

## Unusual Metalloporphyrins. XVIII. The First Heterodinuclear Metalloporphyrin.

[Tricarbonyltechnetium(I)]- $\mu$ -[mesoporphyrin IX dimethyl esterato]-[tricarbonylrhenium(I)]

Sir:

Several dinuclear metalloporphyrins in which one porphyrin binds with two metal ions have been reported.<sup>1-11</sup> In some of these complexes the porphyrins act as di-, tri-, or hexadentate ligands which are considered to be nonclassical coordination numbers for them. However, most of these novel metalloporphyrins are classified as homodinuclear complexes.<sup>1-4,7</sup> The others are either unstable heterodinuclear metalloporphyrins with two different metals bound to the porphyrin nitrogens<sup>6,8-11</sup> or stable heterodinuclear metalloporphyrin  $\pi$  complexes containing a metallo group bound to an aryl substituent of the porphyrin ring.<sup>5</sup> To our knowledge, no stable heterodinuclear metalloporphyrin has been found with two different metals bound to the porphyrin nitrogens.

Because of the current interest in finding new binding modes of porphyrins with metal ions, in the locations of metal ions on porphyrins, and in other aspects of unusual metalloporphyrin chemistry, unsuccessful attempts were made to isolate heterodinuclear metalloporphyrins. For example, the incorporation of additional metal ions such as  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$  was attempted with porphyrin complexes containing a single rhenium ion. The desired complexes were detected spectroscopically but could not be characterized.<sup>6</sup> We have, however, successfully isolated tricarbonyltechnetium(I)- $\mu$ -[mesoporphyrin IX dimethyl esterato]-tricarbonylrhenium(I),  $(\text{OC})_3\text{TcMPRe}(\text{CO})_3$  (the first heterodinuclear metalloporphyrin), and wish to report its preparation and characterization.

[Monohydrogen mesoporphyrin IX dimethyl esterato]tricarbonylrhenium(I) and ditechneium decarbonyl<sup>12</sup> in 1 to 0.6 mol ratio were mixed in decalin<sup>13</sup> and refluxed under argon. When absorptions at 397 (soret) and 513 nm reached maxima, the reaction was stopped. The decalin solution was cooled, centrifuged, and decanted, and the supernatant was evaporated to dryness under vacuum. The resulting solid was then extracted with dichloromethane several times. Finally, the combined extracts were evaporated to dryness and washed with *n*-hexane to give an air-stable, dark red solid (I), mp 238-240°. *Anal.*<sup>14</sup> Calcd for  $\text{ReTc}$ -

(1) D. Ostfeld, M. Tsutsui, C. P. Hrun, and D. C. Conway, *J. Amer. Chem. Soc.*, **93**, 2548 (1971).

(2) D. Cullen, E. Meyer, T. S. Srivastava, and M. Tsutsui, *ibid.*, **94**, 7603 (1972).

(3) H. Ogoshi, T. Omura, and Z. Yoshida, *ibid.*, **95**, 1666 (1973).

(4) Z. Yoshida, H. Ogoshi, T. Omura, E. Watanade, and T. Kuro-saki, *Tetrahedron Lett.*, 1077 (1972).

(5) N. J. Gogan and Z. U. Siddiqui, *Can. J. Chem.*, **50**, 720 (1972).

(6) D. Ostfeld, M. Tsutsui, C. P. Hrun, and D. C. Conway, *J. Coord. Chem.*, **2**, 101 (1972).

(7) M. Tsutsui and C. P. Hrun, *Chem. Lett.*, in press.

(8) P. Rothmund and A. R. Menotti, *J. Amer. Chem. Soc.*, **70**, 1808 (1948).

(9) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Amer. Chem. Soc.*, **73**, 4315 (1951).

(10) P. Hambricht, *J. Inorg. Nucl. Chem.*, **32**, 2449 (1970).

(11) E. B. Fleischer, E. I. Choi, P. Hambricht, and A. Stone, *Inorg. Chem.*, **3**, 1284 (1964).

(12)  $\text{Tc}_2(\text{CO})_{10}$  obtained from Pressure Chemical Co.  $^{44}\text{Tc}^{99}$ :  $\beta^-$ , 0.292 MeV; lifetime,  $2.12 \times 10^5$  years.

(13) For the purification of decalin, see M. Tsutsui, R. A. Velapoldi, K. Suzuki, F. Vohwinkel, M. Ichikawa, and T. Koyano, *J. Amer. Chem. Soc.*, **91**, 6262 (1969).

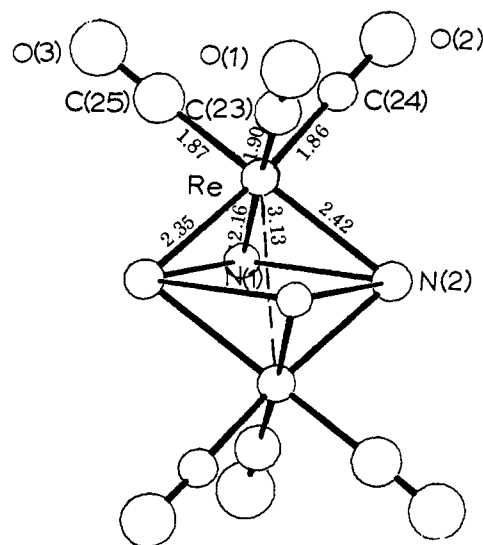


Figure 1. Coordination sphere showing bond distances around the Re atoms of [meso-tetraphenylporphinato]bis[tricarbonylrhenium(I)] (IV).

$\text{C}_{42}\text{H}_{40}\text{N}_4\text{O}_{10}$ : C, 48.30; H, 3.85; N, 5.36; Re, 17.80; Tc, 9.47; mol wt, 1046.0. Found: C, 48.25; H, 3.77; N, 5.15; Re, 17.90; Tc, 9.18; mol wt, 1024 (measured by vapor pressure osmometry in chloroform). The infrared spectrum of I in the solid phase (KBr) showed three strong metal-carbonyl stretching bands at 2045, 2030, and 1925  $\text{cm}^{-1}$  and two sharp ester carbonyl peaks at 1740 and 1720  $\text{cm}^{-1}$ . The mass spectrum<sup>15</sup> of I showed a parent peak at  $m/e$  1046;  $(M - 5\text{CO})^+$ ,  $(M - 6\text{CO})^+$ , and several doubly charged peaks were also observed. The visible spectrum of I in dichloromethane had absorption maxima at 513 nm ( $\log \epsilon$ , 4.462); 480 (3.795), shoulder; 397 (5.039); and 375 (4.398), shoulder.

The visible absorption spectrum of I was identical with those of  $\mu$ -[mesoporphyrin IX dimethyl esterato]-bis[tricarbonylrhenium(I)],  $\text{MP}[\text{Re}(\text{CO})_3]_2$ , II, and  $\mu$ -[mesoporphyrin IX dimethyl esterato]bis[tricarbonyltechnetium(I)],  $\text{MP}[\text{Tc}(\text{CO})_3]_2$ , III, except for anticipated shifts of the positions of the soret band and an absorption band at 513 nm (Table I).

Table I. Visible Absorption Maxima for  $(\text{OC})_3\text{TcMPRe}(\text{CO})_3$  (I),  $\text{MP}[\text{Re}(\text{CO})_3]_2$  (II), and  $\text{MP}[\text{Tc}(\text{CO})_3]_2$  (III) (in  $\text{CH}_2\text{Cl}_2$ )<sup>a</sup>

Complexes	Soret, nm	$\lambda(\text{max})$ , nm	Ref
II	400 (375 sh)	520 (480 sh)	1
I	397 (375 sh)	513 (480 sh)	
III	396 (375 sh)	507 (480 sh)	7

<sup>a</sup> sh indicates shoulders.

A crystallographic study of  $\mu$ -[meso-tetraphenylporphinato]bis[tricarbonylrhenium(I)],<sup>2</sup> IV, has shown that each Re ion is bonded to three nitrogen atoms, with both rhenium atoms on opposite sides of a single porphyrin (Figure 1). Because of the similarities in physical and chemical properties among II, III, and IV,

(14) Elemental analyses and molecular weight determination were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. 11377.

(15) CEC 21-104 mass spectrometer.

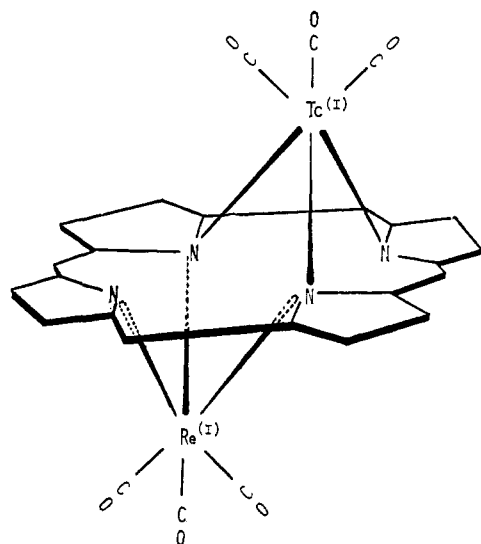


Figure 2. Schematic picture of  $(OC)_3TcMPRe(CO)_3(I)$ ; the alkyl substituents on the porphine ring are left out of the figure for clarity.

structures identical with that of IV were proposed for II<sup>1</sup> and III.<sup>7</sup> For the same reason, the structure shown in Figure 2 is proposed for I.

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## Indole Alkaloid Rearrangements in Acetic Acid

Sir:

Scott and Qureshi in 1968<sup>1</sup> claimed the conversion of (-)-tabersonine into (±)-catharanthine (12% yield) and (±)-pseudocatharanthine (28%), and of (+)-stemmadenine into (±)-tabersonine (12%), (±)-catharanthine (9%), and (±)-pseudocatharanthine (16%) in refluxing glacial acetic acid over periods ranging from 16 to 72 hr; even after extensive exchange of experimental information with the above authors we were unable to reproduce these results, indeed we failed to observe even traces of the rearrangement products claimed. With reluctance, we eventually felt obliged to publish our findings,<sup>2</sup> more recently with full experimental details.<sup>3,4</sup> One simple example of a result which could not be affected by experimental factors such as added boiling chips, external bath temperature, etc., is our observation that, on a 500-mg scale, catharanthine survives to the extent of less than 1% in refluxing acetic acid after 12 hr,<sup>3</sup> and that on a 5-mg scale it ceases to be detectable by tlc even after only 30 min; this makes the

(1) A. A. Qureshi and A. I. Scott, *Chem. Commun.*, 947 (1968).

(2) R. T. Brown, J. S. Hill, G. F. Smith, K. S. J. Stapleford, J. Poisson, M. Muquet, and N. Kunesch, *Chem. Commun.*, 1475 (1969).

(3) R. T. Brown, J. S. Hill, G. F. Smith, and K. S. J. Stapleford, *Tetrahedron*, 27, 5217 (1971).

(4) M. Muquet, N. Kunesch, and J. Poisson, *Tetrahedron*, 28, 1363 (1972).

isolation of the order of 10% of (±)-catharanthine<sup>1</sup> under such conditions difficult to understand.

We wish to state quite simply that none of the experimental work now described in preliminary form by Scott and Wei<sup>5a,c,d</sup> contradicts our findings; there is mention of general factors on which the success of the original rearrangements apparently depends, but these factors are not quantified,<sup>5a</sup> and we still await the full experimental details of the original work of Scott and Qureshi.<sup>1</sup>

It must be pointed out that the only reaction in acetic acid described in the four papers is that of (-)-tabersonine, from which only the isolation of allocatharanthine is now reported,<sup>5c</sup> in keeping with our own observations<sup>2,4</sup> and not with those of Scott and Qureshi.<sup>1</sup> The remaining reactions<sup>5a,c,d</sup> are carried out under *completely different* conditions (four on silica at 150° and one in methanol) and in any case on *none* of the original compounds studied by us (stemmadenine, tabersonine, and catharanthine). We wish to refrain from commenting on this new work.

The substance referred to by Scott as the "levorotatory preparation to which they allude as pseudocatharanthine" was prepared as described by Gorman *et al.*,<sup>6</sup> except that it was not crystallized, and was fully characterized spectrally;<sup>3</sup> the fact that the recrystallized material handled by Scott is fully racemic is not surprising, as the ~10% excess of one of the enantiomers in the total material would not be expected to cocrystallize. Our ~90% racemic pseudocatharanthine was not used at all by us as a reference compound in the sense indicated by Scott<sup>5b</sup> for the simple reason that pseudocatharanthine, whether partially or fully racemic, never turned up in the reactions of stemmadenine and tabersonine; Scott's criticisms are thus void.

Scott states that "the manipulation of microgram quantities in biomimetic experiments is an art which, in our experience, has oft-times required several hundred trials before declaring a negative result";<sup>5b</sup> whatever this statement may mean, it has no relevance to our work, which was carried out on the larger scale of 5–20 mg, with the exception of the preparative experiments, which approached the gram scale.

(5) (a) A. I. Scott and C. C. Wei, *J. Amer. Chem. Soc.*, 94, 8266 (1972); (b) A. I. Scott, *ibid.*, 94, 8262 (1972); (c) A. I. Scott and C. C. Wei, *ibid.*, 94, 8263 (1972); (d) *ibid.*, 94, 8264 (1972).

(6) M. Gorman, N. Neuss, and N. J. Cone, *J. Amer. Chem. Soc.*, 87, 93 (1965).

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## Direct Observation of Oxaphosphetanes from Typical Wittig Reactions

Sir:

Nonstabilized phosphorus ylides attack simple ketones or aldehydes at -70° to form 1:1 adducts which decompose into triphenylphosphine oxide and olefins above 0°. This sequence of events is traditionally explained by assuming that a betaine such as 1 or its