1226 *Organometallics* 1982, *1*, 1226–1229

Bridged Ferrocenes. 9.[1] Lithiation and Subsequent Reactions of 1,1′-Trimethyleneferrocene

Manny Hillman,*[2] Linda Matyevich, Etsuko Fujita, Uttam Jagwani, and Jefferson McGowan

*Chemical Sciences Division, Department of Energy and Environment, Brookhaven National Laboratory,
Upton, New York 11973*

Received May 11, 1982

Dilithiation of a trimethylene-bridged ferrocene with *n*-butyllithium and TMEDA selectively metalated the ring at the 2,2′- or the 3,3′-positions. The dilithio derivatives were converted to the dicarboxylic acid, the dibromo, and the diiodo derivatives.

Introduction

For several anticipated applications such as the formation of an additional bridge under alkaline conditions[3,4] (formation of a bridge from a propionic acid using trifluoracetic anhydride causes rearrangement of a bridge of 1,1′,2,2′,4,4′-tris(trimethylene)ferrocene-3-propionic acid),[5] Ullmann type coupling of dihalo derivatives to form bridged [0,0]ferrocenophanes,[6,7] and the formation of bridged [1,1]ferrocenophanes,[8] it is desirable to able to place a pair of substituents on the corresponding positions of each ring of a bridged ferrocene. Friedel–Crafts acetylation of 1,1′-trimethyleneferocene, I (see Figure 1 for structures), have been found to form all of the disubstituted products but 2,2′-diacetyltrimethyleneferrocene and 3,3′-diacetyltrimethyleneferrocene.[9] However, since dilithiation of ferrocene using *n*-butyllithium and TMEDA[10] was shown[11] to involve an intermediate holding the two lithiums as part of a bridge spanning the two rings, it would appear that the steric requirements of dilithiation of any trimethylene-bridged ferrocene would give a product whose lithium atoms are on the corresponding positions of each ring. This paper reports an investigation of this reaction.

Results

The trimethyleneferrocene, I, was lithiated with *n*-butyllithium and TMEDA, followed by reaction with CO_2, $BrCF_2CF_2Br$, or I_2 to give mixtures of the mono- and dicarboxylic acids, bromides, or iodides. Since the carboxylic acids were difficult to purify, they were converted to their methyl esters. Chromatographic separation gave the pure products later identified as the 2-carbomethoxy, bromo, or iodo derivative, IIa–c, the corresponding derivatives with the substituents on the 3-position, IIIa–c, the disubstituted derivatives with substituents on the 2- and 2′-positions, IVa–c, and the disubstituted derivatives with substituents on the 3- and 3′-positions, Va–c.

When potassium *tert*-butoxide was used as a base instead of TMEDA, very little of IVa or IVb was formed and new minor disubstituted derivatives were observed, tentatively identified as VIIIa,b. This reaction was not carried out by using iodine. However, the VIIIc was isolated from that reaction mixture using TMEDA as a minor product.

Discussion

The structural assignments of the disubstituted products were based primarily on the NMR spectra but also on the comparison of one of the products with a sample of the compound with one of the two alternative structures. Analysis of the ^{13}C NMR spectrum (both coupled and decoupled with ^{1}H) of Va narrowed consideration to four possible isomers, the 2,2′, the 2,5′, the 3,3′, and the 3,4′ isomers. This interpretation was based on the detection of nine different carbon atoms with the expected couplings. The other possible isomers have lower symmetry with 11 or 17 different carbon atoms. The ^{1}H NMR spectrum of Va contains two different ring protons in the ratio of 2:1 with the more abundant protons downfield (δ 4.82) from the others (δ 4.15). The downfield protons are the ones vicinal to the carbomethoxy groups. Since there are twice as many of these, Va must be either the 3,3′ or the 3,4′ derivative. The reverse is true for IVa. The downfield ring protons are half the abundance of the others, and this confirms the assignment of IVa as either the 2,2′ or the 2,5′ derivative.

Further examination of the ^{1}H NMR spectra of IVa and Va are suggestive that these compounds are in fact the 2,2′- and the 3,3′-dicarbomethoxy derivatives. The bridge protons of I are found as a single sharp peak, even at 360 MHz, despite the fact that the α- and β-protons differ. In Va, at 80 MHz the bridge protons form a broad peak which becomes a pair of broad multiplets at 360 MHz separated by 0.1 ppm. In IVa, the bridge protons have been modified from I by an even greater extent, forming a pair of broad multiplets separated by 0.6 ppm. This behavior can be explained if the carbomethoxy groups are on the corresponding positions of each ring. The aposition of the carbomethoxy groups, even though on different rings, is accompanied by a repulsion and a consequent change in the ring-tilting geometry from that in I. The carbomethoxy groups in the 2- and 2′-positions exert an even greater distortion on the bridge than those on the 3- and 3′-positions. This is evident in the ^{1}H NMR spectra as a greater separation of the bridge-proton peaks in IVa than in Va.

This interpretation requires that the interaction of carbomethoxy groups on the 3- and 4′-positions do not

---

[1] Paper 8: Fujita, E.; Gordon, B.; Hillman, M.; Nagy, A. G. *J. Organomet. Chem.* **1981**, *218*, 105–114.

[2] To whom correspondence should be addressed.

[3] Barr, T. H.; Watts, W. E. *Tetrahedron* **1968**, *24*, 3219–3235.

[4] Mock, W.; Richards, J. H. *J. Org. Chem.* **1962**, *27*, 4050–4051.

[5] Hillman, M.; Gordon, B.; Weiss, A. J.; Guzikowski, A. P. *J. Organomet. Chem.* **1978**, *155*, 77–86.

[6] Hedberg, F. L.; Rosenberg, H. *J. Am. Chem. Soc.* **1969**, *91*, 1258–1259.

[7] Cowan, D. O.; LeVanda, C. *J. Am. Chem. Soc.* **1972**, *94*, 9271–9272.

[8] Cassens, A.; Eilbracht, P.; Nazzal, A.; Prossdorf, W.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1981**, *102*, 6367–6372.

[9] Winstead, J. A.; McGuire, R. R.; Cochoy, R. E.; Brown, A. D., Jr.; Gauthier, G. J. *J. Org. Chem.* **1972**, *37*, 2055–2060.

[10] Rausch, M. D.; Ciappenelli *J. Organomet. Chem.* **1967**, *10*, 127–136; Kovar, R. F.; Rausch, M. D.; Rosenberg, H. *Organomet. Chem. Synth.* **1970–1971**, *1*, 173–181.

[11] Walczak, M.; Walczak, K.; Mink, R.; Rausch, M. D.; Stucky, G. *J. Am. Chem. Soc.* **1978**, *100*, 6382–6388.

0276-7333/82/2301-1226$01.25/0 © 1982 American Chemical Society

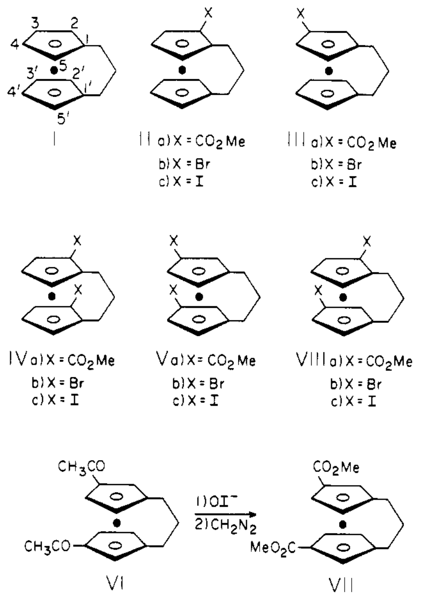

Figure 1. Structures of ferrocene derivatives. The filled circles are the iron atoms.

exert a strong influence on the bridges. Confirmation was obtained by the synthesis of a sample of the 3,4′-dicarbomethoxy derivative, VII, from VI, and the examination of its ^{1}H NMR spectrum. Not only did the spectrum differ from that of Va, but also the influence of the carbomethoxy groups on the bridge protons is small. A single, though slightly broadened, peak is found for the bridge protons even at 360 MHz.

Assignment of the structures of the dibromide and diiodides was corroborated by similar arguments concerning the deformation of the bridge-proton signals in the ^{1}H NMR spectra. In both cases, the bridge protons had signals of greater complexity for the 2,2′ than for the 3,3′ derivatives. The relative positions of the ring protons were the same for IVb and Vb as for IVa and Va. The downfield shift caused by the bromine is not as great as that caused by the carbomethoxy group. The influence of the iodine atoms in IVc and Vc is not as clear, and it is possible that the iodide in some cases acts as an electrophobe. The ring protons of the dibromides and the diiodides were better resolved than those of the dicarbomethoxy groups, and the assignments were easier; e.g., in IVb,c triplets exist with ortho coupling (J = 2.5–2.7 Hz) consistent with the 4,4′ protons and in Vb,c triplets exist with meta coupling (J = 1.2 Hz) consistent with the 2,2′ protons. Tentative assignments of all of the ring protons that are consistent with the structures are given in the Experimental Section.

The monocarbomethoxy derivatives IIa and IIIa had properties that resemble those in the literature and the structural assignments were made accordingly. The structure assignments of IIb,c and IIIb,c were deduced from the ^{1}H NMR spectra by the greater deformation of the bridge protons in the 2-substituted derivatives (IIb,c) than in the 3-substituted derivatives (IIIb,c) and by the observance of a triplet with ortho coupling in IIc. In addition, the structural assignments of all of the compounds are consistent with the observation[9] that the order of elution on chromatography follows the pattern that derivatives of I with substituents in the 2-position are eluted before derivatives with substituents in the 3-position.

Thus, dilithiation of I with *n*-butyllithium and TMEDA places the lithium atoms on corresponding positions of each ring. The use of other bases are expected to enhance the speed of the reaction but are expected to be not as selective in the positioning of the metal atoms.[12] In an adaptation of Osborne's[12] and Schlosser's[13] methods, *n*-butyllithium was used together with potassium *tert*-butoxide as the base in a reaction with I. The results for bromination and carboxylation were essentially the same except that either no or very little 2,2′ derivative was formed and small amounts of new products, VIIIa,b, were isolated. Since a corresponding diiodination product VIIIc was isolated from the reaction by using TMEDA, it appears that the formation of the new dibromo and dicarboxy derivatives was not induced by the presence of potassium *tert*-butoxide but that isolation was made easier by the absence or negligible presence of IVa,b as products.

A tentative assignment of the structures was made essentially on the basis of the ^{1}H NMR spectrum of VIIIa and VIIIc. In VIIIa there are two methyl groups, indicating that the compound is asymmetrical. The presence of the somewhat broad bridge protons indicates substitution in the 2-position. Of the four possibilities, 2,3, 2,4, 2,3′, and 2,4′, the last two derivatives are each expected to have a ring proton with a triplet with ortho coupling and a ring proton with a triplet with meta coupling, as does the observed spectrum of VIIIa. Since the formation of a dilithio derivative with lithium on neighboring atoms appears to be preferred, the dicarbomethoxy derivative is assigned the structure shown for VIIIa. A similar interpretation may be made for the diiodo derivative, and the structure VIIIc is assigned. Two triplets, one with ortho coupling and one with meta, can be discerned except that the suggested triplet with meta coupling is not well resolved. The positions of the peaks are different from those of VIIIa as would be expected if the carbomethoxy group is electron withdrawing and the iodo is electron donating. An interpretable ^{1}H NMR spectrum was not obtained for the dibromo derivative, probably due to the presence of impurities. The tentative assignment VIIIb is made by analogy. No further work was done with any of these three compounds.

Osborne[12] suggested that the potassio derivative was formed when potassium menthoxide was used as a base, while Schlosser[13] assumed that when potassium *tert*-butoxide was used, a lithio derivative was formed, but one that is more loosely bound. Since the only major product formed was the 3,3′ derivative, an association of metal atoms in the dimetallo intermediate seems plausible. This favors the loose dilithio but does not rule out the dipotassio derivative.

Experimental Section

Compounds I and VI were prepared according to literature procedures.[9,14] A sample of VI was generously donated by Dr. T. E. Bitterwolf. ^{1}H NMR spectra were obtained on a Varian CFT-20 spectrometer equipped with a dual 80-MHz proton and 20-MHz carbon probe and on a Bruker WH-360 spectrometer. ^{13}C NMR spectra were obtained at 90.52 MHz on a Bruker WH-360 spectrometer. The NMR data are given in parts per million (intensity, multiplicity, coupling constant, position). All preparations were carried out under N_2. Absorption grade alumina (Fischer) and 80–200 mesh silica gel (Baker) were used for the chromatography. Hexane and ether for the reactions were dried over CaH_2. After the reaction of the metallo derivative was complete, a N_2 atmosphere was not used further.

Preparation of the Dilithio Derivative of I. (a) With TMEDA. The *n*-butyllithium–tetramethylethylenediamine complex was formed in the addition funnel by adding 1.67 mL TMEDA (11 mmol) to a solution of 7.0 mL of 1.57 M *n*-butyl-

---

[12] Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1978**, *162*, 79–81.

[13] Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9–16.

[14] Rinehart, K. L., Jr.; Curby, R. J., Jr.; Gustafson, D. H.; Harrison, K. G.; Bozak, R. E.; Bublitz, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 3263–3269.

lithium (11 mmol) in 20 mL of dry hexane. This mixture was then added at room temperature to a solution of 1.0 g (4.5 mmol) of I in 30 mL of hexane. Stirring was continued for 20 h.

(b) With Potassium *tert*-Butoxide A solution of 7.0 mL of 1.57 M *n*-butyllithium in 10 mL of dry hexane was added at room temperature to a stirred suspension of 1.12 g (10 mmol) of KO-*t*-Bu and 1.0 g (4.5 mmol) of I in 40 mL of hexane. Stirring was continued for 2–3 h.

Reaction of the Dilithio Derivative. (a) With CO_2. Dry ice was placed in a reservoir in the N_2 inlet stream. The N_2 source was turned off, and the CO_2 gas was allowed to pass over the stirred reaction mixture cooled by a dry ice–acetone bath until CO_2 was no longer absorbed. The reaction mixture was warmed to room temperature. A 50-mL sample of water was added; the layers were separated; the aqueous layer was extracted with benzene; the hexane layer was washed with H_2O. The combined organic layers were dried over Na_2SO_4 and evaporated to dryness to give 545 mg of I when TMEDA was used and 261 mg of I when KO-*t*-Bu was used. The aqueous layer was acidified with 6 N HCl. The precipitate was separated and air dried to give 891 mg of a mixture of carboxylic acids when TMEDA was used and 851 mg of the mixture when KO-*t*-Bu was used.

(b) With Dibromotetrafluoroethane ($C_2F_4Br_2$). A solution of 1.3 mL (2.91 g, 11.1 mmol) of $C_2F_4Br_2$ in 10 mL of dry hexane was added to the reaction mixture cooled by a dry ice–acetone bath. Stirring of the cooled mixture was continued for 3 h. The mixture was warmed to room temperature. A 2-mL sample of H_2O was added followed by 35 mL of CH_2Cl_2. The solution was filtered, dried over Na_2SO_4, and evaporated to dryness to give 1.79 g of the crude product when TMEDA was used and 1.56 g when KO-*t*-Bu was used. The crude product was chromatographed on a 3.5 cm × 80 cm alumina column with hexane. When TMEDA had been used, four bands developed. The first was 287 mg of a mixture of I and IIb. The second was 143 mg of crude IIIb as an oil, the third, eluted with 1–2% C_6H_6 in hexane, was 504 mg of IVb, and the fourth band, eluted with 5% C_6H_6 in hexane, was 337 mg of Vb. The mixture of I and IIb was rechromatographed on a 2 cm × 38 cm column of silica gel with hexane. Two bands developed. The first was 32.1 mg of IIb as an oil, and the second was 238 mg of I. When KO-*t*-Bu had been used, the chromatographic separation was not clear except for the last band containing 632 mg of Vb. Repeated chromatographs of various groups of fractions gave 22 mg of I, 34 mg of IIIb, and 66 mg of VIIIb. No IVb was detected. IIb was recrystallized from pentane at −20 °C to give an orange solid: mp 158–158.5 °C; ^1H NMR δ 4.31 (2 H, m), 4.01 (1 H, t, J = 2.4 Hz, 4), 3.96 (3 H, m), 1.87–2.44 (6 H, m). Anal. $C_{13}H_{13}BrFe$: C, H. IIIb was recrystallized from pentane at −20 °C to give an orange solid: mp 67–68 °C; ^1H NMR δ 4.27, 4.30 (4 H, m), 3.92 (2 H, m), 3.79 (1 H, m), 1.92 (6 H, s). Anal. $C_{13}H_{13}BrFe$: C, H. IVb was recrystallized from 1:1 C_6H_6:hexane to give large orange-brown needles: mp 242 °C dec; ^1H NMR δ 4.32, 4.34, 4.36, 4.37 (2 H, dd, J = 2.5 Hz, 3,3′), 4.06, 4.10, 4.13 (2 H, t, J = 2.5 Hz, 4,4′), 3.96, 3.98, 4.00, 4.01 (2 H, dd, J = 2.6 Hz, 5,5′), 1.82–2.45 (6 H, m). Anal. $C_{13}H_{12}Br_2Fe$: C, H. Vb was recrystallized from 1:1 C_6H_6–hexane to give small orange-brown needles: mp 184.5–186 °C; ^1H NMR δ 4.30–4.37 (4 H, m, 2,2′,4,4′), 3.93–3.98 (2 H, m, 5,5′), 1.91, (6 H, s). Anal. $C_{13}H_{12}Br_2Fe$: C, H. VIIIb was obtained as an oil and was not purified: ^1H NMR δ 4.28 (2 H, m), 4.06 (1 H, m), 3.91 (1 H, m), 3.86 (1 H, m), 3.78 (1 H, m), 1.72–2.38 (6 H, m).

(c) With Iodine. A solution of 2.49 g (9.8 mmol) of I_2 in 30 mL of ether was added to the reaction mixture (only TMEDA was used for these runs) cooled with a dry ice–acetone bath. Stirring of the cooled mixture was continued for 2 h. After the mixture was warmed to room temperature, 3 mL of H_2O was added followed by 15 mL of CH_2Cl_2. (Note: This addition of H_2O and CH_2Cl_2 was accompanied by decomposition. In a much larger run not used for determining yields, the addition of H_2O was eliminated, and the decomposition was not observed. However, the solubility of LiI in CH_2Cl_2 complicated the subsequent workup.) The mixture was filtered, dried over Na_2SO_4, and evaporated to dryness to give 1.43 g of a crude product. The product was chromatographed on a 2.5 cm × 23 cm alumina column with hexane. Three bands developed. The first was eluted with hexane and contained 421 mg of a mixture of I, IIc, and IIIc. The second was eluted with 1:3 C_6H_6–hexane to give 524 mg of a mixture (by TLC), and the third was eluted with 1:1 C_6H_6–hexane to give 89.5 mg of Vc. The product from the first band was rechromatographed to give 214 mg of I, 68 mg of IIc, and 76 mg of IIIc in addition to 76 mg of a mixture of the three compounds. Rechromatography of the product of the second band gave 234 mg of IVc and an additional 99 mg of Vc and mixtures of the various components. An accumulation of the mixtures from several experiments was rechromatographed in order to recover additional material. From this, 45.8 mg of VIIIc was obtained, emerging from the column between IIIc and IVc. IIc was recrystallized from pentane at −20 °C to give a tan solid: mp 102–103 °C; ^1H NMR δ 4.25–4.32 (2 H, m), 4.09, 4.12, 4.15 (1 H, t, J = 2.5 Hz, 4), 3.96–4.07 (3 H, m), 3.42 (1 H, m), 1.88–2.32 (6 H, m). Anal. $C_{13}H_{13}IFe$: C, H. IIIc was recrystallized from pentane at −20 °C to give a yellow-orange powder: mp 52–53 °C; ^1H NMR δ 4.26, 4.29 (4 H, m), 3.92–3.97 (2 H, m), 3.60–3.66 (1 H, m), 1.93 (6 H, s). Anal. Calcd for $C_{13}H_{13}IFe$: C, 44.36. Found: C, 45.02 (this compound appeared to be less stable than the others). IVc was recrystallized from 1:1 C_6H_6–hexane to give orange-brown needles: mp 224 °C with dec; ^1H NMR δ 4.29–4.34 (2 H, m), 4.17, 4.20, 4.30 (2 H, t, J = 2.5 Hz, 4,4′), 4.02–4.06 (2 H, m), 1.73–2.11 (6 H, m). Anal. $C_{13}H_{12}I_2Fe$: C, H. Vc was recrystallized from 1:1 C_6H_6–hexane to give orange-brown plates: mp 182.5–183 °C; ^1H NMR δ 4.28–4.32 (2 H, m), 4.19, 4.21, 4.23 (2 H, t, J = 1.2 Hz, 2,2′), 3.98–4.02 (2 H, m), 1.93 (6 H, s). Anal. $C_{13}H_{12}I_2Fe$: C, H. VIIIc was obtained as an oil and was not purified: ^1H NMR δ 4.29, 4.32, 4.35 (1 H, t, J = 2.5 Hz, 4), 4.21, 4.23, 4.24, 4.26 (1 H, dd, J = 2.3 Hz, 3), 3.90 (1 H, m, 4) 3.87 (2 H, m, 5,5′), 3.58, 3.60, 3.62 (1 H, t, J = 1.2 Hz, 2′), 1.91–2.29 (6 H, m).

Esterification of Carboxylic Acids. The mixture of carboxylic acids formed using TMEDA (649 mg, 2.07 mmol) was refluxed in 1000 mL of methanol and 6 mL of concentrated H_2SO_4 for 24 h. The reaction mixture was cooled, and unreacted acid was recovered by filtration. The unreacted acid was esterified in the same way by using proportionate amounts of reactants. Water was added to the methanol which was made alkaline with 5% NaOH. The mixture was extracted with CH_2Cl_2 which was dried over Na_2SO_4 and evaporated to dryness to give 594 mg of a mixture of esters. This was chromatographed on a 2.5 cm × 22 cm column of silica gel using benzene as solvent. Four bands developed. The first contained 26.7 mg of IIa as an oil (lit.[15,16] oil, mp 41–44 °C), the second 39 mg of IIIa as an oil, the third 247 mg of IVa as an orange solid, and the fourth 252 mg of Va as an orange solid. When KO-*t*-Bu had been used, the yield of crude esters was 844 mg from 851 mg of acids. Chromatography on silica gel gave 35.4 mg of IIa, 152 mg of IIIa, 21.7 mg of IVa, 53 mg of VIIIa, and 412 mg of Va in that order. IIIa was recrystallized from hexane at −20 °C to give a tan solid: mp 73.5–74 °C (lit.[16] mp 55–56 °C); 1H NMR δ 4.64, 4.66 (2 H), 4.17–4.25 (3 H, m), 3.92–3.97 (2 H, m), 3.74 (3 H, s, CH_3), 1.98 (6 H, m). IVa was recrystallized from hexane to give a reddish brown solid: mp 145–146 °C; ^1H NMR δ 4.83, 4.86, 4.88 (2 H, m, 3,3′), 4.16, 4.19 (4 H, m, 4,4′,5,5), 3.75 (6 H, s, CH_3), 1.86–2.36, 2.36–2.86 (6 H, m). Anal. $C_{17}H_{18}O_4Fe$: C, H. Va was recrystallized from benzene to give a brown solid: mp 162–163 °C; ^1H NMR δ 4.81, 4.83 (4 H, 2,2′,4,4′), 4.13, 4.15, 4.18 (2 H, 5,5′), 3.76 (6 H, CH_3), 1.87–2.00, 2.00–2.13 (6 H, m); ^{13}C HMR δ 163.0 (s, C═O), 89.7 (s, 3,3′), 74.6 (s, 1,1′), 73.5, 72.4, 71.7 (3 d, J = 183 Hz, 2,2′,4,4′,5,5′), 53.6 (q, J = 143 Hz, CH_3), 38.2 (t, J = 127 Hz, β-CH_2), 28.2 (t, J = 127 Hz, α-CH_2). Anal. $C_{17}H_{18}O_4Fe$: C, H. VIIIa was obtained as an oil and was not purified: ^1H NMR δ 4.60 (1 H, m), 4.55 (1 H, m), 4.30, 4.33, 4.36 (1 H, t, J = 2.7 Hz, 4), 4.25 (1 H, t, J = ∼1.1 Hz, 2′), 4.07, 4.08 (2 H, m), 1.49–2.71 (6 H, m).

3,4′-Dicarbomethoxy-1,1′-trimethyleneferrocene (VII). The procedure of Rinehart et al.[17] was used to convert VI to the dicarboxylic acid. A mixture of 100 mg (0.32 mmol) of VI, 200 mg (0.79 mmol) of I_2, and 2 mL of pyridine was stirred under nitrogen at room temperature for 20 h. The mixture was then heated on a boiling water bath for 1.5 h, 15 mL of 0.6 N NaOH was added, and the mixture again was stirred at room temperature

---

(15) Falk, H.; Hofer, O.; Schlögl, K. *Monat. Chem.* **1969**, *100*, 624–648.

(16) Rapic, V.; Schlögl, K.; Steinitz, B. *J. Organomet. Chem.* **1975**, *94*, 87–98.

(17) Rinehart, K. L., Jr.; Motz, K. L.; Moon, S. *J. Am. Chem. Soc.* **1957**, *79*, 2749–2754.

for 60 h. After being left sitting in a hot water bath for 1 h, the mixture was filtered. The crystals were washed with 0.6 N NaOH, and the combined wash and filtrate were extracted with ether and then acidified with 10 mL of 6 N HCl to precipitate the dicarboxylic acid, crude yield 55.7 mg.

A 2 M solution of CH_2N_2 in 4 mL of ether (8 mmol) was added to a solution of the dicarboxylic acid in 250 mL of ether, and the mixture was kept in a refrigerator at 0 °C for 3 days. Excess CH_2N_2 was destroyed by adding 10 mL of glacial acetic acid, and the mixture was then extracted with 5% NaOH. The ether layer was washed with H_2O, dried over Na_2SO_4, and evaporated to dryness to give the crude diester VII. The crude diester was chromatographed on a 1 cm × 20 cm silica gel column with benzene. Four bands developed. The third and major band was eluted with 1:99 ethyl acetate–benzene mixture to give 44.5 mg of crude VII. Recrystallization from hexane at −20 °C gave a yellow-orange solid: mp 93–93.5 °C; ^{1}H NMR δ 4.61, 4.63, 4.64 (2 H, dd, J = 1.3, 1.3 Hz, 2,5′), 4.50, 4.52, 4.53, 4.55 (2 H, dd, J = 1.3, 2.6 Hz, 3,4), 4.39, 4.41, 4.42, 4.44 (2 H, dd, J = 1.3, 2.7 Hz, 2′,5), 3.73 (6 H, s, CH_3), 1.97 (6 H, s, CH_2). Anal. $C_{17}H_{18}O_4Fe$: C, H.

Acknowledgment. We wish to thank Mr. Donald Lawler for the ^{13}C NMR and the 360-MHz ^{1}H NMR spectra and Drs. J. J. Eisch and T. E. Bitterwolf for valuable discussions. The NSF financed the time that U.J. spent at Brookhaven National Laboratory. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. DE-AC02-76CH00016.

Registry No. I, 12302-04-4; IIa, 56800-49-8; IIb, 82522-08-5; IIc, 82522-09-6; II (X = Li), 82522-13-2; IIIa, 82544-14-7; IIIb, 82544-15-8; IIIc, 82544-16-9; III (X = Li), 82544-23-8; IVa, 82522-10-9; IVb, 82522-11-0; IVc, 82522-12-1; IV (X = Li), 82522-14-3; Va, 82544-17-0; Vb, 82544-18-1; Vc, 82544-19-2; V (X = Li), 82544-24-9; VI, 41558-92-3; VIIIa, 82544-20-5; VIIIb, 82544-21-6; VIIIc, 82544-22-7; VIII (X = Li), 82544-25-0.

Substituent Effects in Cationic Bis(arene)chromium Compounds. Electronic and Electron Spin Resonance Spectra and an X-ray Structure of Bis(1,3,5-triisopropylbenzene)chromium(I) Iodide

Tomi Ting-Tung Li, Wei-jen Kung, Donald L. Ward, Beth McCulloch, and Carl H. Brubaker, Jr.*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received March 31, 1982

For a series of monosubstituted bis(arene)chromium cations, the UV ligand–metal charge-transfer (LMCT) bands and electron spin resonance (ESR) parameters do not depend on the nature or ring substituents. However, as the number of electron-donating groups on the arene ring are increased inductive effects become more significant. X-ray crystallography has been applied to determine the molecular structure of bis(1,3,5-triisopropylbenzene)chromium(I) iodide. The staggered conformation was found to be stabilized by steric factors. Crystal data for bis-(1,3,5-triisopropylbenzene)chromium(I) iodide are as follows: space group $P\bar{1}$ (triclinic), unit-cell dimensions a = 9.988 (3) Å, b = 16.199 (3) Å, c = 9.479 (2) Å, α = 91.08 (2)°, β = 106.92 (2)°, and γ = 96.33 (2)°, and ρ_{calcd} = 1.340 g cm^{-3} for Z = 2. The final R factor is 0.037 for 5358 observed independent reflections. The ring angle at the substituted carbon has an average value of 118.6°, consistent with the electron-donating nature of isopropyl groups as predicted by Domenicano[28] for uncomplexed benzene rings.

Introduction

Charge-transfer spectra have been measured for $Cr(C_6H_6)_2$ and $Cr(C_6H_6)_2^+$ and assignments are clearly tentative.[1,2] The effects on the shifts of charge-transfer spectra induced by substitution in the bis(arene)chromium cations are investigated here in order to examine the assignment of the ligand to metal ($e_{1u} \rightarrow a_{1g}$) charge-transfer bands.

Substituent effects on the ESR data in cationic bis(arene)chromium complexes have been the subject of several reports,[3-5] dealing primarily with alkyl-substituted bis(benzene)chromium compounds.[4,5] It is instructive to examine these results in the light of ESR data and the nature of the substituents in the arene ring.

To avoid the impurities formed in the synthesis by the Friedel–Crafts method, bis(1,3,5-triisopropylbenzene)chromium has been prepared by using the cocondensation of chromium vapor with 1,3,5-triisopropylbenzene at −196 °C. Oxidation of the complex in air in presence of an aqueous KI solution gives the iodide of bis(1,3,5-triisopropylbenzene)chromium(I) which was obtained in the crystalline state and used for the X-ray structure study. The structure of bis(benzene)chromium(I) iodide,[7] bis(toluene)chromium(I) iodide,[8] bis(ethylbenzene)chromium iodide,[9] η^{12}-[3,3](paracyclophane)chromium(I) triiodide,[10]

---

[1] Warren, K. D. *Struct. and Bonding (Berlin)* **1976**, *27*, 45 and references therein.

[2] (a) Hillier, I. H.; Canadine, R. M. *Discuss Faraday Soc.* **1969**, *38*, 27. (b) Weber, J.; Geoffroy, M.; Goursot, A.; Penigault, E. *J. Am. Chem. Soc.* **1978**, *100*, 3995. (c) Anderson, S. E., Jr.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 1564.

[3] Burdorf, H.; Elschenbroich, Ch. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 94.

[4] Elschenbroich, Ch.; Mockel, R.; Zenneck, U.; Clack, D. W. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1008.

[5] Gribov, B. G.; Kozyrkin, B. I.; Krivospitskii, A. D.; Chirkin, G. K. *Dokl. Chem. (Engl. Transl.)* **1970**, *193*, 457.

[6] Reviews to conventional synthetic method for the chemistry of bis(arene)chromium, see: Sneeden, R. P. E. "Organochromium Compounds"; Academic Press: New York, 1975.

[7] Morosin, B. *Acta Crystallogr., Sect. B* **1974**, *B30*, 838.

[8] Starovskii, C. V.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1961**, *2*, 161.

0276-7333/82/2301-1229$01.25/0 © 1982 American Chemical Society