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COMMUNICATION

SYNTHESIS, STRUCTURE AND LIGAND EXCHANGE REACTIONS OF Ru(TTP)(NO)(OMe)*

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Abstract—A facile, novel preparation of the useful synthon Ru(TTP)(NO)(OMe) is reported and it has been characterized by a range of techniques, including single crystal X-ray diffraction. Subsequent methoxide substitution reactions led to the preparation in high yield and purity of a wide variety of new complexes including a mercaptide complex which is the first reported analogue of the diamagnetic nitrosyl adducts of the P-450 monooxygenases. Copyright © 1996 Elsevier Science Ltd

Although ruthenium has an extensive coordination chemistry of both nitric oxide[1,2] and porphyrinato dianions,[3,4] the chemistry of Ru(porphyrin)(NO)X remains largely unexplored.[5–8] In part this is due to a lack of a practical efficient general synthesis of this class. There is currently considerable interest in these compounds due to the recently recognized pervasive biological role that the nitrosyl adducts of haeme proteins have in intercellular communication.[9,10] Herein we report: (1) a high yield general synthesis of Ru(TTP)(NO)(OMe) directly from Ru(TTP)(CO)(MeOH); (2) the structure of this useful synthon; (3) derivatization/substitution reactions with a wide range of anionic ligands such as chloride, mercaptide, imidazolide and nitrite.

When Ru(TTP)(CO)(MeOH) is treated with nitric oxide under the mild conditions depicted in Scheme 1, Ru(TTP)(NO)(OMe), (**1**) is isolated in 87% yield as air-stable red–purple crystals by recrystallization from dichloromethane/methanol.‡

*Abbreviations used include: TTP, for the porphyrinato dianion of *meso*-tetrakis(5,10,15,20-*p*-tolyl) porphyrin; DBU, for 1,8-diazabicyclo[5.4.0]undec-7-ene.

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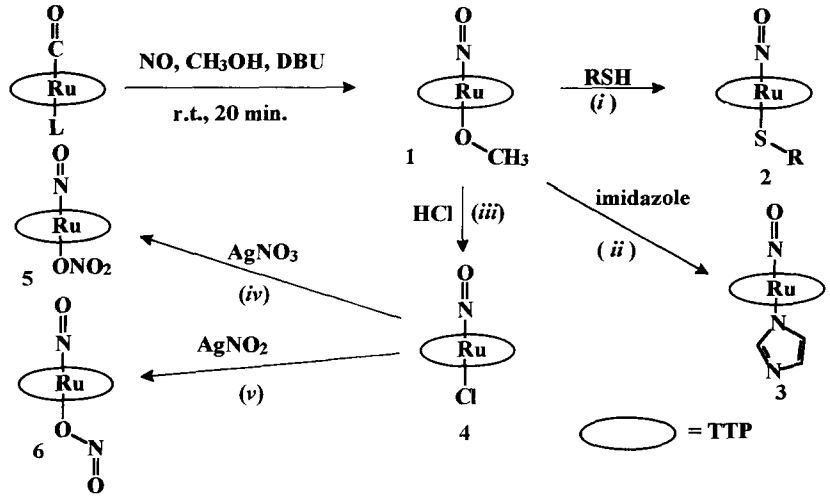
‡ Characteristic spectroscopic data for new compounds, all bands strong unless otherwise indicated. IR (KBr, cm^{-1}): ν(NO): **1** 1800, **2** 1784, **3** 1846, **4** 1842, **5** 1860, and **6** 1835. Other IR bands: **5** (NO_3) 1212m ν(NO), 1273s $\nu(NO_2)_a$ and 964m $\nu(NO_2)_s$; and (NO_2) 1511m $\nu(NO_2)_s$, 927m $\nu(NO_2)_a$ and $\delta(NO_2)$ 845w. NMR spectra were measured at 22°C in C_6D_6 and are referenced to TMS (^{1}H) and HNO_3 (^{15}N). ^{1}H NMR (400 Mhz, ppm): **1** 9.16 (s, 8H, H_β), 8.10 (d, $^3J_{HH}$ = 6.8 Hz, 4H, H_m), 8.00 (d, $^3J_{HH}$ = 7.7 Hz, 4H, $H_{m'}$), 7.24 (t, $^3J_{HH}$ = 6.0 Hz, H_o, $H_{o'}$, partially obscured by C_6D_5H), 2.39 (s, 12H, *p*-CH_3), ligand −1.50 (s, 3H, OCH_3); **2** 9.14 (s, 8H, H_β), 8.09 (d, $^3J_{HH}$ = 7.3 Hz, 4H, H_m), 8.05 (d, $^3J_{HH}$ = 7.3 Hz, 4H, $H_{m'}$), 7.30 (d, $^3J_{HH}$ = 7.3 Hz, 4H, H_o), 7.25 (d, $^3J_{HH}$ = 7.3 Hz, 4H, $H_{o'}$), 2.41 (s, 12H, *p*-CH_3), ligand 3.65 (d, $^3J_{HH}$ = 8.5 Hz, 4H, H_o), 5.92 (d, $^3J_{HH}$ = 8.5 Hz, 4H, H_p), 1.88 (s, 3H, *p*-CH_3); **3** 9.13 (s, 8H, H_β), 8.07 (d, $^3J_{HH}$ = 7.2 Hz, 4H, H_m), 7.87 (d, $^3J_{HH}$ = 7.1 Hz, 4H, $H_{m'}$), (H_o and $H_{o'}$ are obscured by C_6D_5H), 2.41 (s, 12H, *p*-CH_3), ligand 4.93 (s, 1H, broad), 2.55 (s, 1H, broad), 0.54 (s, 1H, broad); **4** 9.16 (s, 8H, H_β), 8.11 (d, $^3J_{HH}$ = 7.1 Hz, 4H, H_m), 7.91 (d, $^3J_{HH}$ = 7.7 Hz, 4H, $H_{m'}$), (H_o and $H_{o'}$ are obscured by C_6D_5H), 2.39 (s, 12H, *p*-CH_3), **5** 9.19 (s, 8H, H_β), 8.09 (d, $^3J_{HH}$ = 7.3 Hz, 4H, H_m), 7.95 (d, $^3J_{HH}$ = 7.3 Hz, 4H, $H_{m'}$), 7.24 (t, $^3J_{HH}$, H_o and $H_{o'}$ are partially obscured by C_6D_5H), 2.39 (s, 12H, *p*-CH_3); **6** 9.15 (s, 8H, H_β), 8.10 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, 4H, H_m), 7.81 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, 4H, $H_{m'}$), 7.26 (d, $^3J_{HH}$ = 7.3 Hz, 4H, H_o), 7.20 (d, $^3J_{HH}$ = 7.3 Hz, 4H, $H_{o'}$), 2.38 (s, 12H, *p*-CH_3). ^{15}N NMR (40.4 MHz, ppm): **6** 236.6 (s, $^{15}NO_2$), −26.2 (s, ^{15}NO).



Scheme 1. Syntheses of new compounds under the following conditions; (i) C_6H_6 excess *p*-tolylSH, 25°C, 1 min; (ii) neat excess imidazole (melt), 90°C, 20 min; (iii) CH_2Cl_2, HCl_g, 25°C, 5 min; (iv) 2 equiv. $AgNO_3$ in CH_3CN, 25°C, 30 min; (v) 1 : 1 C_6H_6/CH_3CN at reflux, 4 equiv. $AgNO_2$, 20 min.

Weakly coordinating bases such as DBU increase the yield and rate of formation of **1**, possibly by accelerating proposed key reductive nitrosylation steps in these preparations.[11,12] The position of the ν(N≡O) in the IR suggests that the nitric oxide adopts a linear conformation in this complex[13] and this has been confirmed by X-ray crystallography (Fig. 1).* Although disorder limits meaningful interpretation of the axial ligand bond lengths, the methoxide orientation, which bends toward the *meso* positions of the porphyrin ring with a Ru—O—C bond angle of 137.7(31)°, is typical of the conformation found for other axial ligands in group 8 metalloporphyrins.[14] The ruthenium is

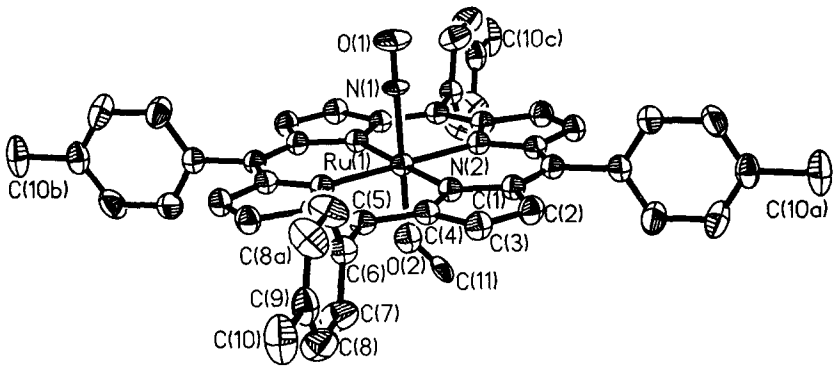


Fig. 1. View of one orientation for the disordered axial ligands in **1**. Important bond lengths (Å) and angles (°) include: Ru(1)—N(1) 1.84(4), Ru(1)—N(2) 2.050(3), Ru(1)—O(2) 1.80(5), Ru(1)—O(2)—C(11) 137.7(31).

*Crystallographic data for **1**: $[C_{49}H_{39}N_5O_2Ru]$, $M = 830.9$, tetragonal space group $I4/m$, $a = 14.805(2)$, $c = 9.753(2)$ Å, $U = 2137.7(6)$ Å^3, $Z = 2$, $D_c = 1.291$ g cm^{-3}, μ(Mo-K_α) = 0.411 mm^{-1}, $F(000) = 856$, $T = 295$ K. Laue symmetry $4/m$-$C4h$ leaves $I4$, $I\bar{4}$ or $I4/m$ as possible space groups with $I4/m$ assigned based upon successful full refinement with the absence of substantial correlation between symmetry-related carbon atoms in the tolyl rings. In this model three of the axial atoms, O(1), N(1) and O(2), are refined as having equal occupancy on either side of the porphyrin along the four-fold axis and the fourth atom, C(11) of the methyl group, is crystallographically disordered over eight positions around this axis and on either side of the plane. Anisotropic refinement for all non-hydrogen atoms (Hs fixed; 95 variables) using 890 reflections with $F > 6\sigma(F)$, from 1300 unique data collected on a Siemens R3m/V diffractometer from the omega scan method ($4.0 \leqslant 2\theta \leqslant 55.0$), gave $R = 0.038$, $R_w = 0.048$.

crystallographically restricted to the plane defined by the porphyrin ring.

In parallel with the known reactions of Ru(porphyrin)(CO)(MeOH), which undergoes fast ligand substitution of methanol by a wide range of neutral two electron donor ligands,[3] the methoxide ligand in **1** is rapidly substituted by HX {HX = HS(*p*-tolyl), HNCHNCHCH, and HCl} to give **2–4**, Scheme 1, respectively. The chloride ligand of Ru(TTP)(NO)Cl (**4**) undergoes facile metathesis with either silver nitrate or nitrite to give Ru(TTP)(NO)(ONO_2) (**5**) and Ru(TTP)(NO)(ONO) (**6**), respectively. The latter product is formulated as containing an oxygen bound (nitrito) ligand on the basis of the IR data* due to the large difference in $\nu(NO_2)_s$ and $\nu(NO_2)_a$ of 584.4 cm^{-1}.[15] In addition, the ^{15}N NMR spectrum which has two resonances at $\delta = 236.6$ and -26.2 ppm, which are assigned to a downfield shifted nitrite with a bent ligand geometry and the linear nitrosyl, respectively.[16] The nitrosyl-nitrito complex **6** also results from a disproportionation of nitric oxide when the metal–metal bonded dimeric complex $[Ru(TTP)]_2$ is treated with nitric oxide at room temperature under rigorously oxygen free conditions, eq. (1).

$$[Ru(TTP)]_2 \xrightarrow{NO,\ 5\ min.\ 1\ atm} 2[Ru(TTP)(NO)(ONO)] \quad (1)$$

The bis-nitrosyl complex is ruled out by the presence of two well separated $\nu(NO_2)$ stretches in the IR[15] and the lack of a downfield peak in the ^{15}N NMR spectrum between 350 and 850 ppm corresponding to a nitrosyl coordinated with a bent geometry.[16] Although a variety of complexes promote nitric oxide disproportionation,[17] proposed mechanisms usually suggest a metal-mediated coupling of two *cis* nitrosyl ligands.[18] The *cis* coordination of two nitrosyl ligands is, however, very unlikely for ruthenium metalloporphyrin complexes and the mechanism in eq. (1) may involve a direct attack of nitric oxide on the bent nitrosyl ligand in an intermediate such as $Ru(TTP)(NO)_2$.[19] A similar reaction has been proposed for Fe(TPP)(NO) and nitric oxide but the product, formulated as *N*-bound nitro complex, was stable only in solution in the presence of excess nitric oxide and was not isolated.[20]

The mercaptide complex **2** is a second row analogue of the metal site present in the nitric oxide adducts of the heme proteins cytochrome P-450 and nitric oxide synthase.[21,22] Although Fe(porphyrin)(NO)(X) analogues to those described herein have been reported for highfield ligands such as methyl and phenyl,[23,24] the corresponding mercaptides have not been reported. In part this may be due to the intrinsic instability of the mercaptide adducts of the ferric porphyrins which tend to undergo facile autoxidation and reductive elimination of disulfide.[25,26] In contrast, **2** is thermally stable to prolonged thermolysis at 180°C or to ligand displacement at reflux in pyridine. Finally, the pronounced thermal stability is in contrast with the corresponding high valent mercaptides such as $Os(TTP)(S\text{-}p\text{-tolyl})_2$, which readily eliminate disulfide under these conditions.[27]

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REFERENCES

1. F. Bottomley, *Coord. Chem. Rev.* 1978, **26**, 7.
2. A. A. Svetlov and N. M. Sinitsyn, *Zh. Neorg. Khim.* 1986, **31**, 2902.
3. S. Ariel, D. Dolphin, G. Domazetis, B. R. James, T. W. Leung, S. J. Rettig, J. Trotter and G. M. Williams, *Can. J. Chem.* 1984, **62**, 755.
4. J. P. Collman, C. E. Barnes, P. J. Brothers, T. J. Collins, T. Ozawa, J. C. Gallucci and J. A. Ibers, *J. Am. Chem. Soc.* 1984, **106**, 5151.
5. A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc.* 1978, **100**, 3015.
6. T. S. Srivastava, L. Hoffman and M. Tsutsui, *J. Am. Chem. Soc.* 1972, **94**, 1385.
7. M. Massoudipour and K. K. Pandey, *Inorg. Chim. Acta* 1989, **160**, 115.
8. J. W. Buchler and P. D. Smith, *Chem. Ber.* 1976, **109**, 1465.
9. L. J. Ignarro, *Biochem. Soc. Trans.* 1992, **20**, 465.
10. J. R. Stone and M. A. Marletta, *Biochem.* 1994, **33**, 5636.
11. B. B. Wayland and L. W. Olson, *J. Am. Chem. Soc.* 1974, **96**, 6037.
12. K. G. Caulton, *Coord. Chem. Rev.* 1975, **14**, 317.
13. D. M. P. Mingos and D. J. Sherman, *Adv. Inorg. Chem.* 1989, **34**, 293.
14. c.f. W. R. Scheidt and M. E. Frisse, *J. Am. Chem. Soc.* 1975, **97**, 17.
15. M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev.* 1982, **42**, 55.
16. L. K. Bell, D. M. P. Mingos, D. G. Tew, L. F. Larkworthy, B. Sandell, D. C. Povey and J. Mason, *J. Chem. Soc., Chem. Commun.* 1983, 125.
17. F. Bottomley, *Reactions of Coordinated Ligands* (Edited P. S. Braterman), p. 115. Plenum Press, New York (1989).

* Refer to footnote on previous page.

18. S. Bhaduri, B. F. G. Johnson, A. Khair, I. Ghatak and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* 1980, 1572.
19. C. D. Meyer and R. Eisenberg, *J. Am. Chem. Soc.* 1976, **98**, 1364.
20. T. Yoshimura, *Inorg. Chem. Acta* 1984, **83**, 17.
21. J. Wang, D. L. Rousseau, H. M. Abu-Soud and D. J. Stuehr, *Proc. Natl. Acad. Sci. (USA)* 1994, **91**, 10512.
22. S. Hu and J. R. Kincaid, *J. Am. Chem. Soc.* 1991, **113**, 2843.
23. G. Lagrange, P. Cocolios and R. Guilard, *J. Organomet. Chem.* 1984, **260**, C16.
24. R. Guilard, G. Lagrange, A. Tabard, D. Lançon and K. M. Kadish, *Inorg. Chem.* 1985, **24**, 3649.
25. J. P. Collman, T. N. Sorrell and B. M. Hoffman, *J. Am. Chem. Soc.* 1975, **97**, 913.
26. S. Koch, S. C. Tang, R. H. Holm and R. B. Frankel, *J. Am. Chem. Soc.* 1975, **97**, 914.
27. J. P. Collman, D. S. Bohle and A. K. Powell, *Inorg. Chem.* 1993, **32**, 4004.

Note added in proof. The chemistry of several nitrosyl derivatives of ruthenium tetraphenylporphyrin have recently been described: Kadish, K. M.; Adamian, V. A.; Caemelbecke, E. V.; Tan, Z.; Tagliatesta, P.; Bianco, T.; Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* 1996, **35**, 1343.