

# Evidence for a common Ru(P)(NO)<sub>2</sub> intermediate in photochemical and synthesis pathways involving Ru(TmTP)(NO)(ONO) and excess nitric oxide

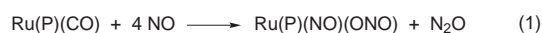
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Optical and IR spectra of the intermediate formed from the reaction of Ru(CO)(TmTP) with NO are compared with transient UV-VIS and FTIR spectra of photochemical intermediates formed from the photolysis and recovery of Ru(TmTP)(NO)(ONO) in the presence of NO; comparison reveals that the two pathways share a common intermediate, which IR spectral properties suggest to be *trans*-Ru(TmTP)(NO)<sub>2</sub>.

The reaction chemistry of nitric oxide has drawn renewed attention owing to the established biological roles of NO and its interactions with metal centers in mammalian cardiovascular systems, in immunology and in various human disease states.<sup>1-4</sup> In this context we have been studying reactions of NO with metal porphyrin complexes,<sup>5-7</sup> and we and others have shown that the reaction of Ru<sup>II</sup>(CO)(P) (P<sup>2-</sup> = a porphyrinato dianion) with excess NO in hydrocarbon solvents forms the nitrito nitrosyl complex Ru(P)(NO)(ONO).<sup>5,8</sup> The other product is 1 equiv. of N<sub>2</sub>O [eqn. (1)].<sup>8</sup> Other metal centers have long been known to facilitate the NO disproportionation in the presence of excess nitric oxide.<sup>9,10</sup>



Stopped flow kinetics studies in this laboratory with P = TmTP (tetra-*m*-tolylporphyrinate) or OEP (octaethylporphyrinate) have shown that the reaction in eqn. (1) proceeds by several steps.<sup>6</sup> There is a discernable intermediate **X** with a composition consistent with that of Ru(P)(NO)<sub>2</sub>, and this reacts further by a pathway second order in [NO] to give Ru(P)(NO)(ONO).



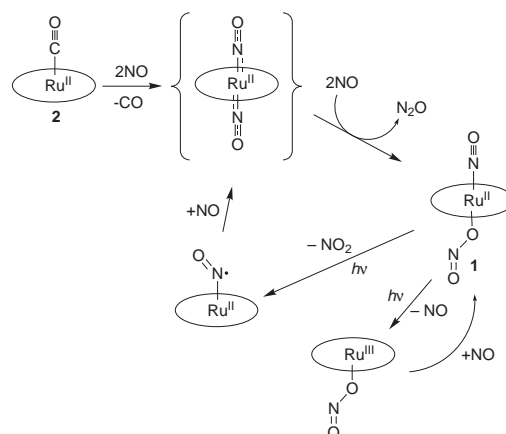
Parallel work in this laboratory has been concerned with the photochemistry of various Ru(P)(NO)(ONO).<sup>11</sup> Flash photolysis in benzene was shown to give two primary photoproducts, which were proposed to be Ru<sup>III</sup>(P)(ONO) (resulting from photolabilization of NO) and Ru<sup>II</sup>(P)(NO) (resulting from photolabilization of NO<sub>2</sub>) both of which react with the excess NO to reform Ru(P)(NO)(ONO). Reformation of Ru(TmTP)(NO)(ONO) **1** from Ru<sup>III</sup>(TmTP)(ONO) was shown to proceed by second order recombination with NO ( $k_A = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). The regeneration of **1** from Ru(TmTP)(NO) **2** proved to be more circuitous; first there is a second order reaction of **2** with NO ( $k_B = 4.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) to form yet another transient species **Y**, then a much slower reaction of **Y** with excess NO to give **1**.<sup>11</sup>

On the basis of similarities in their optical spectra and reactivities, **X** and **Y** were suggested to be the same species, namely Ru(TmTP)(NO)<sub>2</sub>. The OEP complex behaves similarly.<sup>11</sup> We present here a comparison of the UV-VIS and IR spectra of the photochemically prepared intermediate **Y** to those of **X** which was prepared by rapid mixing techniques in the thermal reaction of Ru(TmTP)(CO) plus NO. These data

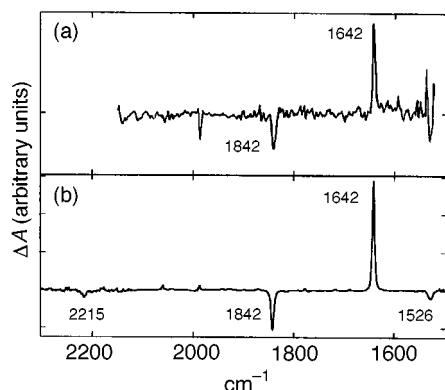
provide compelling evidence that the thermal and photochemical routes do indeed share a common intermediate. Also, IR analysis of the transient species of the thermal reaction confirms that N<sub>2</sub>O production occurs during the second step of the thermal reaction, and that the isomerization of a predicted transient nitrosyl nitro species to **1** (Scheme 1) occurs too quickly to be observed by stopped flow techniques.

The optical spectral changes observed upon rapid mixing of cyclohexane solutions of NO and Ru(TmTP)(CO) are virtually identical in profile and time dependence to the changes observed using toluene as solvent.<sup>6</sup> In short, the carbonyl complex (Q band  $\lambda_{\text{max}}$  at 528 nm;  $\epsilon = 2.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) gives way, within 5 ms after mixing, to an intermediate (546 and 580 nm;  $16 \times 10^4$  and  $5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), which reacts slowly ( $k_{\text{obs}} = 0.3 \text{ s}^{-1}$ ), in a second step, to give **1** (561 nm;  $10.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). Furthermore the difference optical spectrum observed, after flash photolysis of a solution of **1** in cyclohexane in the presence of NO (5 mM) is indistinguishable from the difference spectrum between **X** and **1**.

Fig. 1(a) shows the IR spectral changes associated with the generation of **Y** within 1  $\mu\text{s}$  after flash photolysis of **1** in cyclohexane solutions containing 5 mM NO (previously reported<sup>11</sup> but included here for purposes of comparison). Fig. 1(b) shows IR spectral data generated using a custom built, hand driven stopped-flow reactor to mix Ru(TmTP)(CO) with NO in a 1 mm pathlength IR cell. This difference spectrum was generated by subtracting the product spectrum generated by mixing identical concentrations of NO and Ru(TmTP)(CO) and waiting about 20 s from the initial spectrum seen immediately after mixing. The positive peaks represent the initial species formed, *i.e.* **X**, while the negative peaks can be largely attributed to the ruthenium containing product **1**, although the small peak at 2215  $\text{cm}^{-1}$  is attributed to the formation of N<sub>2</sub>O. Successive difference spectra show the positive and negative peaks returning to baseline as the intermediate **X** undergoes reaction with NO to form **1** and the transient spectra converge on the product spectrum. The intensities of the negative peaks in Fig. 1(a) represent *ca.* 95% of the maximum  $\Delta A$  possible as determined by subtracting the product solution spectrum from



Scheme 1



**Fig. 1** (a) Long term (8–20  $\mu\text{s}$ ) FTIR difference spectrum observed using a step scan instrument after flash photolysis of a solution of **1** (200  $\mu\text{M}$ ) in cyclohexane in the presence of NO (5 mM).<sup>11</sup> (b) FTIR difference spectrum obtained by subtraction of the product spectrum recorded 15 s after mixing from the transient spectrum in cyclohexane recorded *ca.* 0.2 s after mixing of Ru(CO)(TmTP) (150  $\mu\text{M}$  after mixing) with NO (3.9 mM) in a flow experiment. For both top and bottom spectra, the small peaks observed between 1900 and 2100 are solvent subtraction errors and correspond exactly to cyclohexane peaks.

that of pure cyclohexane. Thus, the subsequent reaction of **X** with NO has proceeded by only *ca.* 5%, and one can use the previously determined rate constant for this process to estimate the elapsed time after mixing at *ca.* 0.2 s. In this time frame, the starting material Ru(TmTP)(CO) would have reacted to completion ( $k_{\text{obs}} = k_1[\text{NO}] = 3.8 \times 10^3 \text{ s}^{-1}$ ).

It is clear from a comparison of Fig. 1(a) with 1(b) that the photolysis of **1** in the presence of NO and the reaction of Ru(CO)(TmTP) with NO generate the same intermediate, *i.e.* that **X** and **Y** are both Ru(TmTP)(NO)<sub>2</sub>. There are several additional implications of these data. First, the negative peaks at 1527 and 1842  $\text{cm}^{-1}$  show the same absorbance ratio (*ca.* 1/5) as observed for independently purified **1** in cyclohexane. This indicates that the negative peak at 1842  $\text{cm}^{-1}$  does not overlap with a positive absorbance arising from **X**. (The small peaks visible at 1790, 1990 and 2060  $\text{cm}^{-1}$  are due to imperfect solvent subtraction and correspond exactly to peaks in the cyclohexane spectrum). The peak at 1642  $\text{cm}^{-1}$  is the sole characteristic absorbance of **X** with appreciable intensity between 2300 and 1500  $\text{cm}^{-1}$ . Therefore the absorption coefficient at 1642  $\text{cm}^{-1}$  may be estimated as 9000  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  by intensity comparison to the negative  $\nu_{\text{NO}}$  peak at 1842  $\text{cm}^{-1}$  (3300  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) for **1**. The integrated intensity of the former is *ca.* 2.3 as strong as the latter.

There still remains some ambiguity with respect to the likely structure of **X**. Two possibilities would be the six coordinate dinitrosyl species implied above by the formula Ru(TmTP)(NO)<sub>2</sub> in either the *cis* or *trans* configurations. The *cis* dinitrosyl appears quite unlikely since it should show two IR active  $\nu_{\text{NO}}$  bands, but only one was detected. In contrast, a linear array of two *trans* NO ligands bound to the metal in a centrosymmetric *ca.*  $D_{4h}$  point group should show a single IR band, the antisymmetric  $A_{2u}$  stretching mode of the two diatomic ligands with roughly twice the transition dipole strength of a single nitrosyl stretch. The symmetric  $A_{1g}$  stretch should not be IR active. Although  $\nu_{\text{NO}}$  frequencies as low as 1600  $\text{cm}^{-1}$  have been reported for linear or near linear metal nitrosyls,<sup>12</sup> the 1642  $\text{cm}^{-1}$  remains unexpectedly low for a linear M–NO, since such bonding is commonly viewed as the result of NO<sup>+</sup> coordination. A possible explanation would be that the two additional electrons necessary for the dinitrosyl formulation of **X** are in  $\pi^*$  molecular orbital(s) delocalized over the five atom ONRuNO structure, thus giving a lower effective NO bond order, hence a lower  $\nu_{\text{NO}}$ . The IR data are also

consistent with a *trans*-Ru(NO)<sub>2</sub> structure with Ru–N–O angles less than 180° if the two NO groups are positioned in a manner to maintain a center of inversion ( $C_{2h}$  symmetry). Observation of but a single, sharp  $\nu_{\text{NO}}$  band would appear to require a strong thermodynamic preference for this centrosymmetric configuration under the reaction conditions, unless there is very poor coupling between two such oscillators positioned on opposite sides of the Ru(P) plane.<sup>13</sup>

The difference spectrum Fig. 1(b) also shows a negative peak at 2215  $\text{cm}^{-1}$  which decays back to baseline on the same time scale as the other negative peaks. This indicates that N<sub>2</sub>O is formed concomitantly with **1** during the second stage in the reaction sequence in approximately the stoichiometry indicated by eqn. (3).<sup>14</sup> Although the final step in the mechanism described by Scheme 1 would be isomerization of an initially formed N-coordinated nitro complex to the O-bound nitrito analogue, the stopped-flow IR experiment gave no indication of intermediates between **X** and **1**. Thus, either this linkage isomerization is much faster than the trimolecular reaction of **X** with NO or this process leads to direct formation of the nitrito product.

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- A referee has suggested another structure for **X**, namely Ru(P)-(N(O)NO), formed by reaction of NO with the coordinated NO of Ru(P)(NO). However, this formulation for **X** would be predicted to give products for the isotopic exchange experiments where Ru(TmTP)-(NO)(ONO) was photolyzed in the presence of <sup>15</sup>N<sup>18</sup>O different from those observed (ref. 11). Those products can indeed be explained on the basis of formation of a dinitrosyl Ru(P)(NO)<sub>2</sub> intermediate. Another argument against this formulation would be that –N(O)NO ligand would also be expected to give two strong  $\nu_{\text{NO}}$  bands yet only one new band was detected in the 1500–2300  $\text{cm}^{-1}$  region. No new bands were seen in the 1000–1500  $\text{cm}^{-1}$  region either; however, in that region there are several windows possibly obscured by solvent interference.
- Based on the estimated absorption coefficients for N<sub>2</sub>O, the yield of nitrous oxide in the second stage of the reaction was *ca.* 65% that of **1**, but the small intensity of the signal at 2215  $\text{cm}^{-1}$  as well as possible pathways for N<sub>2</sub>O loss add to the uncertainty of this value.

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