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Cyclopentadienyliron Carbonyl Complexes of Cyclic Cis Azo Ligands. Diiron Bridging and Cationic Monometallic Compounds

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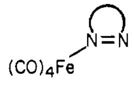
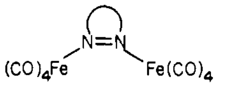
Reaction of the cyclic cis azo ligands 2,3-diazabicyclo[2.2.1]hept-2-ene, $C_5H_8N_2$ (a), 2,3-diazabicyclo[2.2.2]oct-2-ene, $C_6H_{10}N_2$ (b), and pyridazine, $C_4H_4N_2$ (c), with $(C_5H_5)_2Fe_2(CO)_4$ in refluxing toluene or benzene produces the azo-bridged diiron compounds $[(C_5H_5)Fe(CO)]_2L$ (VI, L = a–c) in which the azo linkage serves as a four-electron donor. Oxidation of VI with I_2 or $AgClO_4$ in toluene or benzene yields the cationic iron species $(C_5H_5)Fe(CO)_2L^+$ (VIII, L = a–c) which can be isolated as the tetraphenylborate salts. The cationic species can also be synthesized by the reaction of $(C_5H_5)Fe(CO)_2(OH_2)^+$ and the azo ligand (a–c) in acetone. Benzo[*c*]cinnoline (d) did not react to give either VI or VIII and both *cis*- and *trans*-azobenzene failed to react with $(C_5H_5)Fe(CO)_2(OH_2)^+$.

Introduction

Complexes of iron have played a major role in the investigation of the reactions of azo compounds with metal carbonyl systems.[1,2] In this context one area of recent interest has been the reactions of cyclic cis azo ligands with the iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$.[3-15] To date five types of complexes, I–V, have been characterized in which the original azo linkage and ligand structure remain intact. In these complexes the azo linkage demonstrates the ability to serve as a two-electron donor (type I[3-6]), a four-electron donor (types II[7,8] and III[3,9]), or a six-electron donor (types IV[3,4,10-15] and V[5,7]).



I



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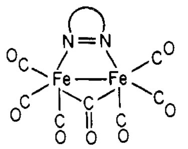

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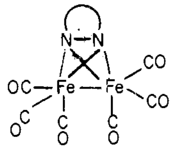

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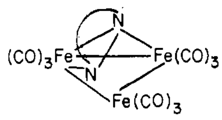
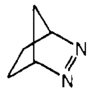
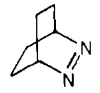


V

As part of our continuing interest in the coordination properties of the cis azo linkage,[16] we have investigated for the first time the reactions of several cyclic azo compounds (a–d) with (dicyclopentadienyl)tetracarbonyldiiron, $(C_5H_5)_2Fe_2(CO)_4$. We now report the characterization of a new type of bridging diiron–azo complex, VI, in which the azo linkage functions as a four-electron donor and only bridging carbonyl groups are present. The oxidation chemistry of these complexes has also been studied and observed to provide cationic iron–azo complexes which were synthesized by an independent method as well.

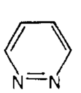


2,3-diaza-
bicyclo[2.2.1]hept-2-ene



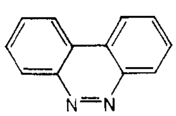
2,3-diaza-
bicyclo[2.2.2]oct-2-ene

b



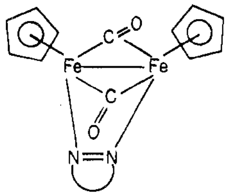
pyridazine

c



benzo[*c*]cinnoline

d



VI

Experimental Section

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Molecular weights were determined by osmometry in acetonitrile and 1,2-dichloroethane by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer. Proton NMR spectra were recorded on a Varian A-60 spectrometer; samples were sealed in vacuo using degassed solvents. Melting points were taken in open capillaries or on a Kofler hot-stage microscope and are uncorrected.

A nitrogen atmosphere was employed for carrying out all reactions, for filtration and handling of solutions of organometallic compounds, and for filling evacuated flasks. Benzene and hexane were redistilled under nitrogen from sodium benzophenone ketyl. Dichloromethane was distilled from phosphorus pentoxide under nitrogen. All other solvents were purged with nitrogen before use.

Materials. Pyridazine, benzo[*c*]cinnoline, and *trans*-azobenzene were obtained commercially and checked spectroscopically for purity before use. *cis*-Azobenzene was prepared by photolysis of the trans form in glacial acetic acid.[17] The cis and trans isomers were separated by chromatography on Florisil in a darkened room using dichloromethane–hexane mixtures as eluent. 2,3-Diazabicyclo[2.2.1]hept-2-ene, $C_5H_8N_2$ (a),[18] 2,3-diazabicyclo[2.2.2]oct-2-ene, $C_6H_{10}N_2$ (b),[19] and $(C_5H_5)_2Fe_2(CO)_4$[20] were prepared by published procedures.

Preparation of $[(C_5H_5)Fe(CO)]_2L$ (VI). (1) L = $C_5H_8N_2$. A mixture of 1.26 g (3.54 mmol) of $(C_5H_5)_2Fe_2(CO)_4$ and 0.34 g (3.54 mmol) of $C_5H_8N_2$ was refluxed in benzene until the infrared spectrum showed a complete absence of the starting iron compound (15 days). Solvent was removed by aspiration (~25 °C (20 Torr)), and the residue was taken up in dichloromethane and filtered. The solid on the filter was washed with dichloromethane until little additional green color came through in the filtrate. Approximately 100 mL of *n*-hexane was added to the filtrate, the solution volume was reduced by aspiration, and the black crystals were collected by filtration. The crude product was recrystallized again from dichloromethane/*n*-hexane to give an 85% yield (1.19 g, 3.01 mmol) of product. The same reaction run in toluene required only 5 days' reflux time but the yield was reduced to 42%. Anal. Calcd for $[(C_5H_5)Fe(CO)]_2(C_5H_8N_2)$: C, 51.81; H, 4.61; N, 7.11; mol wt 394. Found: C, 51.57; H, 4.64; N, 7.11; mol wt 314.

(2) L = $C_6H_{10}N_2$. The reaction was carried out as for L = $C_5H_8N_2$ except that toluene was used as the solvent. On a scale of 1.75 g (4.96 mmol) of $(C_5H_5)_2Fe_2(CO)_4$ and 0.50 g (4.5 mmol) of $C_6H_{10}N_2$ in 40 mL of toluene reaction was complete after 2 days of refluxing. Workup gave an 81% yield (1.50 g, 3.64 mmol) of black crystals. In benzene the reaction was still incomplete after 8 days on a 2.45-mmol scale. Workup at that time required chromatography on a 2 × 25 cm Florisil column slurry-packed in petroleum ether (bp 30–60 °C). After elution of unreacted $(C_5H_5)_2Fe_2(CO)_4$ with 2:5 dichloromethane/petroleum ether, the product was eluted as a brown band with pure dichloromethane. A 37% yield of analytically pure product was obtained. Anal. Calcd for $[(C_5H_5)Fe(CO)]_2(C_6H_{10}N_2)$: C, 52.98; H, 4.94; N, 6.87. Found: C, 53.08; H, 4.98; N, 6.95.

(3) L = $C_4H_4N_2$. A mixture of 1.24 g (3.5 mmol) of $(C_5H_5)_2Fe_2(CO)_4$ and 0.79 mL (10.5 mmol) of pyridazine was refluxed in 25 mL of toluene. Infrared monitoring showed a product peak only sporadically and the starting iron carbonyl dimer spectrum remained strong even after as long as 3 weeks. The product appears to precipitate from the reaction solution and is usually accompanied by considerable brown decomposition material. Workup of reactions as for L = $C_5H_8N_2$ after 5–7 days reflux gave a black solid in yields of 10–15%. More extended reflux decreased yields further. Several reactions in benzene for 1–3 weeks gave little or no product. Anal. Calcd for $[(C_5H_5)Fe(CO)]_2(C_4H_4N_2)$: C, 50.82; H, 3.74; N, 7.41; mol wt 378. Found: C, 50.70; H, 3.76; N, 7.32; mol wt 296.

Oxidation of $[(C_5H_5)Fe(CO)]_2L$ (VI). (1) Oxidation with I_2. A solution of iodine (155 mg, 0.61 mmol) in 30 mL of toluene was added dropwise over ~1 h to a stirred solution of 250 mg (0.61 mmol) of $[(C_5H_5)Fe(CO)]_2L$ and 590 mg (1.5 mmol) of $NaB(C_6H_5)_4$ in a mixture of 70 mL of toluene and 5 mL of ethanol at 0 °C. The reaction mixture was stirred ~2 h at room temperature and then filtered. The solid was washed with dichloromethane until the yellow product had been extracted. Addition of *n*-hexane to the dichloromethane solution until a solid precipitated followed by cooling to −25 °C gave the yellow product of $[(C_5H_5)Fe(CO)_2L]B(C_6H_5)_4$ (VIII). Recrystallization from dichloromethane/hexane gave yields of 64, 47, and 38% for L = $C_6H_{10}N_2$, $C_5H_8N_2$, and $C_4H_4N_2$, respectively. Variation in the ratio of I_2 to $[(C_5H_5)Fe(CO)]_2L$ from 0.5 to 2.0 did not alter the nature of the product. However, the yield dropped if the ratio fell below 1.0. Anal. Calcd for $[(C_5H_5)Fe(CO)_2(C_5H_8N_2)]B(C_6H_5)_4$: C, 73.00, H, 5.62; N, 4.73; mol wt 592. Found: C, 72.89; H, 5.65; N, 4.79; mol wt 676. Calcd for $[(C_5H_5)Fe(CO)_2(C_6H_{10}N_2)]B(C_6H_5)_4$: C, 73.29; H, 5.82; N, 4.62; mol wt 606. Found: C, 72.95; H, 5.96; N, 4.73; mol wt 524. Calcd for $[(C_5H_5)Fe(CO)_2(C_4H_4N_2)]B(C_6H_5)_4$: C, 72.95; H, 5.07; N, 4.86; mol wt 576. Found: C, 73.00; H, 5.07; N, 4.89; mol wt 582. (Molecular weights found are corrected for an expected two ions per molecule.)

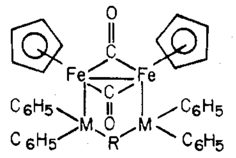
(2) Oxidation with $AgClO_4$. A solution of $AgClO_4$ (156 mg, 0.75 mmol) in 30 mL of benzene was added dropwise over ~1 h to a solution of 0.75 mmol of $[(C_5H_5)Fe(CO)]_2L$ in 70 mL of benzene at room temperature. The mixture was stirred an additional 5 h at room temperature and then filtered to give a green-black solid. Recrystallization from dichloromethane/*n*-hexane gave a yellow-green product which was identified by infrared and NMR spectra as $[(C_5H_5)Fe(CO)_2L]ClO_4$ contaminated with some starting material. Because these cations were available in better yield and quality by another synthetic route, no attempts to obtain analytically pure samples were made.

Preparation of $[(C_5H_5)Fe(CO)_2L]B(C_6H_5)_4$ (VIII). The procedure was similar for all ligands and will be described for $C_5H_8N_2$ only. A solution containing 2.4 mmol of $[(C_5H_5)Fe(CO)_2(OH_2)]BF_4$ was generated using the method of Dombek and Angelici.[21] To this was added 250 mg (2.6 mmol) of $C_5H_8N_2$ in 15 mL of acetone followed by 1.02 g (3.0 mmol) of $NaB(C_6H_5)_4$ in 40 mL of acetone. The solution was stirred ~1 h and filtered, and the filtrate was stripped by aspiration (~25 °C (20 Torr)). The product was extracted into dichloromethane to give a yellow solution. Hexane was added until a precipitate formed, the solvent volume partially reduced by aspiration, and the solution cooled to −25 °C. The yellow solid was collected in 49% (695 mg, 1.17 mmol) yield. Further crystallizations as needed were done from dichloromethane/hexane mixtures. On the same scale the reaction with L = $C_4H_4N_2$ gave a 35% yield; on a 1.0-mmol scale L = $C_6H_{10}N_2$ provided yields of 15 and 30%.

The above procedure was also employed in attempts to isolate products from benzo[*c*]cinnoline and *cis*- and *trans*-azobenzene. Several modifications were also tried including carrying out the reaction at 0 °C, using methanol in place of acetone as the solvent, and washing the stripped reaction mixture with chloroform prior to extraction with dichloromethane. All were without success.

Results and Discussion

Refluxing the cyclic azo ligands $C_5H_8N_2$ (a), $C_6H_{10}N_2$ (b), and $C_4H_4N_2$ (c) with $(C_5H_5)_2Fe(CO)_4$ in benzene or toluene provides complexes of the type $[(C_5H_5)Fe(CO)]_2L$ (L = a–c). The compounds are black air-stable solids; they decompose above ~130 °C but the dark color prohibited any accurate determination of the temperature. They are insoluble in saturated hydrocarbons but moderately soluble in aromatic and polar organic solvents in which they exhibit a green color. On the basis of spectroscopic and analytical data structure VI, in which the azo ligand has replaced the terminal carbonyls in $(C_5H_5)_2Fe_2(CO)_4$, is proposed for these compounds. This structure is similar to an analogous set of complexes in which L is a bridging diphosphine or diarsine, VII (M = P, As; R = hydrocarbon bridge) synthesized in a similar manner.[22]



VII

The bridging azo structure, VI, is amply supported by the spectroscopic data (Table I). The single cyclopentadienyl resonance in the NMR spectrum requires that the iron atoms be equivalent, while symmetric coordination of the azo linkage is indicated by the single signal for the ligand 1,4 bridgehead protons in VIa and VIb. The infrared spectra reveal the presence of only bridging carbonyl groups. By assuming local C_{2v} symmetry, two infrared-active carbonyl modes ($A_1 + B_1$) are predicted for structure VI. The observed relative intensities are as expected if the $Fe_2(CO)_2$ portion of the molecule is nearly planar.[22,23] The spectrum of VIc in KBr shows a strong peak at 1430 cm^{-1} attributable to a pyridazine mode. This feature, which does not appear in free pyridazine, has been found to be characteristic of complexes in which pyridazine acts as a bridging ligand.[9,24]

The azo linkage serves as a four-electron donor in VI with coordination involving only the lone-pair electrons of each nitrogen atom. The Fe—Fe and N=N bonds are expected to be collinear with a planar Fe_2N_2 unit. The only previous examples of this geometry in an iron–azo system are the compounds $Fe_2(CO)_7L$, III,[9] although this has not been confirmed by an x-ray structure determination. Compounds in which the azo linkage serves as a six-electron donor (IV) are well documented to have a tetrahedral Fe_2N_2 unit.[25,26] Confirmation of the retention of the nitrogen–nitrogen double bond in VI was sought in the infrared spectra. On group frequency grounds $\nu(N{=}N)$ is expected to lie in the 1400–1600-cm^{-1} range. Although the free ligands (a–c) and their complexes (VIa–c) all exhibit bands in this region (Table I), complications from the presence of CH modes made a firm assignment of $\nu(N{=}N)$ impossible without ^{15}N isotopic data.[27]

Replacement of the terminal carbonyl groups in $(C_5H_5)_2Fe_2(CO)_4$ by a bridging azo group results in a reduction in the bridging carbonyl frequencies and an upfield shift in the NMR of the cyclopentadienyl resonance and the 1,4 bridgehead protons of a and b. These changes parallel those observed in the analogous arsine and phosphine complexes, VIII,[22] and are attributed, similarly, to effects on the nearly planar $Fe_2(CO)_2$ group when the terminal carbonyls are replaced with a poorer π-acceptor ligand.[16,28] The marked shift of the bridgehead protons is compatible with the previously proposed ring current in a delocalized π system of the $Fe_2(CO)_2$ unit.[22] The upfield shift occurs if these protons are located below the $Fe_2(CO)_2$ plane. We conclude that the azo complexes VIa–c lend considerable support to the earlier interpretation of the bonding in the $Fe_2(CO)_2$ moiety.

The synthesis of the complexes $[(C_5H_5)Fe(CO)]_2L$ (L = a–c) provides the first examples of a bridged iron–azo system with an iron–cyclopentadienyl group. The lower reactivity of $(C_5H_5)_2Fe_2(CO)_4$ compared with that of the iron carbonyl

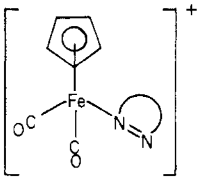
Table I. Spectroscopic Data

	IR features,[a] cm^{-1}		^{1}H NMR,[d] ppm		
Compd	ν(CO)[b]	1400–1600 cm^{-1} region[c]	Solvent	C_5H_5	Other signals
$[(C_5H_5)Fe(CO)]_2(C_5H_8N_2)$ (VIa)	1785 w, 1742 s	1455 m, 1430 mw, 1417 m	*e*	5.35 s	6.43 s (H(1), H(4)); 8.5–9.1 m (H(5)–H(7))
$[(C_5H_5)Fe(CO)]_2(C_6H_{10}N_2)$ (VIb)	1775 w, 1728 s	1442 m, 1427 mw, 1413 mw	*e*	5.37 s	6.88 s (H(1), H(4)); 8.68 s, br (H(5)–H(8))
$[(C_5H_5)Fe(CO)]_2(C_4H_4N_2)$ (VIc)	1770 w, 1730 s	1498 m, 1430 s, 1392 w	*e*	5.35 s	*g*
$[(C_5H_5)Fe(CO)_2(C_5H_8N_2)]B(C_6H_5)_4$ (VIIIa)	2071 s, 2028 s	1580 m, 1480 ms, 1460 w, 1440 w, 1427 ms, 1415 w, sh	*f*	4.53 s	4.75 s, 4.93 s (H(1), H(4)); 8.0–9.1 m (H(5)–H(7)); 2.5–3.4 m (C_6H_5)
$[(C_5H_5)Fe(CO)_2(C_6H_{10}N_2)]B(C_6H_5)_4$ (VIIIb)	2071 s, 2027 s	1578 m, 1510 m, 1476 ms, 1462 w, 1448 w, 1426 ms, 1415 w, sh	*f*	4.48 s	4.69 s, 5.01 s (H(1), H(4)); 8.2–8.6 m (H(5)–H(8)); 2.5–3.4 m (C_6H_5)
$[(C_5H_5)Fe(CO)_2(C_4H_4N_2)]B(C_6H_5)_4$ (VIIIc)	2078 s, 2032 s	1576 m, 1562 m, 1475 ms, 1445 m, 1423 ms, 1412 w	*f*	4.50 s	0.59 s, br, 0.95 s, br (H(3), H(6)); 2.1–3.4 m (H(4), H(5), C_6H_5)
$(C_5H_5)_2Fe_2(CO)_4$	1976 s, 1953 m, 1772 s	1430 w, 1415 m	*e*	5.21 s	
$C_5H_8N_2$ (a)		1482 m, 1435 m	*e*		4.88 s (H(1), H(4)); 8.2–9.3 m (H(5)–H(7))
$C_6H_{10}N_2$ (b)		1517 m, 1446 m	*e*		4.87 s (H(1), H(4)); 8.2–8.9 m (H(5)–H(8))
$C_4H_4N_2$ (c)		1569 m, 1563 m, 1444 w, 1413 ms	*e*		0.72 t (H(3), H(6)); 2.44 t (H(4), H(5))

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] In CH_2Cl_2. [c] KBr pellet. [d] τ scale; tetramethylsilane internal standard. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. [e] Chloroform-*d*. [f] Acetone-d_6. [g] Solubility too low to confidently detect other than the sharp cyclopentadienyl resonance.

sources $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ required the use of more vigorous reaction conditions which are likely to restrict the potential range of complexes that can be obtained. On the basis of our work, nonaromatic systems such as $C_5H_8N_2$ and $C_6H_{10}N_2$ give the most stable products. But even in these cases an attempt to reduce reaction time by using toluene in place of benzene as the solvent led to a significantly lower yield for the thermally less stable $C_5H_8N_2$.[27] Complexes of cyclic aromatic azo ligands are significantly less stable as evidenced by the low yield of VIc and the failure of benzo[*c*]cinnoline (d) to give any product. Under similar reaction conditions the acyclic azo ligand *trans*-azobenzene gives only the ortho-metalated product, $(C_5H_5)Fe(CO)(C_6H_4N{=}NC_6H_5)$.[29]

With the view of making further comparisons between the bridging azo (VI) and bridging diphosphine (VII) complexes, we have studied the oxidation chemistry of the azo compounds. Treatment of the complexes VIa–c with iodine or silver perchlorate in benzene readily produced the cationic complexes $(C_5H_5)Fe(CO)_2L^+$ (VIII, L = **a**–**c**) which were isolated as the tetraphenylborate or perchlorate salts. They are yellow air-stable solids which decompose around 160 °C. Variation of the ratio of oxidizing agent to complex VI did not change the product, although the oxidation was incomplete if the ratio was below 1:1. Periodic monitoring of the reaction by infrared spectroscopy during the slow addition of the oxidizing agent to a solution of VI showed features due to VI, VIII, and, with use of iodine, a bit of $(C_5H_5)Fe(CO)_2I$. A weak, high-frequency feature around 2100 cm^{-1} is presumed to be $(C_5H_5)Fe(CO)_3^+$ (the other CO band would be masked) formed as a minor decomposition product.[30] This chemistry contrasts with that of the bridging diphosphine complexes (VIII, M = P) where similar oxidation studies permitted isolation of the cationic diiron species $[(C_5H_5)Fe(CO)]_2(C_6H_5)_2PRP(C_6H_5)_2^+$ and two iodine-containing species $[(C_5H_5)Fe(CO)I]_2(C_6H_5)_2PRP(C_6H_5)_2$ and $[(C_5H_5)Fe(CO)]_2(I)(C_6H_5)_2PRP(C_6H_5)_2$ depending upon the identity of R and the relative amount of oxidizing agent used.[23] The last compound is thought to contain a bridging iodine atom. Compounds believed to be of the type $(C_5H_5)Fe(CO)_2L^+$ (L = monocoordinated diphosphine) were also isolated but could not be obtained analytically pure. If similar diiron species are formed in the oxidation of the azo complexes (VIa–c), they must decompose immediately to VI. This difference between the bridging azo and diphosphine compounds may simply reflect the poorer ligand qualities of the azo linkage. Ligand flexibility may also be an important factor. The oxidized diiron species have a weakened or completely severed iron–iron bond which is expected to increase the iron–iron distance. The backbone of the longer and more flexible diphosphine chain can respond to these changes in geometric requirements while the rigid cyclic azo ligands cannot.



VIII

The two strong carbonyl bands above 2000 cm^{-1} in the infrared spectrum and the cyclopentadienyl resonance around τ 4.5 in VIIIa–c are typical spectroscopic features of $(C_5H_5)Fe(CO)_2L^+$ type complexes.[21] Coordination of the azo ligand through the lone pair of only one nitrogen atom is confirmed by the two NMR resonances observed for the 1,4 bridgehead protons in VIIIa and VIIIb. The complexity of the 1400–1600-cm^{-1} region in these tetraphenylborate salts prevents assignment of ν(N=N). Complexes VIIIa–c were also synthesized conveniently in good yield by the addition of the free azo ligand to an acetone solution of $(C_5H_5)Fe(CO)_2(OH_2)$.$^{+}$[21]

Attempts were made to isolate bridging cationic species of the type

$$[(C_5H_5)(CO)_2Fe\overparen{N{=}N}Fe(CO)_2(C_5H_5)]^{2+}$$

by carrying out the oxidation with iodine under a carbon monoxide atmosphere and by reaction of the free azo ligand with excess $(C_5H_5)Fe(CO)_2(OH_2)^+$. In each case only VIII was obtained.

Although benzo[*c*]cinnoline (d) did not form a bridging complex (VI), we tried to make the cationic species VIIId using the alternative synthetic procedure. Despite variation in temperature and use of both acetone and methanol as solvent, all efforts to isolate this compound failed. We were likewise unsuccessful in extending this reaction to the acyclic azo compounds *cis*- and *trans*-azobenzene. A salmon-colored solid was isolated in each case, but it gave a variable analysis and contained no nitrogen. Further attempts to characterize it were fruitless.

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Registry No. VIa, 62066-93-7; VIb, 62066-94-8; VIc, 62085-23-8; VIIIa, 62066-96-0; VIIIb, 62066-98-2; VIIIc, 62077-02-5; $(C_5H_5)_2Fe_2(CO)_4$, 12154-95-9; a, 2721-32-6; b, 3310-62-1; c, 289-80-5; $[(C_5H_5)Fe(CO)_2(OH_2)]BF_4$, 62077-08-1.

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Solvent-Exchange Kinetics in Iron(II) Solutions of *N,N*-Dimethylformamide and Dimethyl Sulfoxide Studied by Nuclear Magnetic Resonance Line Broadening

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Measurements have been made of the temperature dependence of the solvent proton line broadening and shift for solutions of iron(II) perchlorate in *N,N*-dimethylformamide (DMF) and in dimethyl sulfoxide (Me_2SO) and Me_2SO–nitromethane solutions. In DMF chemical-exchange effects are observed on both line broadening and shifts and the kinetic parameters for DMF exchange were found to be $k(25\ °C) = 1.7 \times 10^6\ s^{-1}$, $\Delta H^* = 11.7 \pm 0.6$ kcal mol^{-1}, $\Delta S^* = 9.2 \pm 2$ cal mol^{-1} deg^{-1}. No exchange effects were observed in Me_2SO, but at low temperature in Me_2SO–D_3CNO_2 solution Me_2SO exchange was measurable and found to give $k(25\ °C) = 1 \times 10^6\ s^{-1}$, $\Delta H^* = 11.3 \pm 0.6$ kcal mol^{-1}, and $\Delta S^* = 6.9 \pm 2$ cal mol^{-1} deg^{-1}. No detectable effect of solvent Me_2SO concentration on the exchange rate was noted.

Introduction

Despite the wide distribution and importance of iron(II) there has been relatively little work on the substitution reactions of this ion especially when compared to cobalt(II), nickel(II), and manganese(II).[2a] The water-exchange rate on $Fe(OH_2)_6^{2+}$ was studied by Swift and Connick[2b] and the results indicate that iron(II) and cobalt(II) are of comparable lability. More recently solvent-exchange rates have been reported for iron(II) in methanol,[3] *N,N*-dimethylformamide (DMF),[4] acetonitrile,[5] and dimethyl sulfoxide (Me_2SO).[6]

A comparison of the kinetic parameters for ligand substitution and solvent exchange[7-10] is being used increasingly to test the dissociative ligand substitution mechanism[11] for first-row dipositive transition metal ions. It is hoped that this study may provide further necessary points of comparison for such tests. One problem with this type of mechanistic test is the embarrassingly large range of kinetic parameters obtained from NMR studies ostensibly on the same system. This problem might be alleviated if the variation of solvent-exchange rate with solvent and metal ion could be anticipated approximately in some way. For example, there is reference in the literature to activation enthalpies of 5.3 and 4.16 kcal mol^{-1} for solvent exchange in the Fe(II)–DMF and Fe(II)–Me_2SO systems, respectively. Comparison of these values to other solvent-exchange parameters on iron(II) and other metal ions clearly shows that these iron(II) values are peculiar. Of course, this is hardly grounds for doubting their validity in the absence of a more quantitative way of predicting the ΔH^* values but it seemed justification for a reinvestigation. With the results of the present study in hand, some attempt will be made to correlate the activation enthalpies for solvent exchange on manganese(II), iron(II), cobalt(II), and nickel(II).

Experimental Section

An excess of iron wire (99.9%) was treated with 2 M perchloric acid until hydrogen evolution ceased. The excess iron was removed by filtration and the solvent removed from the filtrate by vacuum distillation to yield crystals of hydrated ferrous perchlorate. A portion of this product was dissolved in a large excess of the required solvent,