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ELECTRONIC EFFECTS IN DIENETRICARBONYLIRON DERIVATIVES
I. THE RELATION BETWEEN ν(C≡O) AND HAMMETT'S σ_p

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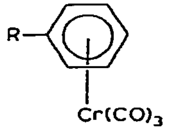
SUMMARY

The synthesis and spectral properties of a variety of *para*-substituted 1-phenyl-1,3-butadienes and their tricarbonyliron complexes are recorded. The C≡O stretching frequencies in the IR spectra are found to be linearly related to σ_p of the *para*-substituent. The effect is related to the degree of d_π–p_π bonding from the metal to the CO group.

INTRODUCTION

The relation between IR vibrational frequencies and substituent groups in benzene derivatives is a well-known phenomenon. In benzene derivatives of the type RC_6H_4X, where X is the functional group being examined and R is a *meta* or *para* substituent, linear relations have been found between the Hammett σ of R and the vibrational frequency of X[1-4].

IR spectral studies have been carried out on π-arenetricarbonylchromium compounds, of type (I), in the C–O stretching region[5,6].



(I)

These compounds also show sensitivity of the C–O absorption to the substituent group and have been related to the Hammett σ function. Of significance is the information that can be deduced on the bond-order for the C–O bond from the IR absorption maxima. Observable shifts occur toward higher or lower frequencies of the C–O stretching region when electron-withdrawing or electron-releasing groups are introduced into the benzene ring. The shift towards lower frequencies corresponds to

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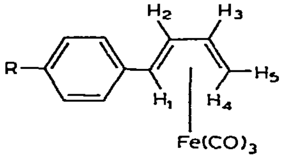
* Taken in part from the Ph.D. Thesis of L. Katz, Adelphi University, 1971.

lower C–O bond orders. This shift with strongly electron-donating groups has been related to the degree of d_π–p_π backbonding of electrons from the metal to the carbon monoxide group[7,8]; thus, the stronger the back-donation that is present, the lower the C–O bond order that results, and the greater the observed shift to lower frequencies that is observed.

In an effort to establish similar relationships for C≡O groups in dienetricarbonyliron complexes, various tricarbonyliron complexes of *para*-substituted 1-phenyl-1,3-butadienes, of type (II), were synthesized and examined in the C≡O region of the IR spectrum.



(II)

RESULTS AND DISCUSSION

The routes to the complexes of type (II) are outlined in Scheme 1. Details for the syntheses are found in the experimental section. Elemental analyses and spectral characteristics of these complexes agree with the assigned structures.

From the data given in Table 1, it can be seen that the C≡O stretching frequencies for complexes (II) varies with the *para*-substituent. From the plot of ν(CO)*vs.* the Hammett σ_p (Fig. 1), the relationship is linear*. This linear correlation of ν(C≡O) with σ_p indicates that the stretching vibration of the C≡O group is sensitive to the presence of substituent groups far removed from the site of C≡O attachment. Interaction arises solely through the ability of the *para*-substituent R to withdraw electrons

TABLE 1

ν(C≡O) OF *para*-SUBSTITUTED (PHENYLBUTADIENE)TRICARBONYLIRON COMPLEXES (II)

p-R	σ_p^a	ν(C≡O)^b (cm^{-1})		
(a) NH_2	−0.66	2047	1980	1973
(b) OCH_3	−0.268	2048	1983	1975
(c) H	0.00	2049	1986	1979
(d) $NHCOCH_3$	0.00	2050	1986	1979
(e) Br	+0.232	2052	1989	1981
(f) $COCH_3$	+0.502	2053	1990	1982
(g) CN	+0.660	2055	1993	1984

[a] Ref. 16. [b] CCl_4 solvent.

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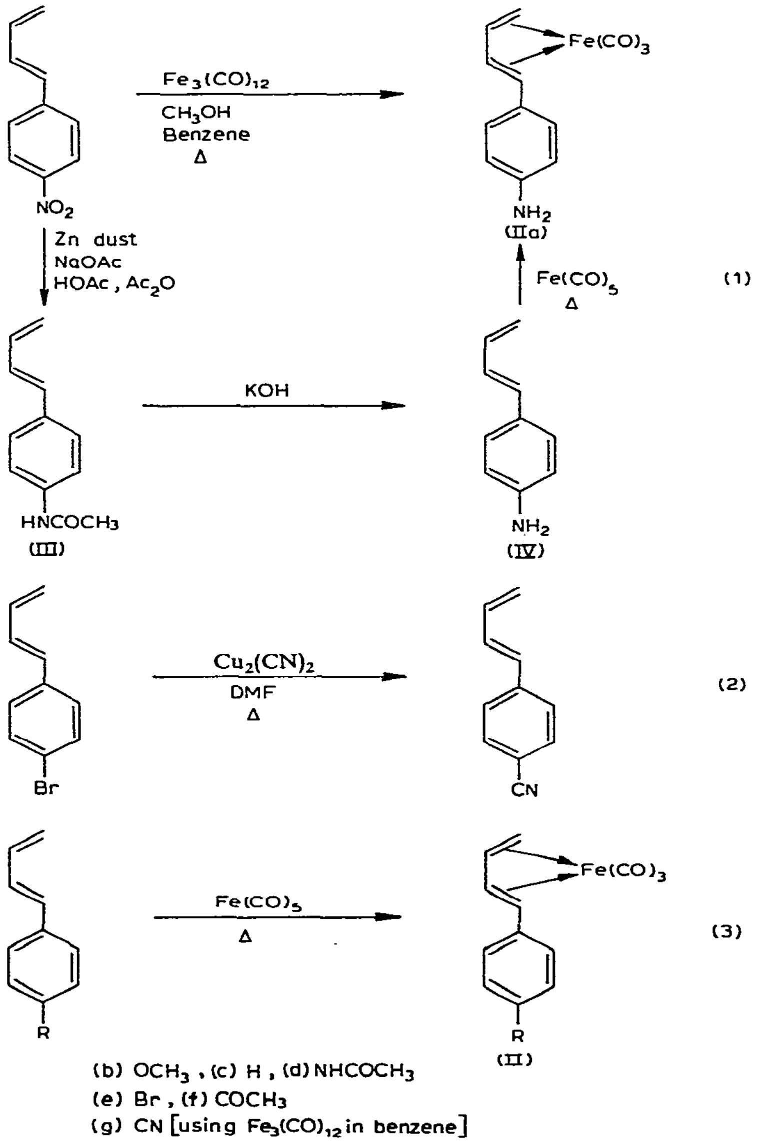
* Two data points appear in Fig. 1 for the high frequency carbonyl band at σ_p=0.00 (groups –NHAc and –H). This is due to the experimental observation of ν=2050 cm^{-1} for acetamido and ν=2049 cm^{-1} for hydrogen. There are single points for the two lower frequency carbonyl bands since the observed ν(C≡O) are identical for both acetamido and hydrogen.

SCHEME 1



from or supply electrons to the metal; the C–O bond order changes according to the *para*-substituent and is reflected in the frequency shifts. The direction is as expected. A lower frequency is observed for amino, a good electron donor, and corresponds to a lower C–O bond order; a higher frequency is observed for cyano, a good electron withdrawer, and corresponds to a higher C–O bond order; intermediate groups show effects consistent with their intermediate electronic character.

The information, thus, determines the relative magnitude of the electronic interaction and establishes the sought after relationship. However, definitive choice

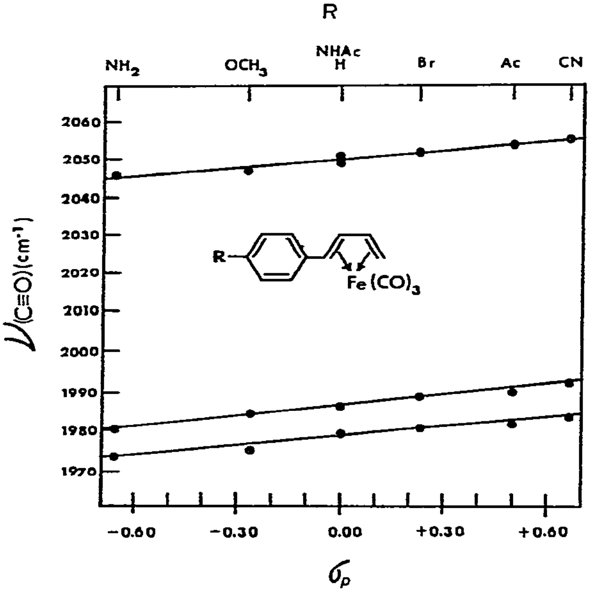


Fig. 1.

as to the character of the electronic interaction, *i.e.* whether inductive or mesomeric, cannot be made. We hope to enlarge upon this through experiments still in progress.

EXPERIMENTAL

General comments

All melting points were taken in capillary tubes using a Thomas Hoover "Uni-melt" apparatus and are uncorrected unless otherwise indicated. The IR spectra, for identification purposes, were recorded on a Perkin–Elmer Model 257 grating spectrophotometer. These were standardized against the 1944 cm^{-1} band of polystyrene for the C≡O region and the 1601 cm^{-1} band of polystyrene for the C=O region and below. For quantitative frequency correlations the IR spectra were recorded using a Beckman IR 7 prism-grating spectrophotometer and regions of the spectra were calibrated with the forementioned bands of polystyrene. Nuclear magnetic resonance (NMR) spectra were carried out on a Varian A-60 spectrometer; the chemical shifts are expressed in parts per million (τ) downfield from tetramethylsilane ($\tau = 10$) used as internal standard; coupling constants (J) are accurate to ±0.5 Hz (where s = singlet, d = doublet, dd = double doublet, m = multiplet, q = quartet). UV spectra were recorded on a Perkin–Elmer Model 202 spectrophotometer and are standardized against the spectra of holmium oxide glass[9].

Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York, and Spang Microanalytical Laboratory, Ann Arbor, Mich.. Column chromatography was carried out using the "Dry Column" method of Loev[10]. The silica gel used was approximately grade III (60–200) mesh. Pentacarbonyliron and dodecacarbonyltriiron were purchased from Alfa Inorganics, Beverly, Mass.

(1-Phenyl-1,3-butadiene)tricarbonyliron (IIc)

This complex was prepared according to the procedure of Mahler[11] from 161 ml (234 g, 1.20 mol) of pentacarbonyliron and 32.2 g (0.247 mol) of 1-phenyl-1,3-butadiene. Upon work-up a solid was obtained, 31.3 g (47%), m.p. 59–61° (lit[11].: m.p. 60–61°).

The spectral characteristics of (IIc) are as follows: IR: $\nu(CCl_4)$ 2049 and 1987 (C≡O), and 1979 cm^{-1} (C≡O); UV: λ_{max} (EtOH) 263 (ε 1.70×10^4) and 315 (ε 0.73×10^4) nm; NMR: τ ($CDCl_3$) 2.72 (s, 5, Ar–H), 4.19 (dd, 1, J 9.5 Hz, J 5 Hz, H_2), 4.50–4.96 (m, 1, H_3), 7.73–8.34 (m, 2, H_1 and H_5), and 9.45 (dd, 1, J 9 Hz, J 2.5 Hz, H_4).

[1-(p-Acetylphenyl)-1,3-butadiene]tricarbonyliron (IIf)[12]

To 430 mg (3.20 mmol) of anhydrous aluminum chloride in 35 ml of dry methylene chloride under nitrogen was added 0.25 ml (375 mg, 3.30 mmol) of acetyl chloride with stirring. The solution was stirred under nitrogen in an ice bath 15 min and then 815 mg (3.00 mmol) of (1-phenyl-1,3-butadiene)tricarbonyliron was added. The resulting deep red mixture was stirred at 5–8° for 1 min. The reaction mixture was then poured over 10 g of ice and stirred 10 min. The organic layer was washed with two 30 ml portions of water and dried (anh. Na_2SO_4). Solvent removal yielded a greenish-brown solid. Recrystallization from pentane gave 550 mg (86%) of yellow powder. Recrystallization from pentane containing 10% ether yielded 352 mg of yellow powder, m.p. 114.5–115.5° (cor.) (lit.[11]: m.p. 116–118°).

The spectral characteristics of (IIf) are as follows: IR: $\nu(CCl_4)$ 2051 and 1990 (C≡O), 1982 (C≡O), and 1690 cm^{-1} (C=O); UV: λ_{max} (EtOH) 288 (ε 1.35×10^4) and 320 (ε 1.17×10^4) nm; NMR: $\tau(CDCl_3)$ 1.88–3.08 [$(AB)_2$ q, d at 2.15, J 8.5 Hz, d at 2.77, J 8.5 Hz, 4, Ar–H], 3.82–4.33 (m, 1, H_2), 4.33–4.85 (m, 1, H_3), 7.46 (s, 3, $-COCH_3$), 8.08 (unsymmetrical d, 2, J 8 Hz, H_1 and H_5), and 9.30 (m, 1, H_4).

[1-(p-Methoxyphenyl)-1,3-butadiene]tricarbonyliron (IIb)

A mixture of 10.4 g (65.0 mmol) of 1-(*p*-methoxyphenyl)-1,3-butadiene[13] and 45.5 ml (66 g, 34 mmol) of pentacarbonyliron was stirred at 116° under nitrogen for 48 h. Excess pentacarbonyliron was removed *in vacuo*. The dark residue was refluxed with four-125 ml portions of hexane. The combined orange hexane solution was filtered and concentrated to yield an orange solid. This was recrystallized from hexane to give 8.3 g (43%) of orange plates, m.p. 96–97° (cor.). (Found: C, 56.25; H, 4.01. $C_{14}H_{12}FeO_4$ calcd.: C, 56.03; H, 4.03%.)

The spectral characteristics of (IIb) are as follows: IR: $\nu(CCl_4)$ 2850 (CH_3), 2048 (C≡O), 1983 and 1975 (C≡O), and 1256 cm^{-1} ($O–CH_3$); UV: λ_{max} (EtOH) 270 (ε 1.14×10^4) and 315 (ε 0.87×10^4) nm; NMR: $\tau(CDCl_3)$ 2.65–3.40 [$(AB)_2$q, d at 2.84, J 9 Hz, d at 3.24, J 9 Hz, 4, Ar–H], 4.21 (dd, 1, J 9.5 Hz, J 4.5 Hz, H_2), 4.47–4.92 (m, 1, H_3), 6.25 (s, 3, CH_3–O), 7.93 (d, 1, J 9.5 Hz, H_1) 8.25 (dd, 1, J 7.5 Hz, J 2.5 Hz, H_5), and 9.45 (dd, 1, J 9 Hz, J 2.5 Hz, H_4).

[1-(p-Bromophenyl)-1,3-butadiene]tricarbonyliron (IIe)

A solution of 30.3 g (0.146 mol) of 1-(*p*-bromophenyl)-1,3-butadiene[13] in 100 ml (140 g, 0.743 mol) of pentacarbonyliron was stirred for 40 h at 105–110° under a nitrogen atmosphere. Excess pentacarbonyliron was removed under reduced pressure and the viscous dark residue was refluxed with five 100 ml portions of ligroin (b.p. 60–90°). The combined ligroin solution was filtered and solvent removed under reduced pressure yielding a yellow-green oil which solidified on cooling. The crude yield of 26.9 g (53 %) was recrystallized from pentane to yield 16.9 g (33 %) of yellow solid, m.p. 82–85°. Column chromatography through Florisil yielded (IIe) in the third fraction with ligroin used as elutant [(IIe) followed fractions of pentacarbonyliron and a dark green material of unknown nature]. The yellow solid was recrystallized from pentane (cooled to −78°), as a yellow powder, m.p. 88–89° (cor.). (Found: C, 45.00; H, 2.81. $C_{13}H_9BrFeO_3$ calcd.: C, 44.75; H, 2.58 %.)

The spectral characteristics of (IIe) are as follows: IR: $\nu(CCl_4)$ 2052 (C≡O), 1989 and 1981 cm^{-1} (C≡O); UV: λ_{max} 259 (EtOH) (ε 1.77×10^4) and 315 (ε 0.89×10^4) nm; NMR: $\tau(CHCl_3)$ 2.50–3.20 [$(AB)_2$ q, d at 2.62, J 11 Hz, d at 2.95, J 11 Hz, 4, Ar–H], 4.17 (dd, 1, J 9.5 Hz, J 5 Hz, H_2), 4.45–4.85 (m, 1, H_3), 7.92–8.29 (m, 2, H_1 and H_5), and 9.38 (dd, 1, J 9.5 Hz, J 3 Hz, H_4).

1-(*p*-*Cyanophenyl*)-1,3-*butadiene*

A mixture of 12.7 g (61.0 mmol) of 1-(*p*-bromophenyl)-1,3-butadiene[13], 6.80 g (38.0 mmol) of cuprous cyanide, and 0.20 g hydroquinone in 80 ml of dimethyl formamide was heated 2.5 h at 150–155°, with stirring, under a nitrogen atmosphere. The hot reaction mixture was poured into a solution containing 157 ml of water and 43 ml of ethylene diamine. The mixture was extracted with three 150 ml portions of petroleum ether (b.p. 30–60°). The extracts were washed with water and dried (anh. K_2CO_3). The extract was filtered, the drying agent washed with ether, the washings and filtrate combined and concentrated *in vacuo*. The resulting clear viscous liquid was dissolved in a small amount of methylene chloride, mixed with a small portion of silica gel and solvent removed *in vacuo*. This residue was placed on top of a column containing 150 g of silica gel.

Elution with ligroin (b.p. 60–90°) yielded 3.53 g of starting material. Elution with carbon tetrachloride yielded 3.90 g (51 %) of a low melting white solid. Further elution with benzene yielded 1.38 g of a viscous amber oil which appeared to be polymeric. An analytical sample of the diene was prepared from the low melting white solid by two recrystallizations from petroleum ether (b.p. 30–60°), white platelets, m.p. 51.5–52.0° (cor.). (Found: C, 85.14; H, 5.78; N, 9.14. $C_{11}H_9N$ calcd.: C, 85.15; H, 5.84; N, 9.04 %.)

The spectral characteristics of 1-(*p*-cyanophenyl)-1,3-butadiene are as follows: IR: $\nu(CCl_4)$ 2233 (C≡N), 1606 cm^{-1}; NMR: $\tau(CCl_4)$ 2.50–3.35 [$(AB)_2$ q, d at 2.80, J 8.5 Hz, d at 3.09, J 8.5 Hz, 4, Ar–H], 3.27–4.12 (m, 3, –HC=CH–CH=), 4.80 (d, 1, J 9 Hz, =CH_2), and 5.00 (d, 1, J 4 Hz, =CH_2).

[1-(*p*-*Cyanophenyl*)-1,3-*butadiene*]*tricarbonyliron* (*IIg*)

A mixture of 3.60 g (23.0 mmol) of 1-(*p*-cyanophenyl)-1,3-butadiene and 10 g of dodecacarbonyltriiron (containing approx. 10 % methanol) in 180 ml of benzene was heated under nitrogen with stirring for 8.5 h. The mixture was filtered and concentrated under reduced pressure to give 4.15 g of viscous liquid. This was dissolved in a small amount of methylene chloride, mixed with a quantity of silica gel and solvent removed *in vacuo*; the residue was placed on a column containing 120 g of silica gel. Elution with petroleum ether (b.p. 30–60°) separated a yellow band. Further elution with carbon tetrachloride removed the yellow band from the column; this was starting material (1.03 g recovered). Continued elution with carbon tetrachloride removed

2.46 g (52%) of (IIg) from the column. Washing the crude complex with pentane resulted in 1.03 g, m.p. 124.5–127.5°. An analytical sample was prepared by recrystallization from hot hexane, gold crystals, m.p. 126.5–128.5° (cor.). (Found: C, 57.09; H, 3.18; N, 5.05. $C_{14}H_9FeNO_3$ calcd.: C, 57.00; H, 3.08; N, 4.75%.)

The spectral characteristics of (IIg) are as follows: IR: $\nu(CCl_4)$ 2232 (C≡N), 2055 and 1993 (C≡O), and 1984 cm^{-1} (C≡O); UV: λ_{max} (EtOH) 277 (ε 1.77×10^4) and 315 (ε 1.08×10^4) nm; NMR: $\tau(CDCl_3)$ 2.21–3.16 [$(AB)_2$ q, d at 2.46, J 8 Hz, d at 2.78, J 8 Hz, 4,Ar–H], 4.09 (dd, 1, J 9.5 Hz, J 4.5 Hz, H_2), 4.32–4.83 (m, 1, H_3), 7.83–8.36 (m, 2, H_1 and H_5), and 9.28 (dd, 1, J 9 Hz, J 3 Hz, H_4).

1-(*p*-*Acetamidophenyl*)-1,3-*butadiene* (*III*)

To a stirred solution of 37.35 g (0.2000 mol) of 1-(*p*-nitrophenyl)-1,3-butadiene[14] in a mixture containing 850 ml of glacial acetic acid, 850 ml of acetic anhydride, and 60 g of sodium acetate, was added 100 g (1.53 g-atom) of zinc dust over 20 min. The solution was stirred an additional 2 h at room temperature. Excess zinc and sodium acetate was removed by suction filtration and the yellow solution concentrated under reduced pressure. The yellow solid which resulted was allowed to stand overnight in contact with one liter of dilute ammonium hydroxide; the solid was broken up, placed in a Büchner funnel, and washed with several liters of water. The solid was then dried by suction, spread out in a large porcelain dish, and allowed to air dry overnight. The dry solid was heated in 800 ml of benzene and insolubles filtered away. The benzene solution was decolorized with Norite, filtered, and cooled in a refrigerator. The yellow crystals were removed by filtration, dried by suction, broken up, and washed with water. After drying the yield was 20.5 g (55%) of yellow solid, m.p. 139–145°. An analytical sample was prepared by recrystallizing twice from benzene to give a very light yellow powder, m.p. 161–163° (cor.) (sealed evacuated tube). (Found: C, 77.09; H, 7.13; N, 7.24. $C_{12}H_{13}NO$ calcd.: C, 77.00; H, 7.00; N, 7.47%.)

The spectral characteristics of (III) are as follows: IR: $\nu(CHCl_3)$ 3434 (NH), 1690 (C=O), 1601, 1588, and 1514 cm^{-1}; NMR: $\tau(DMSO\text{-}d_6)$ 0.06 (broad s, 1, –NH–Ac), 2.20–2.75 [$(AB)_2$ q: d at 2.36, J 9 Hz, d at 2.60, J 9 Hz, 4, Ar–H], 3.10–3.80 (m, 3, –HC=CH=CH=), 4.43–4.97 (m, 2, =CH_2), and 7.90 (s, 3, –$COCH_3$).

[1-(*p*-*Acetamidophenyl*)-1,3-*butadiene*]*tricarbonyliron* (*IId*)

A mixture of 15.2 g (0.0810 mol) of 1-(*p*-acetamidophenyl)-1,3-butadiene and 300 ml (223 g, 1.14 mol) of pentacarbonyliron was heated under nitrogen, with stirring, at 104–109° for 24 h. Removal of the solvent under reduced pressure yielded a dark residue which was extracted with petroleum ether (b.p. 30–60°). Extraction with one liter of acetone resulted in a brown solution which was filtered, and concentrated to a dark brown solid. This solid was extracted with three 500 ml portions of petroleum ether (b.p. 30–60°) in order to remove colored impurities. The residue was heated with 300 ml of refluxing benzene. This benzene solution was filtered and cooled to give 5.62 g of yellow solid, m.p. 174–177°. The benzene mother liquor was then refluxed with the remaining undissolved residue, filtered, and concentrated to a volume of 100 ml; cooling gave 1.37 g of yellow solid, m.p. 169–176°. An additional 1.97 g of solid, m.p. 173–177°, was obtained by concentration of the petroleum ether extracts. Total yield was 8.96 g (34%). An analytical sample was prepared by recrystallizing twice from benzene yielding a yellow power, m.p. 181–183° (decompn.) (cor.). (Found: C, 55.32; H, 4.30; N, 4.54. $C_{15}H_{13}FeNO_4$ calcd.: C, 55.15: H, 4.02; N, 4.28%.)

The spectral characteristics of (IId) are as follows: IR: $\nu(CHCl_3)$ 3436 (NH), 2050 and 1984 (C≡O), 1700 (C=O), and 1685 cm^{-1}; UV λ_{max} (EtOH) 280 (ε 1.79×10^4) and 315 (ε 1.38×10^4) nm; NMR: $\tau(CDCl_3)$ 2.36 (broad s, 1, Ar–NHAc), 2.42–3.00 (m, 4, Ar–H), 4.15 (q, 1, J 10 Hz, J 5 Hz, H_2), 4.43–4.87 (m, 1, H_3), 7.99 (s, 3, $-COCH_3$), 8.02–8.40 (m, 2, H_1 and H_5), and 9.38 (dd, 1, J 9.5 Hz, J 3 Hz, H_4).

1-(*p-Aminophenyl*)-1,3-*butadiene* (*IV*)

A solution of 17.6 g of potassium hydroxide in 12.6 ml of water was diluted to 50 ml with methanol before adding 7.70 g (41.0 mmol) of 1-(*p*-acetamidophenyl)-1,3-butadiene. The mixture was heated 15 min on a steam bath, with stirring, before 5 ml of water was added; heating was then continued for an additional 15 min. Extraction of the cooled solution with ether yielded, upon evaporation of the ether, 4.22 g of a red liquid. This red liquid was distilled in a micro distillation apparatus to yield 2.22 g (37%) of a water white liquid, b.p. 84–86° (0.04–0.05 mm). This was redistilled to give an analytical sample of 1-(*p*-aminophenyl)-1,3-butadiene. (Found: C, 82.60; H, 7.50; N, 9.71. $C_{10}H_{11}N$ calcd.: C, 82.75; H, 7.63; N, 9.65%.)

The spectral characteristics of (IV) are as follows: IR: $\nu(CCl_4)$ 3477 and 3392 (NH_2), 1621, 1616, 1601, and 1516 cm^{-1}; NMR: $\tau(CCl_4)$ 2.88–3.83 [$(AB)_2$ q:d at 3.02, J 8 Hz, d at 3.67, J 8 Hz, 4, Ar–H], 3.51–4.08 (m, 3, –CH=CH–CH=), 4.73–5.31 (m, 2, $=CH_2$), and 6.57 (broad s, 2, Ar–NH_2).

The phenyl thiourea derivative was prepared by heating the amine with an excess of phenyl isothiocyanate. Several recrystallizations from aqueous ethanol gave an off-white solid, m.p. 137–140° (decompn.). (Found: C, 68.66: H, 5.73. $C_{17}H_{16}N_2S \cdot H_2O$ calcd.: C, 68.55; H, 6.08%.)

The spectral characteristics of the phenyl thiourea derivative are as follows: IR: ν(KBr) 3187 (NH), 1581, 1588, and 1530 cm^{-1}; UV: λ_{max} (MeOH) 205 (ε 4.6×10^4) and 277 (ε 2.7×10^4) nm; NMR: τ(DMSO-d_6) 0.36 (s, 2, –NHCSNHPh), 2.46–3.22 (m, 9, Ar–H), 3.22–4.16 (m, 3, –HC=CH–CH=) and 4.78 (d, 2, J 16 Hz, $=CH_2$).

[1-(*p-Aminophenyl*)-1,3-*butadiene*]*tricarbonyliron* (*IIa*)

(*a*). A mixture of 2.16 g (15.0 mmol) of 1-(*p*-aminophenyl)-1,3-butadiene and 15 ml (22 g, 0.11 mol) of pentacarbonyliron was heated under a nitrogen atmosphere, with stirring, at 110–115° for 24 h. Removal of excess pentacarbonyliron yielded a yellow solid which was taken up in acetone. The acetone solution was filtered and the solvent removed yielding a tarry solid. This was refluxed 4 times with 125 ml portions of ligroin (b.p. 60–90°) and the combined solutions cooled to –78°. The solution was filtered and yielded 0.38 g of yellow solid. The volume of the filtrate was reduced and the solution cooled and filtered to yield an additional 0.49 g. Evaporation to dryness followed by recrystallization of the residue from petroleum ether (b.p. 30–60°) yielded an additional 0.53 g. The total yield was 1.40 g (33%), m.p. 77.5–78.5°. A sample was recrystallized from petroleum ether (b.p. 30–60°) and gave a gold colored solid, m.p. 90.5–93°. An analytical sample was prepared by recrystallizing from petroleum ether (b.p. 30–60°) to give a gold solid, m.p. 95.5–96° (cor.). (Found: C, 55.08; H, 3.68; N, 5.21. $C_{13}H_{11}FeNO_3$ calcd.: C, 54.80; H, 3.89; N, 4.92%.)

The spectral characteristics of (IIa) are as follows: IR: $\nu(CCl_4)$ 3482 and 3402

(NH_2), 2047 and 1980 (C≡O), 1973 (C≡O), and 1257 cm^{-1} (C–N); UV: λ_{max} (EtOH) 275 (ε 0.91 × 10^4) and 323 (ε 0.99 × 10^4) nm; NMR: $\tau(CDCl_3)$ 2.65–3.84 [$(AB)_2$ q: d at 2.95, *J* 8 Hz, d at 3.51, *J* 8 Hz, 4, Ar–H], 4.25 (dd, 1, *J* 10 Hz, H_2), 4.46–4.95 (m, 1, H_3), 6.52 (broad s, 2, Ar–H_2), 7.90 (d, 1, *J* 9.5 Hz, H_1), 8.23 (dd, 1, *J* 7.5 Hz, H_5), and 9.48 (dd, 1, *J* 9.5 Hz, *J* 2.5 Hz, H_4).

(*b*). A mixture of 1.75 g (10.0 mmol) of 1-(*p*-nitrophenyl)-1,3-butadiene, 12.0 g of dodecacarbonyltriiron (containing approx. 10% methanol) and 2.5 ml methanol in 100 ml of benzene was stirred at 70° for 15 h[15]. The mixture was filtered, decolorized with charcoal and solvent removed. The solid was triturated with pentane and filtered to give 2.27 g (80%) of yellow gold solid, m.p. 80–86°. Two recrystallizations from petroleum ether (b.p. 30–60°) gave pure sample, m.p. 95.5–96.5° (cor.).

Correlation of ν(C≡O) vs. σ_p

The IR spectra of all the *para*-substituted (phenylbutadiene)tricarbonyliron complexes were recorded on a Beckman IR-7 double-beam, prism-grating IR spectrophotometer equipped with NaCl optics. Solutions were prepared using spectral grade carbon tetrachloride (obtained from J. T. Baker). These solutions then were diluted until the C≡O absorptions were of a suitable intensity for wave number measurements (band positions were not significantly concentration dependent). The spectra of these solutions were recorded *vs.* pure solvent in NaCl micro cavity cells (0.1 mm pathlength; 9 μl capacity). The recorded wave numbers (ν) were all corrected using the 1944 cm^{-1} band of polystyrene as reference; band positions are believed good to better than ± 1.0 cm^{-1}. Spectral data is presented in Table 1; ν(C≡O) *vs.* σ_p is plotted in Fig. 1.

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