

Figure 1.—Low-temperature fractionation column.

column. The pressure in the system is maintained as low as possible by continuous evacuation through a liquid nitrogen cooled trap located as near the head of the column as possible.

The lengths of the columns used have been approximately 1 m and the temperature gradient from top to bottom about 10–30° depending upon the rate of coolant flow (and thus, indirectly, the temperature). Lower temperature gradients can be obtained by applying a silver mirror to the dewar jacket; however, this has been felt unnecessary and less desirable than the ability visually to follow the bands of material on the column walls. Cold gas was supplied from a large dewar of liquid nitrogen in which the rate of heat leakage was regulated by a submerged, Variac-controlled resistance heater. Liquid nitrogen consumption varied from about 3–4 l./hr when operating at temperatures of about –100° to about 1 l./hr in the –30° range. Using well-insulated delivery tubes the lower temperature limit obtainable is nearly that of liquid nitrogen although the consumption becomes quite high.

In the preparation *via* the Grignard method,  $\mu$ -dimethylaminodiborane was condensed into a bulb containing an equimolar quantity of methylmagnesium iodide in diethyl ether solution. The reaction was carried out at room temperature for about 2 hr; only traces of noncondensable gas were detected upon vacuum removal of the volatile products. The bulk of the diethyl ether was stripped off by fractional condensation using a Dry Ice cooled trap and the residue in the trap was further purified as described above.

The purified material had a vapor pressure of 31.0 mm at 0° and a melting range of –94.5 to –95.3° (Stock plunger method). Analysis for boron content was carried out by fuming nitric acid oxidation and titration of the resulting boric acid by the method of identical pH. *Anal.* Calcd: B, 25.5. Found: B, 25.0. Hydridic hydrogen was determined by hydrolysis at 100° and yielded 4.10 mol of hydrogen per mole of sample, in reasonable agreement with 4.0 expected from the reaction  $B_2H_4CH_3N(CH_3)_2 + 5H_2O \rightarrow B(OH)_3 + H_3CB(OH)_2 + HN(CH_3)_2 + 4H_2$ . The vapor density molecular weight, 83.2, agreed adequately with the calculated 84.8 and the mass spectrum showed a sharp cutoff at  $m/e$  85,  $^{11}B_2H_4CH_3N(CH_3)_2^+$ , with only exceedingly weak peaks at higher masses, probably caused by trace impurities.

The 19.3-MHz  $^{11}B$  nmr spectrum of  $\mu$ -dimethylaminomethyl-diborane exhibited an interesting temperature dependence. At temperatures above about –30° the spectrum was composed of, respectively, overlapping doublet and quartet resonances [ $\delta(BF_3 \cdot O(C_2H_5)_2)$ ,  $J(\text{cps})$ ]: 10.0, 126; 14.8, 97. When the sample was cooled below about –34°, the quartet structure began to collapse and at –55° resolved to a 1:2:1 triplet of doublets, while the original doublet resonance had remained unaffected. These changes clearly suggest a change in molecular structure from an unbridged, linear system terminated by  $BH_2$

and  $BHCH_3$  groups at higher temperatures to a cyclic hydrogen-bridged structure at lower temperatures.

In contrast, it should be noted that  $\mu$ -dimethylaminodiborane does not undergo a reversible bridge cleavage until brought to relatively elevated temperatures in the presence of weak Lewis bases.<sup>6–8</sup> The lifetime of the unbridged species under these conditions is also very much shorter since, in the limit, a complete equilibration of boron-bound protons was observed in the nmr time scale (about  $10^{-3}$  sec).<sup>8</sup> The substituted case is strikingly different in that the higher temperature spectra indicate that the lifetime of the unbridged species is at least long compared to milliseconds and also that the bridge opening is always in the same direction, *i.e.*, toward the unsubstituted boron.

**Acknowledgment.**—The authors are grateful to the U. S. Army Research Office (Durham) for support of this work under Grant DA-ARO (D)-31-124-G556.

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## Iron Carbonyl Complexes of Azo Compounds<sup>1</sup>

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Prior to 1963 the literature contained very little information on azo groups involved in delocalized bonding with transition metals apart from some azo dye metal chelates. In 1963, Kleiman and Dubeck reported<sup>3</sup> on the reaction of azobenzene and dicyclopentadienylnickel to yield a complex involving nickel bonded to the azo link and to one aromatic ring. In 1965, Cope and Siekman<sup>4</sup> found similar Pt and Pd complexes of azobenzene and substituted azobenzenes. In the same year Porter and Murray<sup>5</sup> examined  $PdCl_2$  and  $AgNO_3$  complexes of benzo[*c*]cinnoline (1), a compound containing a *cis*-azo link, but did not propose any structure for these complexes. Balch and Petridia<sup>6</sup> recently described azo complexes of Pd in which only one nitrogen was thought to be involved in bonding to the metal. Pauson<sup>7</sup> reported on complexes of Schiff bases and of azobenzene with  $Fe_2(CO)_9$ . The Schiff base complexes are analogous to Cope's complexes involving substitution of iron into the *ortho* position of the aromatic ring. The original communication reported that the azobenzene complex underwent rearrangement to *o*-semidine on lithium aluminum hydride reduction,

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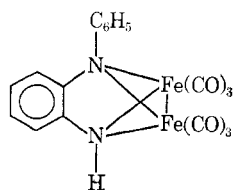
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Subsequent X-ray work by Baikie and Mills,<sup>8</sup> however, established that the complex already has the *o*-semidine structure and that formation of the complex must involve rupture of the N-N bond with each nitrogen being a three-electron donor. Cyclopentadienylcobalt and

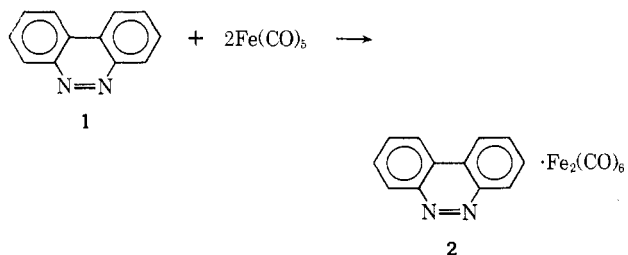


azobenzene also form a complex with an *o*-semidine structure.<sup>9</sup>

Dekker and Knox<sup>10</sup> have reported that the reaction of  $\text{Fe}_2(\text{CO})_9$  and azidobenzene yields a complex based on an azobenzene skeleton. This complex decomposes spontaneously in solution to a urea-based complex and is not an intermediate in formation of the *o*-semidine complex.

More recently, Otsuka and coworkers<sup>11</sup> obtained a related iron carbonyl complex of a conjugated azo olefin from 2-(methylazo)propene and  $\text{Fe}_2(\text{CO})_9$ . Also, Campbell and Rees<sup>12</sup> described the formation of iron carbonyl complexes from *ortho*-substituted phenyl azides and diazides.

We now report some of our investigations on complexes containing a rigid *cis*-azo group. It was found that benzo[*c*]cinnoline (1) will react with 2 mol of iron pentacarbonyl to form a red-orange, crystalline, air-stable complex (2) with the composition  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{Fe}_2(\text{CO})_6$ . The reaction product is easily purified by



chromatography on alumina to yield the pure complex in 79% yield. Diiron nonacarbonyl or triiron dodecarbonyl can also be used.

The complex (2) is diamagnetic, somewhat soluble in organic solvents, and nonconducting ( $\Lambda_{\text{molar}} = 1.2$  mhos) in nitromethane. Oxidation with ceric ammonium nitrate in acetone yields the theoretical amount of benzo[*c*]cinnoline. Reaction of 2 with lithium aluminum hydride gave 2,2'-diaminobiphenyl in 56% yield as the only isolated product. Under the same conditions 1 is stable to lithium aluminum hydride, so the azo link in the complex must be weakened.

The molecular weight (460) and presence of six CO

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(11) S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, **8**, 2514 (1969).

(12) C. D. Campbell and C. W. Rees, *Chem. Commun.*, 537 (1969).

groups were confirmed by mass spectral analysis. Mössbauer analysis<sup>13</sup> indicated that the two iron atoms are in equivalent environments (IS of  $-0.13$  mm/sec. and QS of 0.99 mm/sec). The infrared spectrum shows only terminal metal carbonyl absorptions at 2073, 2033, 1989, and 1972  $\text{cm}^{-1}$  (sh) in  $\text{CS}_2$ . One carbonyl group of the complex is easily displaced by triphenylphosphine in benzene at room temperature and up to 80° to form a new stable complex  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{Fe}_2(\text{CO})_5 \cdot \text{P}(\text{C}_6\text{H}_5)_3$ . No further displacement of CO by triphenylphosphine could be achieved under similar conditions.

The azo link appears to be essential as no complexes could be obtained under similar conditions from phenanthridine or phenanthrene.<sup>14</sup> Also, attempts to form analogous complexes using other metal carbonyls such as Cr, Mo, W, Co, and Ni have been unsuccessful. Manganese carbonyl was not tried. Other complexes which have been prepared are shown in Table I.

TABLE I

Ligand	Complex formula	MP, °C
1,10-Dichlorobenzo[ <i>c</i> ]cinnoline	$\text{C}_{18}\text{H}_8\text{N}_2\text{O}_6\text{Cl}_2\text{Fe}_2$	130 dec
3,8-Dichlorobenzo[ <i>c</i> ]cinnoline	$\text{C}_{18}\text{H}_8\text{N}_2\text{O}_6\text{Cl}_2\text{Fe}_2$	170
3-Phenylcinnoline	$\text{C}_{20}\text{H}_{10}\text{N}_2\text{O}_6\text{Fe}_2$	125
Dibenz[1,4,5]oxadiazepine	$\text{C}_{18}\text{H}_8\text{N}_2\text{O}_7\text{Fe}_2$	160
2,3-Diazabicyclo[2.2.1]hept-2-ene	$\text{C}_{11}\text{H}_8\text{N}_2\text{Fe}_2\text{O}_6$	100 dec
4,5,9,10-Tetraazapyrene	$\text{C}_{24}\text{H}_8\text{N}_4\text{O}_{12}\text{Fe}_4$	140
Azobenzene	$\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}_6\text{Fe}_2$	55 dec

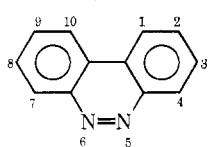
<sup>a</sup> Melting points are approximate as the complexes slowly turn brown in air above 100°.

Azobenzene under these reaction conditions forms an unstable complex which appears, by mass spectra, infrared, and elemental analyses, to be of the same type. This complex slowly degrades in air to azobenzene in contrast to Dekker and Knox's complex. Attempts to purify this complex by chromatography or sublimation led only to azobenzene with no evidence for any *o*-semidine product. Cinnoline formed a colored solution, but no air-stable solid complex could be isolated. Pyridazine appears to form a different kind of complex and bears further investigation.

A study of the nmr spectra of several benzocinnolines and their complexes was undertaken to elucidate the structures. Table II shows some of the results. Benzo[*c*]cinnoline shows two multiplets of four protons each interpreted as protons 4, 7, 1, and 10 in the low-field group and 2, 9, 3, and 8 in the high-field group. Benzo[*c*]cinnoline 5-oxide is included to demonstrate that decreasing the electron density on the nitrogen atom causes an upfield shift of the proton on the adjacent atom (C-4) into the 2,9,3,8 multiplet. Unfortunately, the N,N'-dioxide was too insoluble to be examined. The spectra of the complexes all have the peaks shifted slightly upfield. The signals of the 4 and 7 protons are in each case shifted up into the 2,9,3,8 group indicating a symmetrical molecule involving only the nitrogen atoms in complexing.

(13) We are indebted to Professor R. Herber, Rutgers University, for several Mössbauer analyses and discussions concerning their interpretation.

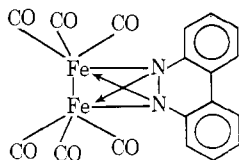
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TABLE II  
NMR SPECTRA

	Ligand		Complex	
	$\tau^a$	H	$\tau$	H
Benzo[c]cinnoline	1.42	4,7	2.15	1,10
	1.79	1,10		
	2.32	2,9,3,8	2.7	4,7,2,9,3,8
3,8-Dichlorobenzo- [c]cinnoline	1.30	4,7	1.66	1,10
	1.58	1,10	2.09	2,9
	2.16	2,9	2.83	4,7
	1.44	4,7	2.5-3.0	
1,10-Dichlorobenzo- [c]cinnoline	2.25	2,9,3,8	Multiplet	
	1.50	7		
Benzo[c]cinnoline 5-oxide	1.99	1,10		
	2.40	2,9,3,8,4		

<sup>a</sup> All of the peaks are multiplets.

On the basis of the above data we proposed<sup>1</sup> a structure analogous to Baikie and Mills' *o*-semidine structure and Dekker and Knox's azobenzene-type structure



wherein the Fe-Fe plane is perpendicular to the benzo-cinnoline plane and the N-N bond is not totally ruptured, but each N atom acts as a three-electron donor. The tetraazapyrene complex presumably has the Fe<sub>2</sub>(CO)<sub>6</sub> structure complexed to each azo link. The infrared spectrum of **2** compared with the spectra of **1** and the N,N'-dioxide in the 1400-1620 cm<sup>-1</sup> region indicates a simplification in the complex compatible with lower N-N bond order.<sup>11,15</sup>

Recent single-crystal X-ray analysis has now confirmed the proposed structure and has been reported on in detail in a separate communication.<sup>16</sup> Preliminary data indicate the N-N bond to be a "normal" single bond of 1.40 Å. These values are similar to another recently reported<sup>17</sup> complex which contains an N-N bond.

#### Experimental Section

Iron pentacarbonyl was purchased from GAF and used as received. The starting azo compounds were obtained commercially or prepared by literature procedures. In each case the complexes were characterized by elemental analysis and nmr (Varian A-60), ir (PE-221), and mass spectra (AEI MS-9). A general procedure, used for preparing all of the complexes, is given below. Column chromatography was the preferred purification procedure although some complexes could be sublimed.

**Benzo[c]cinnolinehexacarbonyldiiron (2).**—A mixture of benzo-[c]cinnoline (2.04 g, 0.0113 mol) and iron pentacarbonyl (4.43 g, 0.0226 mol) in decalin (50 ml) was heated with stirring at 150° until gas evolution ceased (about 1 hr). The mixture was cooled and filtered and the red filtrate chromatographed on alumina. Petroleum ether (bp 30-60°) was used to elute the decalin. Petroleum ether-benzene (4:1) eluted the complex, dark red

(15) We gratefully acknowledge the assistance of Mr. Norman Colthup in interpreting the infrared spectra.

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crystals, 4.1 g (79%), mp 145° dec. *Anal.* Calcd for C<sub>15</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>Fe<sub>2</sub>: C, 46.99; H, 1.75; N, 6.09; O, 20.87; Fe, 24.28. Found: C, 47.38; H, 1.79; N, 6.24; O, 20.73; Fe, 24.18.

**3,8-Dichlorobenzo[c]cinnolinetriphenylphosphinepentacarbonyldiiron.**—3,8-Dichlorobenzo[c]cinnolinehexacarbonyldiiron (0.21 g, 0.0004 mol) and triphenylphosphine (0.10 g, 0.0004 mol) in benzene (35 ml) were heated at reflux for 2 hr. The solution was cooled and the solvent was evaporated under vacuum. The red solid product was triturated with petroleum ether and ethanol resulting in an orange solid, 0.2 g (66%), mp 215° dec. *Anal.* Calcd for C<sub>35</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub>Cl<sub>2</sub>PF<sub>2</sub>: C, 55.08; H, 2.77; N, 3.67; Cl, 9.29; P, 4.06; Fe, 14.64. Found: C, 55.11; H, 2.80; N, 4.08; Cl, 9.32; P, 4.36; Fe, 14.92.

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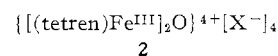
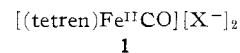
### Complexes of Tetraethylenepentamine with Iron(II) and Iron(III). An Iron(II) Carbonyl Derivative

BY L. RUSSELL MELBY

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Tetraethylenepentamine (tetren) forms well-characterized complexes with Co(II), Co(III), Cr(III),<sup>1-4</sup> and Cu(II).<sup>5</sup> Stability constants with other transition metal ions<sup>6-8</sup> and several nontransition metal ions<sup>8</sup> have been determined, but published work with iron has been limited to a stability constant measurement and unsuccessful attempts to prepare complexes with Fe(II) and Fe(III)<sup>6</sup> and an examination of the Fe(III) derivative, in solution, as a catalyst for hydrogen peroxide decomposition.<sup>9</sup>

This note describes the isolation of crystalline complexes of tetraethylenepentamine with Fe(II) wherein carbon monoxide occupies the sixth coordination position (**1**) and of acidotetraethylenepentamine complexes of Fe(III) wherein the two iron atoms are presumably oxygen bridged to form the dimeric species **2**.<sup>10</sup>



#### Experimental Section

Tetraethylenepentamine was vacuum distilled and the fraction of bp 155-160° (1.0-1.5 mm) was used. Hydriodic acid

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