

PHTHALAZINE IRON CARBONYL COMPLEXES

HOWARD ALPER

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901 (U.S.A.)

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SUMMARY

Reaction of phthalazine with diiron enneacarbonyl in benzene at room temperature and with triiron dodecacarbonyl in hot benzene gives mono- and binuclear complexes where the nitrogen atoms behave as two- or three-electron donor ligands. 1,2-Dihydrophthalazine and a binuclear iron carbonyl derivative are formed when the triiron dodecacarbonyl reaction is effected in methanolic benzene.

Recent publications on iron carbonyl complexes of pyridazines^{1,2} and 1-pyrazolines³ prompt the author to report on the first metal carbonyl complexes of the related phthalazine system.

Treatment of phthalazine (I, Scheme 1) with diiron enneacarbonyl [$\text{Fe}_2(\text{CO})_9$] in benzene at room temperature for 36 h, followed by chromatography on Florisil, gave beautiful red-brown crystals of phthalazine iron tetracarbonyl (II) as the major

SCHEME 1

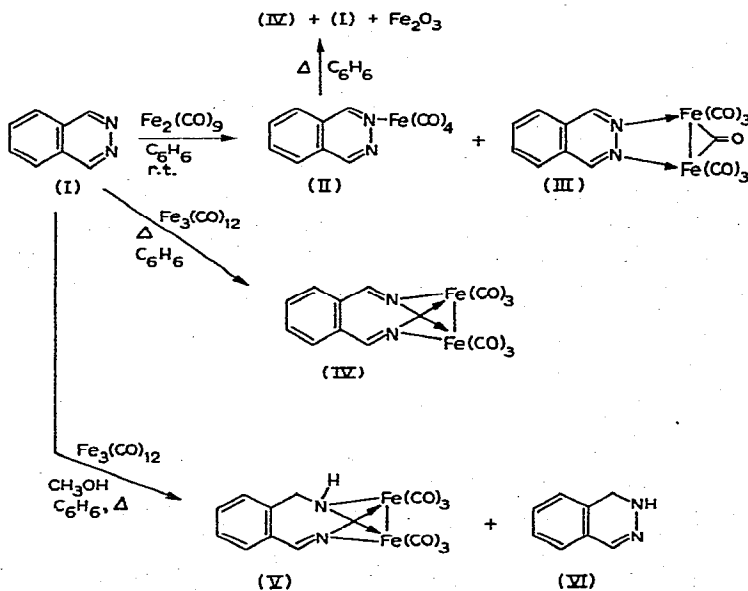


TABLE 1

PHTHALAZINE IRON CARBONYL COMPLEXES

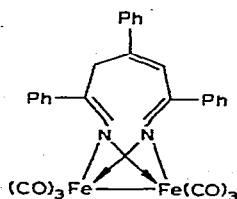
Compound	M.p. (dec.) (°C)	$\nu(\text{CO})$ (cm^{-1})	Highest ion peak m/e (no. of CO's)	$^1\text{H NMR}(\text{ppm})^a$
(I)				7.92 (s, 4H), 9.56 (s, 2H) [CDCl_3]
(II)	128	2054 m, 1982 s, 1955 s, 1935 s (C_6H_{14}), 2056 s, 1998 m, 1957 vs, 1919 vs (KBr)	298(4)	7.97 (s, 4H), 9.20 (s, 1H) 9.72 (s, 1H) [CDCl_3]
(III)	173	2059 s, 2010 s, 1990 vs, 1925 s, 1748 ms (KBr), 1771 ms (CH_2Cl_2)	410(6)	
(IV)	^b	2059 s, 2038 vs, 2001 ms, 1981 s, 1972 m (C_6H_{14}), 2058 s 2022 vs, 1990 s (sh), 1982 vs, 1945 w (KBr)	410(6)	7.20–8.00 (m) [(CD_3) $_2$ CO]
(V)	158	2068 s, 2021 vs, 1984 vs, 1961 m, 1951 mw (KBr)	412(6)	

^a Chemical shifts measured in ppm using tetramethylsilane as internal standard. ^b Decomposed without melting at temperature $>90^\circ$.

product (58% yield) and the binuclear complex III (26% yield). Melting points and pertinent spectral data for the complexes are given in Table 1. The $^1\text{H NMR}$ spectrum of II shows the expected non-equivalence of the two protons on the heterocyclic ring carbons. Complexes analogous to II have been reported to be obtained in poor yield by reaction of pyridazine and 3,6-dimethylpyridazine with $\text{Fe}_2(\text{CO})_9$ ¹.

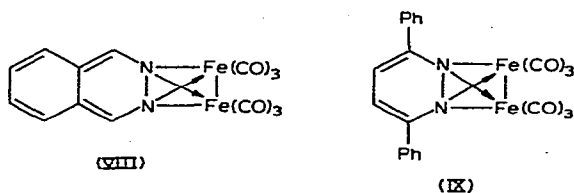
Bridging (1748 cm^{-1}) as well as terminal metal carbonyl stretching was observed in the IR spectrum of the complex assigned structure III. The mass spectrum of III did not show the expected molecular ion peak at m/e 438 (highest fragment appeared at m/e 410) but molecular weights of 436 and 443 were obtained from vapor phase osmometric determinations. The structure of III is quite analogous to that assigned to the binuclear complex isolated from the reaction of 3,5-diphenyl-4,4-dimethyl-1,2-diaza-2,5-cyclopentadiene with excess $\text{Fe}_2(\text{CO})_9$ in *n*-pentane⁴.

Reaction of I with triiron dodecacarbonyl [$\text{Fe}_3(\text{CO})_{12}$] in refluxing benzene gave IV, assigned on the basis of analytical data and spectral results, particularly the similarity of the position of the terminal metal carbonyl stretching bands when compared with VII⁵. In addition, repetition of the experiment using $\text{Fe}_3(\text{CO})_{12}$ moistened



(VII)

with methanol gave the interesting complex V in low yield (1,2-dihydrophtalazine (VI) was the major product and hence this reaction represents a new, simple method for effecting reduction of the carbon–nitrogen double bond)⁶. While the alternate structure, VIII, is possible for complex IV (3,6-diphenylpyridazine gave IX on treatment with $\text{Fe}_2(\text{CO})_9$)⁷, no such analog is possible for V. Note, however, that VIII has an *ortho*-xylylene structure while IV is benzenoid in nature and IX is a diaza-1,3-cyclohexadiene.



Phthalazine, small amounts of IV, and iron oxide were obtained when II was heated in benzene for 12 h.

In summary, phthalazine reacts with iron carbonyls to form a number of different and interesting complexes whose use as intermediates in the synthesis of novel organic heterocycles is under active investigation.

EXPERIMENTAL

Phthalazine (Aldrich Chemical Co.) and the three iron carbonyls (Pressure Chemical Co.) were commercial products. All reaction and work-up solvents were dried prior to use. All reactions were carried out under a nitrogen atmosphere.

Elemental analyses were carried out by Hoffmann-LaRoche, Nutley, N.J., and Meade Microanalytical Lab, Amherst, Mass. Melting points were determined in sealed tubes using a Gallenkamp apparatus. A Perkin–Elmer 521 spectrometer was used for IR determinations. Nuclear magnetic resonance spectra were recorded using a Varian A-60 spectrometer.

Reactions of phthalazine (I)

(i) *With $\text{Fe}_2(\text{CO})_9$* . A mixture of I (1.85 g, 15.0 mmol) and $\text{Fe}_2(\text{CO})_9$ (7.28 g, 20.0 mmol) in dry benzene (60 ml) was stirred at room temperature for 36 h. The solution was filtered, the filtrate concentrated to a small volume, and then chromatographed on Florisil. Elution with benzene first gave 2.60 g (58%) of II. Anal. Found: C, 48.34; H, 2.21; N, 9.33; Fe, 19.01. $\text{C}_{12}\text{H}_6\text{N}_2\text{FeO}_4$ calcd.: C, 48.36; H, 2.03; N, 9.39; Fe, 18.74%.

Further elution with benzene gave 1.73 g (26%) of III. Anal. Found: C, 41.03; H, 1.67; N, 6.77; Fe, 26.90, 26.44. $\text{C}_{15}\text{H}_6\text{N}_2\text{Fe}_2\text{O}_7$ calcd.: C, 41.14; H, 1.38; N, 6.40; Fe, 25.51%. Molecular weight found: 436, 443; calcd. 438.

(ii) *With $\text{Fe}_3(\text{CO})_{12}$ and methanol in benzene*. A mixture of I (1.32 g), $\text{Fe}_3(\text{CO})_{12}$ (6.50 g), dry methanol (3.0 ml), and benzene (50 ml) was refluxed with stirring for 19 h. The solution was cooled, filtered, and the filtrate evaporated *in vacuo*. The residue was dissolved in benzene and chromatographed on Florisil. Elution with benzene gave 0.33 g of V. Anal. Found: C, 40.75; H, 2.09; N, 6.63; Fe, 27.07. $\text{C}_{14}\text{H}_8\text{N}_2\text{Fe}_2\text{O}_6$ calcd.: C, 40.92; H, 1.96; N, 6.80; Fe, 27.11%.

Elution with benzene-ether (1/1) gave 0.72 g (54%) of 1,2-dihydrophthalazine, m.p. 83.5–85.0° (lit.⁸ m.p. 84.0–85.0°).

(ii) *With Fe₃(CO)₁₂ in benzene.* A mixture of I (1.23 g) and Fe₃(CO)₁₂ (6.50 g) in benzene (50 ml) was refluxed with stirring for 9–15 h. The solution was cooled, filtered, and the filtrate evaporated *in vacuo*. The residue was treated with petroleum ether (b.p. 38–52°), filtered, the filtrate concentrated to a small volume, and then chromatographed on Florisil. Elution with petroleum ether–benzene gave IV. Anal. Found: C, 40.79; H, 1.44; N, 6.48; Fe, 27.61. C₁₄H₆N₂Fe₂O₆ calcd.: C, 41.02; H, 1.47; N, 6.83; Fe, 27.25%.

Thermal Decomposition of II

A benzene (20 ml) solution of II (0.13 g) was refluxed with stirring for 12 h. The solution was cooled, filtered from iron oxide, and the filtrate concentrated *in vacuo*. Chromatography of the residue from filtrate evaporation gave I and then IV on elution with petroleum ether.

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