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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The attempts of the synthesis of rhenium carbonyl, chromium and ruthenium carbonyl phthalocyanine complexes are reported. The difficulties were in the isolation.		

Metal Carbonyl Complexes of Phthalocyanine

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I. Introduction

Our laboratory has been engaged in the synthesis and characterization of "Novel Metalloporphyrins" for the past decade. In 1966, we developed a new method¹ for synthesis of metalloporphyrins using metal carbonyls of organometallic compounds as the metal source. Several new metalloporphyrins, particularly metallocarbonylporphyrins were prepared for the first time using this method. The first novel metalloporphyrin prepared in this laboratory was chromium (II) mesoporphyrin IX dimethyl ester which shows a metal-metal interaction in the solid state (μ_{eff} : 2.84 BM). Although no carbonyl ligand is attached to the chromium porphyrin complex, a number of metalloporphyrin complexes prepared from metal carbonyl and porphyrin have carbonyl ligands. Metal carbonyl porphyrin complexes with rhodium,^{2,3,4,5} iridium,^{2,6} ruthenium,^{7,8} rhenium,⁹ and technetium¹⁰ have been prepared. In all of these complexes except the rhodium complex, the bonding of the metal-carbonyl is very strong and removal of the carbonyl ligand from the complex cannot be effected by the usual means.

Phthalocyanine complexes of the above metals are known to be prepared by the reactions of respective metal halides and phthalonitrile.¹¹ Although porphyrins and phthalocyanines have a similar macrocyclic structure and aromatic character, some properties are clearly different. One of them could be bonding of carbonyl ligand to the metal in the complex. A number

of metallocarbonylporphyrin complexes are known, and yet, to our knowledge, metallocarbonylphthalocyanines have not been isolated. Therefore, application of the synthetic method of metallocarbonylporphyrin to preparation of metal-phthalocyanine would be desirable. Moreover, the expected metallocarbonylphthalocyanines may possess properties such as good solubility towards organic solvents which is lacking to metallophthalocyanines and relative ease of removal of carbonyl ligand from the complex. If metallocarbonylphthalocyanine complexes have such properties, they could be used in the synthesis of one dimensional metallophthalocyanine polymers.

II. Results and Discussions

Since metallocarbonylporphyrin complexes are known to be prepared from reactions of porphyrin ligands and metal carbonyls or metallic carbonyl halides in appropriate solvents, one may anticipate that reactions of phthalocyanine ligands and metal carbonyls or metallic carbonyl halides would yield new metallocarbonylphthalocyanine complexes. In these reactions selection of solvent is the key to success. A number of low boiling solvents such as dichloromethane, chloroform, benzene, tetrahydrofuran, etc. were utilized. It was found that these solvents were not appropriate for synthesis of metallocarbonylphthalocyanine complexes. Therefore, higher boiling point solvents were investigated. Such solvents were 1,4-dioxane, N,N-dimethylformamide, n-butylether, diglyme, etc. Among these solvents, n-butylether was found to have sufficient solubility towards both dilithium phthalocyanine and metal carbonyls or metallic carbonylhalides.

Our results now have shown that air stable metal carbonyl phthalocyanines, $\text{PcLi}_2[\text{Cr}(\text{CO})_3]_2$ and $\text{Pc}[\text{Re}(\text{Co})_3]_2$ can be prepared from the reaction

of dilithium phthalocyanine and chromium hexacarbonyl and dirhenium deca-carbonyl, respectively, with n-butyl ether as the solvent.

The tricarbonylchromium complex is stable in air at ambient temperature, but decomposes at elevated temperature after prolonged heating. The compound does not sublime at 280°C *in vacuo* and decomposition to dilithium phthalocyanine results. Attempts to crystallize this compound failed since its solubility towards organic solvents is very low, and visible spectral evidence indicated that the tricarbonylchromium complex decomposes in α -chloronaphthalene solution. The complex shows strong carbonyl stretching absorptions in the infrared spectrum (KBr) at 1960 and 1900 cm^{-1} as is expected for the tricarbonylchromium moiety. The above data, together with the elemental analyses, show that the structure of the complex should be similar to tricarbonylchromium π -complexes of metallotetraphenylporphyrin, $\text{M-TPP}[\text{Cr}(\text{CO})_3]_2$.¹² Chromiumtricarbonyl units attach to the phenyl rings on opposite faces of the phthalocyanine ligand (Fig. 2). Elemental analyses of these phthalocyanine complexes prepared in this laboratory are admittedly outside of normal error limits except in a few cases. Phthalocyanines are well known to be thermally very stable and at the same time are known to be sublimable. Older publications often reported that elemental analyses did not fit the molecular formula well with the exception of one or two elements.

Attempts to prepare $\text{PcLi}_2[\text{M}(\text{CO})_3]_2$ (where $\text{M} = \text{Mo}, \text{W}$) were not successful by this method. The synthesis of molybdenum and tungsten complexes require more rigorous reaction conditions than chromium complexes. For instance, chromium arene complexes can be prepared at one atmosphere of pressure while syntheses of molybdenum and tungsten arene complexes required reaction in a fused tube or at high pressure. Therefore, the above molybdenum and tungsten complexes

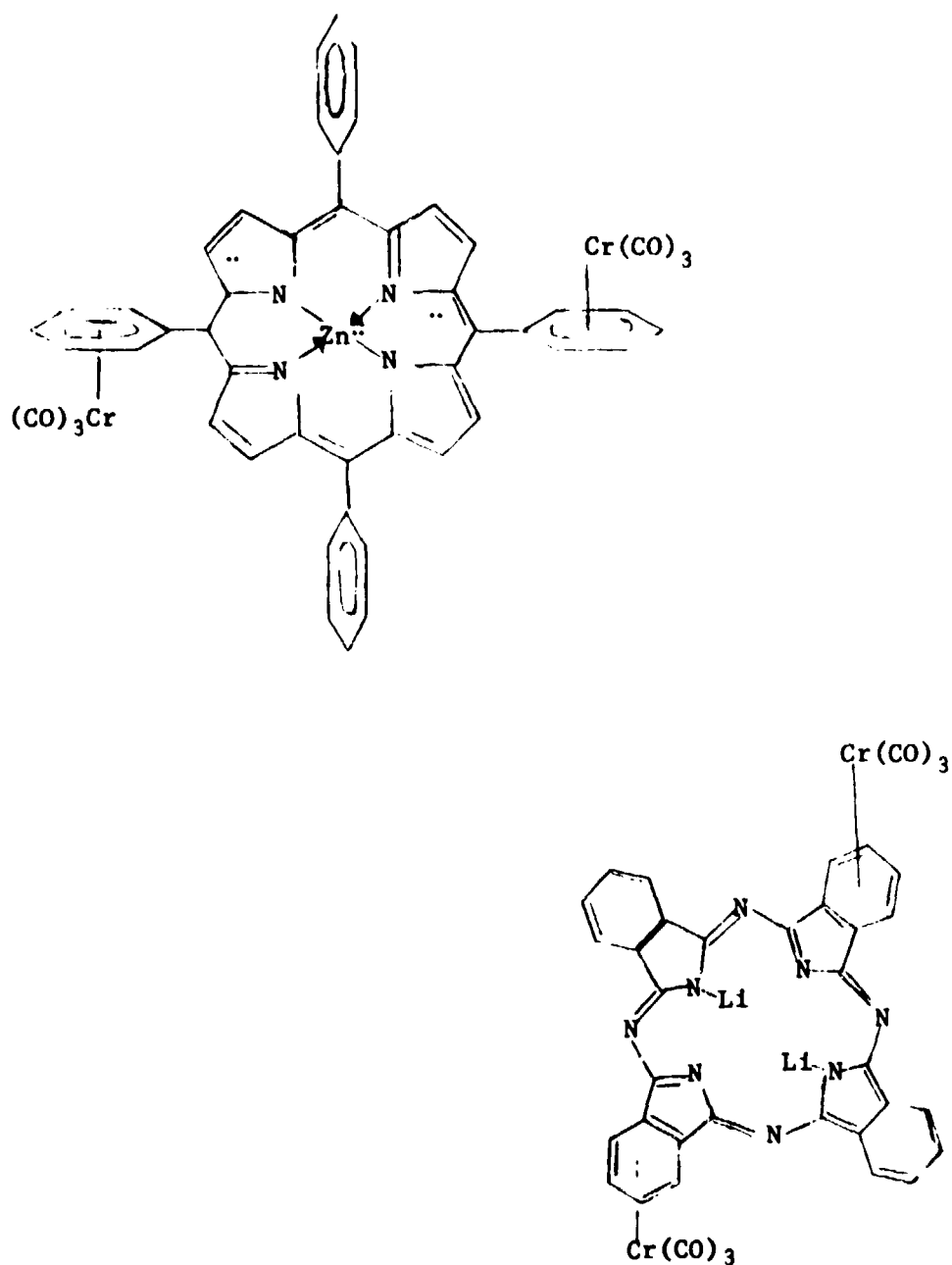


Figure 2. Structure of bis-(π -Cr(CO)₃)-Zn(TPP) and the proposed structure of PcLi₂(Cr(CO)₃)₂

might be obtainable if the reactions were carried out at high pressure. Iron pentacarbonyl, chlorodicarbonylrhodium(I) dimer and triruthenium dodecacarbonyl were also used in the attempted syntheses of the corresponding dilithium phthalocyanine adducts because these metal sources were utilized to form metalloporphyrin and metalcarbonylporphyrin complexes.^{5,7} However, none of the trials were successful, probably because dilithium phthalocyanine was used. If free phthalocyanine was used in analogy to the use of free base porphyrin in metalcarbonylporphyrin syntheses, the desired products might have been obtained. The choice, however, of solvent is a critical factor for success.

III. Experimental

Tricarbonylchromium π -complexes of Dilithium Phthalocyanine

Dilithium phthalocyanine (0.2g) and chromiumhexacarbonyl (0.25g) were allowed to reflux in di-n-butyl ether (200 mL) for 6 hours under argon. The initial purplish color of the reaction mixture turned dark blue after 6 hours of heating. The reaction mixture was condensed to 40 ml *in vacuo* and was allowed to cool to room temperature. The resulting precipitate was isolated by filtration and then was washed twice with 20 mL of pentane and dried in a desiccator. The infrared spectrum (KBr) of the product shows two strong carbonyl bands at 1900 and 1960 cm^{-1} . Attempts to take a visible spectrum appeared to be unsuccessful due to the insolubility of the product towards most organic solvents. In fact, visible spectra that were obtained in chloronaphthalene, acetone, etc., were almost identical with the spectra of dilithium phthalocyanine in the same solvents. The product was dried at 120°C in an Abderhalden drying apparatus for 3 hours.

The infrared spectrum (KBr) of the dried product is identical with that of the product obtained before drying. The dried product was suspended in 60 ml of 1-propanol and stirred for 5 minutes under argon in order to remove any unreacted dilithium phthalocyanine. The resulting solid was filtered, washed three times with 10 mL of n-pentane, and dried in a Abderhalden drying apparatus.

This reaction was run several times, and elemental analysis data of the resulting products are presented in Table I.

Table I. Elemental Analysis Data for Tricarbonylchromium π -Complexes of Dilithium Phthalocyanine^a

	C	H	N	Li	Cr	Cr to N ratio
Calcd. for $C_{38}H_{16}N_8O_8Li_2Cr_2$	57.16	2.02	14.03	1.74	13.02	2.00 : 8.00
Calcd. for $C_{38}H_{16}^{1/4}O_8Li_2Cr_2$ - ($C_4H_9-O-C_4H_9$)	59.48	3.69	12.07	1.49	11.20	2.00 : 8.00
Attempt 1	-	-	11.03	-	11.63	2.27 : 8.00
Attempt 2	50.55	3.95	10.90	1.23	15.53	3.07 : 8.00
Attempt 3 ^b	58.85	3.94	14.87	1.54	4.18	0.60 : 8.00
Attempt 4 ^b	55.11	3.78	13.78	-	7.88	1.23 : 8.00

^aRef. 13^bThese attempts included an additional extraction with hot hexane.

The Reaction of Molybdenum Hexacarbonyl with Dilithium Phthalocyanine

Dilithium phthalocyanine (0.21g) and molybdenum hexacarbonyl (0.31g) were stirred at 100°C in di-n-butylether for 4 hours under argon. The reaction mixture was allowed to cool to room temperature. The resulting purple solid was isolated by filtration, washed three times with 10 mL of n-pentane, and dried in a desiccator. The infrared spectrum (KBr) of the product shows no carbonyl bands in the region of 2100-1800 cm^{-1} . The remainder of the spectrum is similar to that of dilithium phthalocyanine. This reaction was attempted twice more in boiling di-n-butyl ether and in refluxing decalin. In each case no reaction occurred.

The Reaction of Tungsten Hexacarbonyl with Dilithium Phthalocyanine

Dilithium phthalocyanine (0.13g) and tungsten hexacarbonyl (0.23 g) were allowed to reflux in di-n-butyl ether for 4 hours under argon. The reaction mixture was allowed to cool to room temperature. The resulting purple solid was isolated by filtration, washed three times with 10 mL of n-pentane, and dried in a desiccator. The infrared spectrum (KBr) of the product shows no carbonyl stretching bands in the region of 2100-1800 cm^{-1} .

In another attempt, refluxing the reaction mixture for 24 hours in di-n-butyl ether again resulted in no reaction.

Reaction of Iron Pentacarbonyl and Dilithium Phthalocyanine

Dilithium phthalocyanine (0.25g) and iron pentacarbonyl (0.71g) were stirred at 100°C in di-n-butyl ether for 21 hours under argon. After the reaction mixture was allowed to cool to room temperature, the resulting purple solid was isolated by filtration, washed three times with 10 mL of n-hexane, and dried in a desiccator. The infrared spectrum (KBr) of the product shows no carbonyl stretching bands in the region of 2100-1800 cm^{-1} .

An attempt in refluxing di-n-butyl ether resulted in no reaction.

μ -[Phthalocyanato]-bis-[tricarbonyl rhenium(I)]

Dilithium phthalocyanine (0.052g) and dirhenium decacarbonyl (0.136g) were allowed to reflux in a decalin for 24 hours under argon. After standing and cooling to room temperature, the resulting black solid was filtered, washed five times with 10 mL of n-pentane, and dried in a desiccator.

The infrared spectrum (KBr) of the product shows strong absorptions at 2000, 1940, and 1900 cm^{-1} . Further purification was attempted by sublimation at 320°C and 0.025 mm Hg. The product sublimate was collected until the residue shows no carbonyl band in its infrared spectrum (KBr). Elemental analysis data of several attempts are reported in Table II. The melting point of the product was greater than 340°C.

Table II. Elemental Analysis Data for μ -[Phthalocyanato]-bis-[tricarbonyl rhenium (I)]^a

	C	H	N	Li	Cr	Ratio of Elements
Calcd. for $C_{35}H_{16}N_8O_3LiRe$	53.23	2.04	14.19	0.88	23.58	1.00 : 8.00 ^b
Calcd. for $C_{38}H_{16}N_8O_3Re_2$	43.35	1.53	10.64	-	35.37	2.00 : 8.00 ^b
Attempt 1	-	-	-	0.66	17.24	.97 : 1.00 ^c
Attempt 2	54.42	3.10	10.89	-	15.8	.87 : 8.00
Attempt 3 ^d	37.93	2.73	8.63	-	28.44	1.98 : 8.00

^aRef. 13^bRe to Li^cRe to N^dIn this attempt a mixture of di-n-butyl ether and decalin was used and the resulting precipitate was washed with benzene and n-hexane

The Reaction of Chlorodicarbonylrhodium(I) Dimer with Dilithium Phthalocyanine

Dilithium phthalocyanine (0.11g) and an excess of chlorodicarbonyl rhodium(I) dimer were stirred in absolute ethanol at ambient temperature for 26 hours under argon. A large excess of hexane was added to the reaction mixture, and then the mixture was allowed to stand and cool to room temperature. The resulting precipitate was isolated by filtration, washed with hexane, and dried in a desiccator. The infrared spectrum (KBr) of the product shows no carbonyl stretching bands in the region to $2100\text{--}1800\text{ cm}^{-1}$.

Other attempts using 1-pentanol as the reaction solvent at room temperature and using di-n-butyl ether as the reaction solvent at 100°C for 24 hours resulted in no reaction as indicated by the absence of metal carbonyl stretching bands.

The Reaction of Triruthenium Dodecacarbonyl with Dilithium Phthalocyanine

Dilithium phthalocyanine (0.11g) and an excess of triruthenium dodecacarbonyl were allowed to reflux in di-n-butyl ether for 30 hours under argon. After standing and cooling to room temperature, the resulting precipitate was isolated by filtration, washed with hexane, and dried in a desiccator. The infrared spectrum (KBr) of the product shows no carbonyl bands in the region of $2100\text{--}1800\text{ cm}^{-1}$.

An attempt in refluxing decalin also failed.

Reaction of Phthalonitrile and Triruthenium Dodecacarbonyl

Phthalonitrile (0.54 g) was heated to reflux with triruthenium dodecacarbonyl for 4 hours under argon. After standing and cooling to room temperature, the reaction mass was dissolved in tetrahydrofuran, and the solution was diluted with n-hexane, and dried in a desiccator. The infrared spectrum (KBr) shows two carbonyl bands at 2000 and 1930 cm^{-1} . A TLC test indicated that the crude product contains three metallophthalocyanine compounds and

other impurities. Further experiments on the isolation and characterization of this complex will be reported.

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References and Notes

1. M. Tsutsui, M. Ichikawa, F. Vohwinkel and K. Suzuki, J. Amer. Chem. Soc., **88**, 854 (1965).
2. N. Sadasivan and E. B. Fleischer, J. Inor. Nucl. Chem., **30**, 591 (1968).
3. H. Ogoshi, T. Omura, Z. Yoshida, J. Amer. Chem. Soc., **95**, 1666 (1973).
4. E. B. Fleischer, Account Chem. Res., **3**, 105 (1970).
5. H. Ogoshi, J. Setsune, T. Omura and Z. Yoshida, J. Amer. Chem. Soc., **97**, 6461 (1975).
6. D. Ostfeld, M. Tsutsui, C. P. Hsung and D. C. Conway, J. Amer. Chem. Soc., **93**, 2548 (1971).
7. M. Tsutsui, D. Ostfeld and L. M. Hoffman, J. Amer. Chem. Soc., **93**, 1820 (1971).
8. B. C. Chow and I. A. Cohen, Bioinorg. Chem., **1**, 57 (1971).
9. D. Ostfeld, M. Tsutsui, C. P. Hsung and D. C. Conway, J. Coord. Chem., **2**, 101 (1972).
10. M. Tsutsui and C. P. Hsung, J. Coord. Chem., **3**, 193 (1973).
11. F. H. Moser and A. L. Thomas, "Phthalocyanine compounds," ACS Monograph 157, Reinhold, New York, 1973.
12. N. J. Gogan and Z. U. Siddiqui, Can. J. Chem., **50**, 720 (1972).
13. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. 11377.

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