Synthesis and Reactivity of a Monomeric 14-Electron 'Bare' Ruthenium(II) Porphyrin Complex; Reversible Binding of Dinitrogen to form Mono- and Bis-dinitrogen Complexes

Mark J. Camenzind, Brian R. James,* and David Dolphin*

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

The 14-electron species Ru(TMP), obtained *via* vacuum pyrolysis of $Ru(TMP)(MeCN)_2$, reacts with a plethora of ligands to form bis-ligated species, including the first bis(dinitrogen) metalloporphyrin complex [TMP = the dianion of 5,10,15,20-tetramesity|porphyrin].

Collman's group¹ have reported that vacuum pyrolysis of the bis(pyridine) complexes $Ru(porp)py_2^+$ yields the metal-metal bonded species $[Ru(porp)]_2$, that are reactive precursors for a range of bis(axial ligand) complexes. We report here on an

extremely reactive, N_2 - and O_2 -sensitive, monomeric, 14electron Ru(TMP) species (1) in which dimerisation is prevented by the sterically encumbered TMP porphyrin ligand.²

The Ru(TMP)S₂ complexes [S = MeCN, tetrahydrofuran (THF), py] were isolated following a standard procedure³ involving photolysis of Ru(TMP)CO (2),² v_{CO} 1937 cm⁻¹, in the appropriate solvent S. While vacuum pyrolysis of the bis(pyridine) complex at 280 °C did not completely remove the

[†] Abbreviations used: porp = dianion of 5,10,15,20-tetraphenyl-(TPP) and octaethylporphyrin (OEP); TMP = dianion of 5,10,15,20-tetramesitylporphyrin, py = pyridine.

Table 1. ¹H N.m.r. chemical shifts (δ) for Ru(TMP) derivatives.^a

Complex	Pyrrole-H	<i>m</i> -H	<i>p</i> -Me	o-Me
Ru(TMP)(1)	8.12	ca. 7.20, ^b 6.93	2.42	2.20, 1.20
Ru(TMP)CÓ (2)	8.79	7.25, 7.10	2.48	2.20, 1.83
$Ru(TMP)(MeCN)_{2}(3)^{\circ}$	8.65	7.27	2.54	2.21
$Ru(TMP)(Et_2O)_2(4)^d$	8.48	7.29	2.53	2.26
$Ru(TMP)(N_2)_2(\bar{5})$	8.82	са. 7.20ь	2.51	2.10e
Ru(TMP)(THF)N ₂ ^f	8.78	7.24, 7.16	2.49	2.13, 2.02
$Ru(TMP)(Et_2O)N_2^{g}$	8.77	7.29, 7.13	2.50	2.25, 1.91
$Ru(TMP)(CO)_2$	8.84	7.15	2.52	2.03
Ru(TMP)(THF) ₂ ^h	8.49	7.26	2.52	2.25
Ru(TMP)(O)2 ⁱ	9.07	7.14	2.46	1.88

^a Measured at 300 MHz in C_6D_6 at ambient conditions *in vacuo*, except for the dinitrogen and bis(CO)₂ systems that were recorded under 1 atm of the appropriate gas; residual benzene used as reference, assigned at δ 7.20; relative integrations for protons are consistent with the assignments (all singlets). All the complexes have been isolated, except Ru(TMP)L₂ (L = Et₂O, CO) which were formed *in situ*. ^b Peak lies under that of residual benzene used as internal reference. ^cRu-NCMe, δ -1.32. ^dRu-OCH₂Me, δ -1.52, q; Me, δ -1.80, t. ^e Broad; 36 Hz at half-height. ^fRu-THF, δ -1.03, m, -1.71, m. ^gRu-OCH₂Me, δ -1.59, q; -Me, δ -1.96, t. ^hRu-THF, δ -0.94, m, -1.37, m. ⁱ The n.m.r. data, and an 821 cm⁻¹ i.r. band (v_{Ru=O}), are in excellent agreement with those reported.²



axial pyridines, heating an amorphous sample of $Ru(TMP)(MeCN)_2$, (3) (v_{CN} 2270 cm⁻¹), for 2 h at 225 °C and 2×10^{-5} Torr gave a quantitative yield of (1). Addition of MeCN to (1) in C_6D_6 regenerated (3) quantitatively as evidenced by ¹H n.m.r. data (Table 1). The two sets of o-Me and *m*-H protons within (1), as with Ru(TMP)CO, reveal that the species is unsymmetrical about the porphyrin plane; the spectrum does not result from the presence of a mono(acetonitrile) species, because no Ru-NCMe resonance is seen and no free nitrile (δ 0.67) is liberated on forming $Ru(TMP)L_2$ by addition of L (Et₂O, CO, py) to a C₆D₆ solution of (1). Table 1 summarizes ¹H n.m.r. data for some of the TMP derivatives described. The shifts for (1) are independent of concentration and are in the correct region for a diamagnetic species (cf. the data listed for the other complexes). This shows that the porphyrin ligand has prevented dimerisation to $[Ru(TMP)]_2$, which would give a paramagnetically-shifted spectrum akin to that shown by [Ru(TPP)]₂ in which, for example, the pyrrole proton is seen at δ -14.2.1b

The inequivalence observed in the C_6D_6 solution structure of (1) could result from: (i) the metal being inherently out of the plane, or (ii) π -complex formation with benzene. The latter seems more likely. A slight broadening of the n.m.r. resonances, evident at ~20 °C, increases on warming the solution, and is consistent with slow exchange with the solvent; further, there is ample precedent in the literature for formation of both 1:1 and 2:1 weak π -complexes between aromatics and the π -system of a porphyrin ring, in the solid state⁴ and in solution.⁵ η^2 -Co-ordination of alkenes can occur at the metal centre of (porphyrinato)ruthenium(II) complexes,^{1a,6} and η^2 (or η^4)-benzene co-ordination is a further possibility, although any such bonding must be relatively weak. Thus, addition of Et₂O at 10^{-2} M to a benzene solution of (1) at 20 °C forms the symmetrical bis(diethyl ether) species (4), which shows no exchange with free Et₂O; at 40 °C, the interaction with benzene (at *ca.* 11 M) becomes competitive, and both (1) and (4) are now observed in the n.m.r. spectrum. That (4) cannot be formed *via* photolysis of (2) in Et₂O solution demonstrates the synthetic utility of the 'bare' Ru(TMP).

A sample of the brown powder (1) opened under N_2 instantly gives the red, bis(dinitrogen) complex (5) ($v_{N=N}$ 2203 cm^{-1}) and small amounts of a mono(dinitrogen) species ($v_{N=N}$ 2137 cm⁻¹). A brown C_6D_6 solution of (1) also reacts instantly and reversibly with 1 atm N_2 to give a red solution, which exhibits broad resonances in the 1H n.m.r. spectrum, indicating rapid N₂ exchange; (1) can be regenerated by flushing the solution with Ar, while evaporation of the red solution under N_2 yields microcrystals of (5). Treatment of (5) with Bun₃P liberated ca. 1.75 equivalents of gas (consistent with two co-ordinated N_2 ligands) and gave the bis(phosphine) species. Interestingly, C_6D_6 solutions of (3) are unreactive toward 1 atm N_2 , while (4) and the THF analogue form red, mono(dinitrogen), $Ru(TMP)(ether)N_2$ (unsymmetrical by n.m.r.) complexes, with concomitant displacement of one equivalent of free ether. The $Ru(TMP)(ether)N_2$ complexes are readily isolated by evaporation of benzene solutions of the bis(ether) complexes under N_2 ; the $v_{N=N}$ stretches are observed at 2116 cm⁻¹, and are comparable to that reported for $Ru(OEP)(THF)N_2$ (2110 cm⁻¹).^{6†} A second, axial (*trans*), π -acceptor N₂ ligand, as expected, will be weakly bound (clearly, less strongly than Et₂O and THF), and this is evidenced by the i.r. data for (5). To our knowledge, no other dinitrogen complex,⁷ mono, bis (*cis* or *trans*), or tris, outside of matrix-stabilised metal atom species,⁸ has such a high $v_{N=N}$ value[‡] (for free N₂, $v_{N \equiv N}$ 2331 cm⁻¹). The Ru(TMP)(CO)₂ complex (v_{CO} 2008 cm⁻¹) similarly loses one carbonyl ligand in the absence of CO, but such behaviour has been

 $[\]ddagger$ A report^{9a} giving $v_{N \ge N}$ values at *ca*. 2220 cm⁻¹ for some supposed Re dinitrogen complexes was shown later to be in error.^{9b}

On exposure to O_2 , Ru(TMP) in C₆D₆ rapidly forms the *trans*-dioxo species Ru(TMP)(O)₂, the recently described catalyst for aerobic epoxidation of alkenes.² Indeed, our isolated complex (1) is a suggested key transient in the mechanism postulated for this reportedly dioxygenase system.²

We thank N.S.E.R.C. and N.I.H. for financial support, and Johnson Matthey Ltd. for the loan of Ru.

Received, 24th March 1986; Com. 391

References

 (a) J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose, and L. J. Wright, *J. Am. Chem. Soc.*, 1985, **107**, 4570; (b) J. P. Collman, C. E. Barnes, P. N. Swepston, and J. A. Ibers, *ibid.*, 1984, **106**, 3500.

- 2 J. T. Groves and R. Quinn, Inorg. Chem., 1984, 23, 3844; J. Am. Chem. Soc., 1985, 107, 5790.
- 3 A. Antipas, J. W. Buchler, M. Gouterman, and P. D. Smith, J. Am. Chem. Soc., 1978, 100, 3015; N. Farrell, D. H. Dolphin, and B. R. James, *ibid.*, 1978, 100, 324.
- 4 W. R. Scheidt and C. A. Reed, Inorg. Chem., 1978, 17, 710.
- 5 F. A. Walker, J. Magn. Reson., 1974, 15, 201; C. D. Barry, H. A. O. Hill, B. E. Mann, P. J. Sadler, and R. J. P. Williams, J. Am. Chem. Soc., 1973, 95, 4545.
- 6 B. R. James, A. W. Addison, M. Cairns, D. Dolphin, N. P. Farrell, D. R. Paulson, and S. Walker, *Fundam. Res. Homog. Catal.*, 1979, **3**, 751.
- 7 S. N. Anderson, D. L. Hughes, and R. L. Richards, J. Chem. Soc., Chem. Commun., 1984, 958; R. H. Morris, J. M. Ressner, J. F. Sawyer, and M. Shiralian, J. Am. Chem. Soc., 1984, 106, 3683, and references therein.
- 8 G. A. Ozin and A. Vander Voet, Prog. Inorg. Chem., 1975, 19, 105.
- 9 (a) J. T. Moelwyn-Hughes and A. W. B. Garner, J. Chem. Soc., Chem. Commun., 1969, 1309; (b) J. T. Moelwyn-Hughes, A. W. B. Garner, and A. S. Howard, J. Chem. Soc. A, 1971, 2361.
- 10 G. R. Eaton and S. S. Eaton, J. Am. Chem. Soc., 1975, 97, 235.

1139