develop stereospecific syntheses of syn and of anti acylated diene complexes.[3] Results of high-yield preparative isomerizations were reported[3] and have been applied by others.[4] Clinton and Lillya have described the two-step conversion of a syn complex, **2b,** to its anti isomer, **1b,**[5] a contrathermodynamic process. DePuy, Jones, and Parton have reported corresponding thermal isomerizations[6] which are apparently accelerated by $Fe_2(CO)_9$.[6b] We report below a study of the mechanism of the acid- and base-catalyzed reactions.

Results

Isomerizations (eq 1) were run in methanol and monitored by liquid chromatography (LC).[7] Rates determined at different acid and base concentrations revealed first-order dependence. Subsequent studies were conducted at constant acid or base concentration, pseudo-first-order conditions. The base-catalyzed reactions were very clean and followed pseudo-first-order behavior for 2 or more half-lives. After 7 half-lives, less than 1% of dienone remained, and over 90% of the starting material could be accounted for as syn dienone. The acid-catalyzed reactions were not this clean but gave reproducible results. To make our relative rates more reliable, most of the compounds reported in a single table were run simultaneously in aliquots from the same methanolic acid or base solution. Results are presented in Tables I and II.



(1)

1, R′ = Me
3, R′ = Ph

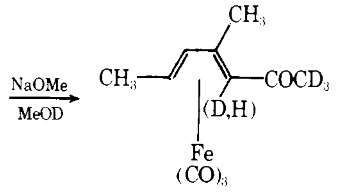
2, R′ = Me
4, R′ = Ph

a, $R_2 = R_3 = R_4 = H$
b, $R_2 = R_3 = H$; $R_4 = Me$
c, $R_2 = R_4 = H$; $R_3 = Me$
d, $R_2 = Me$; $R_3 = R_4 = H$
e, $R_2 = R_4 = Me$; $R_3 = H$
f, $R_2 = R_3 = H$; $R_4 = p\text{-}BrC_6H_4$
g, $R_2 = R_4 = H$; $R_3 = OMe$
h, $R_2 = R_3 = Me$; $R_4 = H$

Isomerization of 10^{-3} M solutions of methyl dienone complexes (**1**) in 0.05 M potassium *tert*-butoxide in *tert*-butyl alcohol was complete after 1 min at 22 °C. However, after 25 min, the concentration of product (**2a**) had decreased by 50%, and LC analysis showed that decomplexation was occurring. In a solution of 10^{-3} M in **1a** and 5×10^{-4} M in potassium *tert*-butoxide ca. 20% isomerization occurred within the first minute at 22°C, but no further change was observed. Subsequent addition of small aliquots of potassium *tert*-butoxide caused additional increments of rapid isomerization. The solution was always neutral to wet litmus 1 min after the addition of potassium *tert*-butoxide. These observations show that *tert*-butoxide is consumed irreversibly with production of uncomplexed dienone among other products.

Isomerization of **1e** in NaOMe/MeOD proceeded with a second-order rate constant of ca. 1.7 L mol^{-1} h^{-1} to give **2e** which was partially deuterated at C_1 (eq 2). Material from a run stopped at 50–65% isomerization showed 46% deuteration at C_1, and a run stopped at 28% isomerization gave 42% deuteration. Unisomerized **1e** isolated from these mixtures showed no deuterium incorporation at C_1. Rates of H–D incorporation at C_1 in syn dienone complexes are reported in Table III. First-order dependence on base concentration was demonstrated in all cases. The base concentration decreased at long reaction times for compound **1e.** Kinetic measurements were made only during the time period that acid titration of aliquots showed an unchanged base concentration.

1e



2e

(2)

Preparation of the anti and syn triphenylphosphine substitution products and their degradation to known isomeric dienones[8] is shown as eq 3. Spectral and analytical data for **5** and **6** (Experimental Section) confirm these structures. Neither of these compounds gave detectable isomerization products

2e

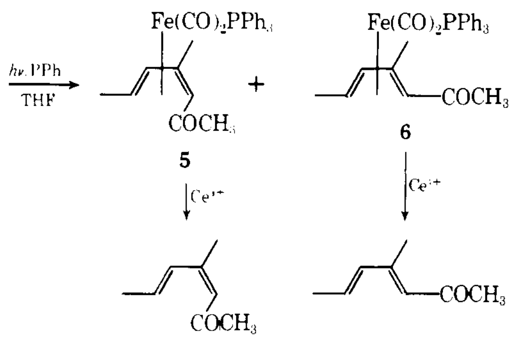


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Table I. Rates of Methoxide-Catalyzed Anti to Syn Isomerization of (Dienone)tricarbonyliron Complexes in Methanol at 22 ± 1 °C[a]

compd	k, L mol^{-1} h^{-1} [b]	k_{rel} [c]
1a	0.72	1.0
1b	0.66	0.9
1c[d]	0.6	0.8
1d[d]	0.4	0.5
1e[e]	0.55	0.8
1f	2.6	3.6
1g	0.3	0.4
3a	1.9	1.0
3b	1.5	0.8
3c[d]	1.1	0.6
3d[d]	1	0.6

[a] All samples, except **1e**, were run simultaneously in one thermostated bath in aliquots of the same 0.070 N methanolic sodium methoxide solution. [b] Probable error ±5% (±10% for **3c** and **3d**). [c] All methyl dienones **1a-g** relative to **1a** as 1.0. All phenyl dienones **3a-d** relative to **3a** as 1.0. [d] Run and analyzed as a mixture of the 2- and 3-methyl derivatives. [e] At 23 ± 1 °C.

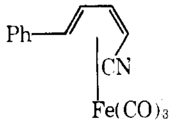
Table II. Rates of Sulfuric Acid Catalyzed Anti to Syn Isomerization of (Dienone)tricarbonyliron Complexes in Methanol at 22 ± 1 °C[a]

compd	k, L mol^{-1} h^{-1} [b]	k_{rel}
1a	6.6	1.0
1b	11	1.7
1c[c]	4.2	0.6
1d[c]	4.0	0.6

[a] Samples were run simultaneously in one thermostated bath in aliquots of the same 0.14 N methanolic H_2SO_4 solution. [b] Probable error ±8%. [c] Run and analyzed as a mixture of the 2- and 3-methyl derivatives.

after 25 h in 0.25 N methanolic sodium methoxide at 25 °C. After 8 days at 23 ± 2 °C in a solution of 3 mL of benzene and 5 mL of 1 N methanolic sodium methoxide, **5** gave a trace of **6** on TLC analysis. Triphenylphosphine and two unidentified minor products were noted. Substantial isomerization can be produced by acid catalysis. Treatment of **5** with methanolic sulfuric acid was accompanied by a slow color change from yellow to colorless. In 0.2 N acid the color change was complete after 4 h, and TLC analysis after 7 days at 23 ± 1 °C showed a small spot with an R_f value identical with that of **6.** In ca. 6 N acid the color change was complete in 1.5 h, and TLC analysis after 24 h at 23 ± 1 °C revealed more of the syn isomer **6** than of **5**.

Reinvestigation of dienonitrile complexes **7** and **8** confirmed the earlier report of Whitlock et al.[9] that H-D exchange at C_1 occurs without isomerization. Treatment of **7** with ca. 0.5 N NaOEt/EtOD at 22 °C for 5 h gave a minimum of 54% exchange, and **8** exchanged completely in 0.4 N NaOEt/EtOD at 23 °C for 16 h. A mixture of 60% **7** and 40% **8** was treated with 0.2 N methanolic sodium methoxide at 23 °C for 72 h. NMR analysis of the product showed that no more than 18% of the original **7** could have been isomerized to **8**. A similar test of pure **8** gave an upper limit of 10% isomerization. Owing to analytical difficulties, finite isomerization was confirmed in neither case.



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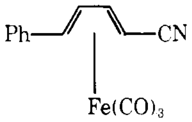

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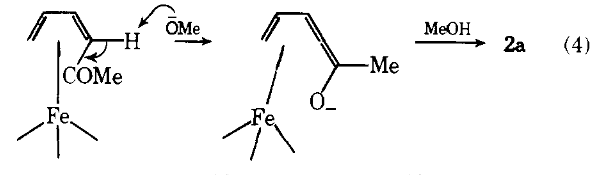
Discussion

We have considered explicitly the three mechanisms shown as eq 4-6 for methoxide catalysis. The proton abstraction mechanism, eq 4, is the simplest. The behavior of terminal carbons in (diene)tricarbonyliron complexes as saturated carbons in some regards[10] suggests the feasibility of this process. The "Michael addition" mechanism, eq 5, is derived from that suggested for H-D exchange at C_1 (e.g., via **10**) of syn (dienone)tricarbonyliron and related complexes by Whitlock et al.[9] Nucleophilic attack at iron, eq 6, gives an analogue of the familiar η^3-allyl-Fe(CO)$_3$X compounds.[11] The first and third mechanisms, but not the second, maintain coordinative saturation at iron throughout the isomerization process.

Table III. Rates of Base-Catalyzed H-D Exchange at C_1 for Syn (Dienone)tricarbonyliron Complexes

compd	solvent	temp, °C	k, L mol^{-1} h^{-1}
2b	EtOD	25 ± 1[a]	0.63 ± 0.5
2e	EtOD	25 ± 1[a]	1.5 ± 0.1
2e	MeOD	23 ± 1	0.43 ± 0.02

[a] Samples were run simultaneously in one thermostated bath in aliquots from the same ethanolic sodium ethoxide solution.



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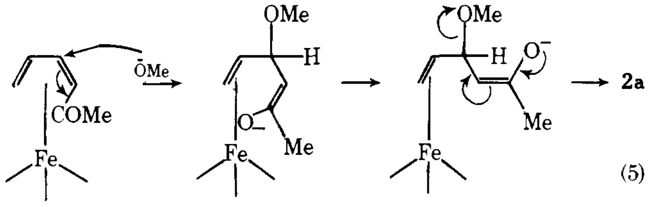
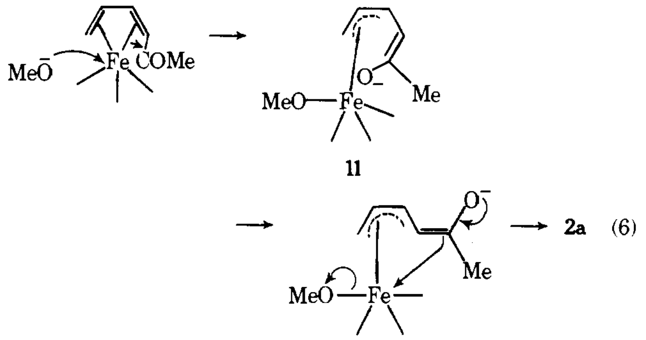


(5)

9 **10**



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(6)

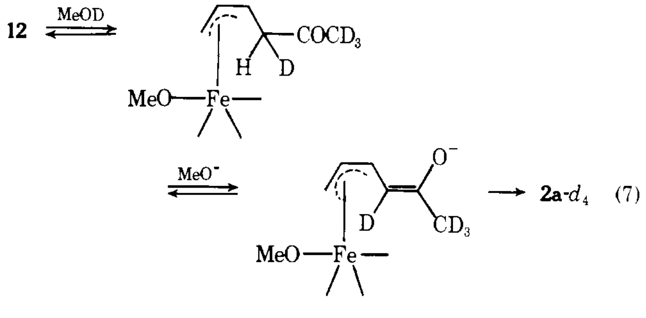
12

The proton-abstraction mechanism, eq. 4, is eliminated by the results of isomerization in MeOD, eq. 2. Since we have observed no exchange without isomerization, this mechanism should give an exchange to isomerization rate ratio of 1.0. Our observations define a maximum value of 0.4 for this rate ratio (exchange in the product after its formation has been ignored).

Nor is the "Michael addition" mechanism in accord with our experimental observations. Rates of Michael additions are decreased dramatically by substitution at C_β, the site of nucleophilic attack which is converted from sp^2 hybridization to sp^3 hybridization. In Michael addition of methanol to the enones MeCOCH=CR$_1$R$_2$ in methanolic sodium methoxide, introduction of a second methyl group at C_β reduces the rate by a factor greater than 290.[13] Crystal structures of relevant dienone-Fe(CO)$_3$ complexes[14] show that 2 substituents lie in or very close to the "diene" plane; thus C_2 in complexed dienones is sp^2 hybridized. The observed substituent effects (Tables I and II) are small, however. A report that the 2,3-

dimethyl derivative, **1h**, resists acid-catalyzed isomerization[15] finds no parallel in our data. Both 2- and 3-substituted derivatives isomerize readily in both acid and base. Introduction of a methyl group at C_2, the site of rate-determining nucleophilic attack in the Michael mechanism, causes the isomerization rate to decrease only by factors of 2 (**1a** and **1d**), 1.2 (**1b** and **1e**), and 1.9 (**3a** and **3d**). The drastic rate decrease caused by triphenylphosphine substitution is also in conflict with this mechanism. Replacement of the small CO ligand with a large triphenylphosphine should accelerate rate-determining formation of **9** owing to the attendant decrease of coordination number and crowding at iron.[16] Because of its better σ-donor and poorer π-acceptor properties, substitution of triphenylphosphine for CO might also stabilize an electron-deficient intermediate like **9** electronically. *Stable* 16-electron (η^3-cycloalkenyl)FeL_3 cations, L = $P(OMe)_3$, have been reported recently.[17]

Our observations are in complete accord with nucleophilic attack at iron, eq. 6. The rate-determining step should be formation of **11** by nucleophilic displacement at iron. The substituent effects are in accord with very small increases in electron density at carbons 2–4 in the transition state for this step. Steric crowding at iron will increase significantly on formation of the transition state. Thus, replacement of a small CO ligand with a large triphenylphosphine[15] will slow the reaction just as changes from primary to secondary to tertiary substrates slow bimolecular nucleophilic substitution at carbon.[18] The solvent isotope effect $k(\text{MeOD})/k(\text{MeOH}) \sim 3$ is probably within experimental error of the 2.3 value expected when methoxide is tightly bound in a transition state and its solvation shell dispersed.[19] The relative isomerization rates $k(\text{COPh}) > k(\text{COMe}) \gg k(\text{CN})$ are those expected on the basis of relative carbanion stability (Table IV). Finally, this mechanism provides a basis for understanding partial deuterium exchange at C_1 during isomerization (eq 7).



(7)

The small 2-methyl and large triphenylphosphine effects observed for acid-catalyzed isomerization make a strong case for a similar mechanism. Rapid, reversible protonation of the ketone oxygen followed by rate-determining attack of methanol or bisulfate ion at iron would produce the key intermediate **13** (X = $HOMe^+$ or OSO_2H). This is the same mechanism proposed by Clinton[5] based on a proposal by Mahler and Pettit for the mechanism of trans dienol formation in aqueous quenching of (*cis*-dienyl) tricarbonyliron cations.[20] Demonstration of nucleophilic attack at iron in the present case lends strong support to Mahler and Pettit's mechanism, which has never been proven.

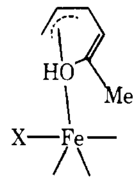


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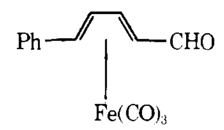
Table IV. Relative Ability of Substituent Groups to Stabilize Carbanions

compd	pK_a	ΔH, kcal/mol, for R-H(g) → R^-(g) + H(g)[a]
PhCOMe	19[b]	45.6
MeCOMe	20[c]	
EtOCOMe	24.5[d]	50.1
N≡CMe	25[c]	52.7

[a] T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 3399 (1976). [b] R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953). [c] W. K. McEwen, *ibid.*, **58**, 1124 (1936). [d] A. Streitwieser, Jr., and C. H. Heathcock, "Introduction to Organic Chemistry", Macmillan, New York, 1976.

H-D exchange at C_1 of 1-substituted (diene)tricarbonyliron complexes was first reported by Whitlock, Reich, and Markezich,[9] who proposed a "Michael mechanism", e.g., formation of **10** followed by deuteration-deprotonation. We can discuss exchange in the light of our data. The small rate increase produced by introduction of methyl at C_2 (Table III) strongly disfavors rate-determining nucleophilic attack at this position. The observation of Whitlock et al. that triphenylphosphine substitution completely suppressed H-D exchange was the genesis of our triphenylphosphine experiments. As pointed out above, the results strongly favor rate-determining nucleophilic attack at iron, not at C_2. The anomalous poor catalysis of exchange by potassium *tert*-butoxide[9] in *tert*-butyl alcohol can now be understood as the result of rapid destruction of the catalyst. H-D exchange of unsaturated ketones and nitriles does proceed via a "Michael" mechanism.[21] Complexation to an $Fe(CO)_3$ fragment slows this exchange only by a factor of ca. 2.[9] We expect a greater rate decrease for the Michael mechanism, since mononuclear iron compounds do not form coordinatively unsaturated species (**9** and **10**) readily. Nucleophilic attack at iron, which preserves coordinative saturation, is in better accord with this observation. Whitlock et al. reported base-catalyzed formation of the monotriphenylphosphine derivative of **14** in methanolic sodium methoxide, a result strongly indicative of the presence of some coordinatively unsaturated species such as **10**. Our attempts to perform similar reactions using **2e** and the aldehyde **15** failed. Typical conditions involved 1–2 equiv (0.16–0.066 M) triphenylphosphine in 0.29 M methanolic sodium methoxide for ca. 70 h (see Experimental Section).



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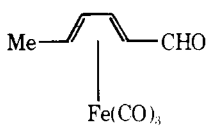

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Whitlock et al. observed the following dependence of exchange rate on the activating group: CN > CHO > COR > CO_2R. With the exception of the nitriles, the relative reactivities are those expected on the basis of relative carbanion stabilities (Table IV). Nitriles exchange much more rapidly than expected if formation of the cyano analogue of enolate **12** is rate determining. This, along with the ability of anti nitrile complexes to undergo exchange without loss of configuration, shows that exchange in nitrile complexes proceeds by a different mechanism.

Experimental Section

General. Infrared spectra were recorded using Beckman IR-10 and Perkin-Elmer 727 instruments. NMR spectra were obtained using Varian A-60 and Perkin-Elmer R-12 instruments, and were calibrated using internal Me_4Si. Mass spectra were recorded at an ionizing voltage of 80 eV using an Hitachi RMU-6L spectrometer. LC analysis of dienone mixtures has been described.[7] Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory. Preparation of most of the dienone complexes has been described.[3]

Synthesis of Triphenylphosphine Derivatives 5 and 6. Syn dienone complex **2e** (1.03 g, 3.92 mmol) and triphenylphosphine (0.974 g, 4.00 mmol) were irradiated in THF under nitrogen in a 200-mL Pyrex flask with a 275-W sunlamp. Reaction progress was monitored by TLC (silica gel/CH_2Cl_2): PPh_3, R_f 1.0; **2e**, R_f 0.8; **6**, R_f 0.6; **5**, R_f 0.4. At 21 h, irradiation was stopped and solvent was evaporated leaving a red oil. Fractionation by dry-column chromatography (neutral alumina Wolem/benzene) gave three orange bands. The band at highest R_f gave 442 mg (43%) of unreacted **2e**. The intermediate band gave 385 mg (35% based on starting material consumed) of **5** as a red oil. Crystallization by solution in CH_2Cl_2, addition of ca. 20% pentane, and cooling to −78 °C gave ((*Z,E*)-4-methyl-3,5-heptadien-2-one)dicarbonyltriphenylphosphineiron (**5**) as a yellow solid: mp 140 °C dec; IR ($CDCl_3$) 1980, 1920 (C≡O), and 1635 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.44 (broad, 15, PPh_3), 5.05 (d, 1, $J_{3,4}$ = 8.5 Hz, H_3), 2.06 (d, 1, J_{PH} = 12 Hz, H_1), 1.75 (s, 3, 2-CH_3), 1.62 (s, 3, $COCH_3$), 1.50 (d of d, 3, J_{4,CH_3} = 6, J_{PH} = 2 Hz, 4-CH_3), ca. 2.0-1.4 (m, ca. 1, H_6); mass spectrum virtually identical with that of **6** reported below.

Anal. Calcd for $C_{28}H_{27}FeO_3P$: C, 67.49; H, 5.46; Fe, 11.21. Found: C, 68.51; H, 5.88; Fe, 11.11.

Oxidative cleavage of **5** in acetone with cerric ammonium nitrate[20] gave (*Z,E*)-4-methyl-3,5-heptadienone identified by VPC[8] by comparison (retention time and peak enhancement by addition of authentic material to cleavage product) with an authentic sample.[22]

The low-R_f band gave 435 mg (39% based on starting material consumed) of **6** as a red oil. Solution in the minimum amount of 9:1 CH_2Cl_2/pentane and cooling to −78 °C gave ((*E,E*)-4-methyl-3,5-heptadien-2-one)dicarbonyltriphenylphosphineiron (**6**) as yellow crystals: mp 148-150 °C; IR (CCl_4) 1990, 1930 (C≡O), 1660 cm^{-1} (C=O); NMR (CCl_4) δ 7.42 (m, 15, PPh_3), 4.75 (d, 1, $J_{3,4}$ = 8.5 Hz, H_3), 2.44 (d, 3, J_{PH} = 2.5 Hz, 2-CH_3), 1.25 (s, 3, $COCH_3$), 0.97 (d, 3, J_{4,CH_3} = 6 Hz, 4-CH_3), ca. 0 (m, 1, H_4), −0.10 (d, 1, J_{PH} = 8.5 Hz, H_1); mass spectrum *m/e* 498 (M), 470 (M − CO), 442 (M − 2CO), 427, 401, 318 ($FePPh_3$), 262 (PPh_3), 240 ($FePPh_3 - C_6H_6$), 183, 124 (dienone ligand). No M − 3CO peak at *m/e* 414 was observed. Anal. ($C_{28}H_{27}FeO_3P$) C, H, Fe. Oxidative cleavage of **6** in acetone with cerric ammonium nitrate gave (*E,E*)-4-methyl-3,5-heptadien-2-one identified by VPC by comparison (see above) to an authentic sample produced by irradiation of the *Z,E* dienone in ether.[8]

Multiple substitution which has attended other photosubstitution reactions of (diene)tricarbonyliron compounds with phosphines[23] was not evident in the reactions described above. Compounds **5** and **6** were also produced when ((*Z,E*)-4-methyl-3,5-heptadien-2-one)tricarbonyliron was irradiated in THF in the presence of triphenylphosphine.

((*Z,E*)-5-Phenyl-2,4-pentadienonitrile)tricarbonyliron (7) and ((*E,E*)-5-Phenyl-2,4-pentadienonitrile)tricarbonyliron (8).[24] (*Z,E*)-5-Phenyl-2,4-pentadienonitrile (2.385 g, 15.4 mmol) and $Fe_2(CO)_9$ (9.8 g, 26.9 mmol) were heated at reflux under nitrogen in 100 mL of ether. After 57 h, TLC (silica gel/benzene) revealed unreacted diene. Additional $Fe_2(CO)_9$ (5.6 g, 15.4 mmol) and 50 mL of benzene were added, and heating at reflux was continued for 21 h, when TLC revealed no unreacted diene. The brown oil obtained after filtration and solvent removal was dissolved in the minimum amount of 4:1 CH_2Cl_2/pentane and was cooled to −78 °C to crystallize the syn isomer **8**. Successive reductions of solution volume and coolings gave a combined yield of 750 mg of **8**: IR (hexachlorobutadiene mull) 2230 (C≡N), 2080, 1995, 1945 cm^{-1} (C≡O); NMR ($CDCl_3$) δ 7.26 (s, 5, Ph), 6.2-5.2 (m, 2, H_2 and H_3), 2.30 (d, 1, $J_{3,4}$ = 9 Hz, H_4), 0.72 (d, $J_{1,2}$ = 7 Hz, H_1).

Dry-column chromatography on the mother liquor gave a center fraction of 550 mg which was rich in anti isomer **7**. Solution in 4:1 CH_2Cl_2/pentane and cooling to −78 °C gave ca. 100 mg of a tacky brown solid shown to be a 4:1 mixture of **7** and **8** by NMR integration: IR (film) 2220 (C≡N), 2080, 1990, 1945 cm^{-1} (C≡O); NMR ($CDCl_3$) δ 7.30 (s, broad, ca. 5, Ph), 6.15 (d of d, 1, $J_{2,3}$ = 5.5, $J_{3,4}$ = 10.5 Hz, H_3), 5.45 (d of d, 1, $J_{1,2}$ = 7.5, $J_{2,3}$ = 5.5, $J_{2,4} \sim$ 1 Hz, H_2), 3.91 (d, broad, $J_{3,4}$ = 10.5, $J_{2,4} \sim$ 1 Hz, H_4) 2.13 (d, 1, $J_{1,2}$ = 7.5 Hz, H_1); mass spectrum *m/e* 295 (M), 267 (M − CO), 239 (M − 2CO), 211 (M − 3CO), 184 (M − 3CO − HCN), 155 (diene ligand), 128 (diene ligand − HCN). The spectrum of pure **8** was virtually identical.

H-D Exchange and Attempted Equilibration of 7 and 8. A mixture 85-90% anti (**7**) was treated under nitrogen with a solution prepared by dissolving 116 mg of sodium in 10.4 mL of ethanol-*O-d* (calcd 0.485 M) at 22 °C for 5 h. Water (30 mL) was added and the organic products were isolated by CH_2Cl_2 extraction. An NMR spectrum of the total crude product showed disappearance of the doublet at δ 2.13 (H_1 of **7**) and collapse of the δ 5.45 quartet to a doublet (H_2 of **7**). Integration of the δ 2.13 region gave a finite signal, probably due to **8** and impurities, which limited our maximum estimate of deuterium incorporation to 54%.

Similar treatment of pure syn isomer, **8**, with 0.37 M NaOEt/EtOD for 16 h at 23 °C gave a product which showed complete disappearance of the NMR doublet at δ 0.72 (H_1) and broadening in the δ 6.2-5.2 region.

Similar treatment of a 3:2 mixture of **7** and **8** (100 mg) with 0.2 M NaOMe/MeOH for 72 h at 23 °C (solution was basic to litmus at 72 h) gave a crude product which was analyzed for **7** and **8** by NMR integration. Interfering impurities allowed only the conclusion that a maximum of 18% the original **7** could have isomerized to **8**. However, little or no isomerization may actually have occurred. An identical experiment starting with the syn isomer (**8**) led to the conclusion that no more than 10% of the original **8** could have isomerized.

Treatment of 2e and 15 with Triphenylphosphine in Base. Dienone **2e** (558 mg) and triphenylphosphine (567 mg, 1.1 equiv, 0.066 M) in 35 mL of 0.287 M NaOMe/MeOH were maintained at room temperature for 75 h. TLC analysis shows no change during this period. Use of authentic **6** demonstrated its absence. Organic material was isolated by an aqueous quench followed by CH_2Cl_2 extraction. Dry-column chromatography gave 365 mg (65.4%) of the original **2e**. The reaction time was equal to 13.5 half-lives for H-D exchange at C_1 in MeOD. Division by 3, to account for the lower reactivity of methoxide in MeOH,[19] gives 4.5 half-lives for conversion of **2e** to the putative coordinatively unsaturated intermediate **10**.

Aldehyde **15** (460 mg, 1.95 mmol) and triphenylphosphine (1.00 g, 4.1 mmol, 0.16 M) were stirred for 66.5 H in 25 mL of 0.287 M NaOMe/MeOH. TLC showed accumulation of small amounts of products at low R_f values. Dry-column chromatography of the products on alumina gave one broad, reddish-brown band which was cut into three equal lengths. The high-R_f fraction was mostly **15** (TLC) and yielded 210 mg (46%) of **15** on rechromatography. The middle fraction contained too little material and too many components to be characterized. The low-R_f fraction contained a small amount of material and was mainly **15** plus two lower R_f spots by TLC. The total sample differed from **15** by having new IR absorptions at 1920, 1880, and 1640 cm^{-1}.

Kinetic Measurements. Spectral quality methanol was dried by heating at reflux for 12 h with magnesium and subsequent distillation.[25] Dienone samples (sufficient to give 10^{-3} M solutions) were weighed into 10-mL volumetric flasks which were then filled with basic or acidic methanol and stoppered. These samples were immersed up to their necks in a thermostated bath at 22 ± 1 °C. At least ten (base) or four points (acid) were taken over 2 half-lives for each compound. Analyses were performed by injection of 1.0-m/L aliquots of the reaction mixtures directly onto the column of a liquid chromatograph.[7] Peak areas were normalized by division by ϵ_{254} (molar absorptivity at the detector wavelength) values determined using Cary 14 and Beckman DU (equipped with a Gilford detector system) spectrophotometers.

H-D exchange kinetics were determined in a similar fashion, except that dienone concentrations were higher and typically four or five aliquots were withdrawn in the 25-75% exchange region. Base concentration was monitored by titration of aliquots with standardized aqueous HCl. Dienones were isolated from aliquots by aqueous quenching followed by CH_2Cl_2 extraction and chromatography on silica gel. Control samples of undeuterated and 100% deuterated dienones were dissolved in deuterated base and immediately run through the isolation procedure. Loss of deuterium from the -$COCD_3$ group during chromatography was apparent, but the deuterium content at C_1 was unaffected. Deuterium content was assessed by NMR. For **2e** the δ 0.9 integral (H_1) was compared to those of the 2-methyl at δ 2.16 and H_3 at δ 5.32, which do not exchange. For **2b** the H_1 integral was compared to the H_2 and H_3 integrals. For this purpose $Pr(fod)_3$ reagent was added to the samples to shift the H_1 signal downfield away from the interfering H_4 and 4-methyl signals.

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Electronic Structure of Tetrahedral Carbonyls and Dinitrogen Complexes of Nickel, Cobalt, and Iron as Calculated by the Multiple-Scattering Method

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Abstract: A comparative study of the isoelectronic complexes $Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$, $Ni(N_2)_4$, $Co(N_2)_4^-$, and $Fe(N_2)_4^{2-}$ is made by the multiple scattering Xα method. The results show clearly a back-donation which increases in the series Ni, Co, Fe in good correlation with the decrease of the N_2 and CO stretching frequencies. The back-donation is of about the same magnitude for the carbonyl and dinitrogen complexes for a given metal. The larger stability of the carbonyls is ascribed to a stronger bonding via 4s and 4p orbitals.

I. Introduction

The nature of the chemical bond in metal carbonyls is subject to much interest in inorganic and theoretical chemistry.[2-3] Quite recently there has been a great interest also in N_2-transition metal complexes.[2] One obvious reason in the latter case is to obtain a deeper understanding of the role of transition-metal atoms in biological and industrial nitrogen fixation processes. In general, a detailed study of the interaction between CO or N_2 and transition-metal atoms is fundamental to the understanding of the bonding not only in numerous organometallic complexes but also in absorption of N_2 and CO on metal surfaces.

There have been a number of theoretical studies on $Ni(CO)_4$ and $Ni(N_2)_4$, by semiempirical,[4-7] multiple scattering,[8] LCAO-Xα,[9] pseudopotential,[10] and ab initio methods.[11-15] The isoelectronic complexes $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ have been studied by semiempirical methods[5] and approximate ab initio methods.[11] The conclusions regarding different bonding mechanisms are at some variance. The back-bonding mechanisms seems to be favored in ab initio and LCAO-Xα calculations[9,11-15] but usually the 4s bonding is considered to be small. The opposite seems to be the case in multiple scattering calculations.[8] The differences between the two methods may well be due to different means of interpreting the calculated molecular wave functions, however. It can be shown that back-bonding and back-donation occurs also in multiple scattering wave functions for $Ni(CO)_4$[16] as well as cyanides.[17]

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