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

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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-tetramesitylporphyrin].

Collman's group[1] 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, 14-electron Ru(TMP) species (**1**) in which dimerisation is prevented by the sterically encumbered TMP porphyrin ligand.[2]

The Ru(TMP)S$_2$ complexes [S = MeCN, tetrahydrofuran (THF), py] were isolated following a standard procedure[3] involving photolysis of Ru(TMP)CO (**2**),[2] ν_{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

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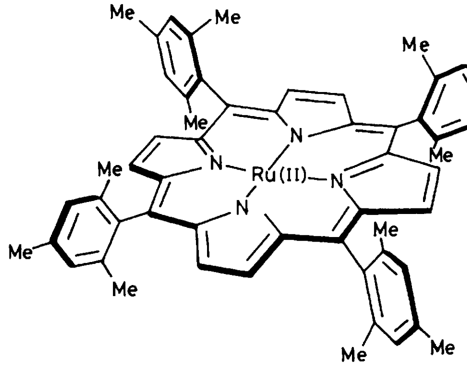
† Abbreviations used: porp = dianion of 5,10,15,20-tetraphenyl- (TPP) and octaethylporphyrin (OEP); TMP = dianion of 5,10,15,20-tetramesitylporphyrin, py = pyridine.

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

Complex	Pyrrole-*H*	*m*-H	*p*-Me	*o*-Me
Ru(TMP) (**1**)	8.12	*ca.* 7.20,[b] 6.93	2.42	2.20, 1.20
Ru(TMP)CO (**2**)	8.79	7.25, 7.10	2.48	2.20, 1.83
Ru(TMP)(MeCN)$_2$ (**3**)[c]	8.65	7.27	2.54	2.21
Ru(TMP)(Et$_2$O)$_2$ (**4**)[d]	8.48	7.29	2.53	2.26
Ru(TMP)(N$_2$)$_2$ (**5**)	8.82	*ca.* 7.20[b]	2.51	2.10[e]
Ru(TMP)(THF)N$_2$[f]	8.78	7.24, 7.16	2.49	2.13, 2.02
Ru(TMP)(Et$_2$O)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)L$_2$ (L = Et$_2$O, CO) which were formed *in situ*. [b] Peak lies under that of residual benzene used as internal reference. [c] Ru-NC*Me*, δ −1.32. [d] Ru–OC*H*$_2$Me, δ −1.52, q; *Me*, δ −1.80, t. [e] Broad; 36 Hz at half-height. [f] Ru–THF, δ −1.03, m, −1.71, m. [g] Ru–OC*H*$_2$-Me, δ −1.59, q; −*Me*, δ −1.96, t. [h] Ru–THF, δ −0.94, m, −1.37, m. [i] The n.m.r. data, and an 821 cm^{-1} i.r. band ($\nu_{Ru=O}$), are in excellent agreement with those reported.[2]



(**1**)

axial pyridines, heating an amorphous sample of Ru(TMP)(MeCN)$_2$, (**3**) (ν_{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 ^{1}H 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-NC*Me* resonance is seen and no free nitrile (δ 0.67) is liberated on forming Ru(TMP)L$_2$ by addition of L (Et$_2$O, CO, py) to a C_6D_6 solution of (**1**). Table 1 summarizes ^{1}H 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 state[4] 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 Et$_2$O 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 Et$_2$O; 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 Et$_2$O 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**) ($\nu_{N\equiv N}$ 2203 cm^{-1}) and small amounts of a mono(dinitrogen) species ($\nu_{N\equiv N}$ 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 ^{1}H n.m.r. spectrum, indicating rapid N$_2$ 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 Bu$^n_3$P 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 $\nu_{N\equiv N}$ 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 N$_2$ ligand, as expected, will be weakly bound (clearly, less strongly than Et$_2$O 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 $\nu_{N\equiv N}$ value‡ (for free N$_2$, $\nu_{N\equiv N}$ 2331 cm^{-1}). The Ru(TMP)(CO)$_2$ complex (ν_{CO} 2008 cm^{-1}) similarly loses one carbonyl ligand in the absence of CO, but such behaviour has been

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

documented for other (porphyrinato)ruthenium(II) systems.[1,10]

On exposure to O_2, Ru(TMP) in C_6D_6 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]

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