The first structurally characterized organometallic nitrosyl porphyrin: structure of [Ru(ttp)(NO)(C_6H_4F-*p*)] (ttp = *meso*-tetratolylporphyrinato dianion)

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Reaction of [Ru(ttp)(NO)Cl] with aryl or alkyl Grignard reagents gives [Ru(ttp)(NO)R] (R = C_6H_4F-*p*, Me); the Ru–C bond in [Ru(ttp)(NO)Me] undergoes insertion by SO_2, and the structure of [Ru(ttp)(NO)(C_6H_4F-*p*)] is determined by X-ray crystallography.

The sole enzymatic receptor for nitric oxide (NO) is guanylate cyclase, which upon binding NO forms a haem–NO derivative.[1] Similar haem–NO compounds form when NO binds to haemoglobin (Hb), myoglobin (Mb) and cytochrome P450.[2] Organic nitroso compounds (RNO; R = alkyl, aryl) are also known to bind Hb, Mb, cytochrome P450 and guanylate cyclase to give metal–RNO adducts.[3–5] We and others have recently reported on the structural characterization of N- and O-bound metalloporphyrin–RNO complexes.[6,7] The structural chemistry of the isomeric metal–RNO and *organometallic* R–metal–NO complexes is also of great interest as far as metal–NO bond formation is concerned.[8]†

Organometallic porphyrins are important synthetic targets due to the observation that metal–carbon bonds play distinct roles in the chemistry of coenzyme B_{12} and cytochrome P450.[9,10] Organoruthenium porphyrins of the type [Ru(por)R_n] (n = 1, 2),[11–15] [Ru(por)R]$^-$,[11,12a] [Ru(oep)Ph(thf)]$^{-/+}$,[16] and [Ru(oep)Ph_2]$^-$,[16] have been prepared previously.‡ The crystal structures of [Ru(oep)Ph],[12b] [Ru(oep)Np][12a] and [{Ru(oep)Np}$_2$(μ-Li)$_2$][12a] have also been described. Although NO binds to ruthenium porphyrins,[17] there were no reports on the synthesis of *organo*-ruthenium nitrosyl porphyrins prior to this study. Indeed, the only reported complexes of the form [M(por)(NO)R] (R = alkyl, aryl) were those of iron, generated from the reaction of [Fe(por)R] with NO gas.[18] We are now pleased to report (*i*) the first synthesis of the novel six-coordinate organoruthenium nitrosyl porphyrins [Ru(ttp)(NO)R] (R = C_6H_4F-*p*, Me), (*ii*) the first crystallographic characterization of an organometallic nitrosyl porphyrin, and (*iii*) that the ruthenium–carbon bond in [Ru(ttp)(NO)Me] (but *not* [Ru(ttp)Me_2]) undergoes an insertion reaction with sulfur dioxide to produce the corresponding sulfinato derivative.

A diethyl ether solution (30 ml) of [Ru(ttp)(NO)Cl] (0.346 g, 0.414 mmol)§ was reacted with MgBr(C_6H_4F-*p*) (0.21 ml, 2.0 mol dm^{-3} in ether, 0.42 mmol) at room temperature for *ca.* 4 h. The mixture was filtered and solvent was removed *in vacuo*. The residue was extracted with benzene (25 ml) and then chromatographed on silica gel using benzene as eluent. The green fraction was collected, and the product crystallized from benzene–hexanes to give [Ru(ttp)(NO)(C_6H_4F-*p*)] (0.237 g, 0.265 mmol, 64% yield; correct analysis for C, H, N) [^{1}H NMR ($CDCl_3$): δ 8.86 (s, 8 H, pyr-H), 8.12 (d, J 8 Hz, 4 H, *o*-H of ttp), 7.99 (d, J 7 Hz, 4 H, *o'*-H of ttp), 7.55 (d, J 8 Hz, 4 H, *m*-H of ttp), 7.52 (d, J 7 Hz, 4 H, *m'*-H of ttp), 4.42 (app t, J 9/9 Hz, 2 H, *m*-H of C_6H_4F-*p*), 2.69 (s, 12 H, CH_3 of ttp), 0.10 (dd, J 9/6 Hz, 2 H, *o*-H of C_6H_4F-*p*)]. The IR spectrum (KBr) shows a ν_{NO} band at 1773 cm^{-1}, which is 64 cm^{-1} lower than that of the chloro precursor. The low-resolution mass spectrum shows a peak at *m/z* 865 due to loss of NO. Crystals of [Ru(ttp)(NO)(C_6H_4F-*p*)] were grown from a benzene–hexanes solution kept at −20 °C for 3 days, and were analysed by a single-crystal X-ray diffraction study (Fig. 1).¶ Importantly, this represents the *first* structural determination of an organometallic nitrosyl porphyrin. The most chemically interesting features of the structure are the *trans* arrangement of the NO and aryl ligands and the bent Ru–N–O angle of 152°. The NO group appears to be influenced by packing forces by a van der Waals' contact from a nearby tolyl group; the Ru–N(1) bond is inclined by 9.8° from the plane perpendicular to that described by the Ru and four porphyrin nitrogens. The average Ru–N(porphyrin) bond length is 2.054 Å, and the Ru–C(axial) bond length of 2.095(6) Å is longer than the Ru–C(sp^2) bond length in the five-coordinate paramagnetic [Ru^{III}(oep)Ph] [S = 1/2, 2.005(7) Å][12b] and is closer to the Ru–C(sp^3) bond length in the five-coordinate [Ru(oep)Np][12a] [S = 1/2, 2.069, 2.12 Å; disordered].

The corresponding alkyl compound [Ru(ttp)(NO)Me] [^{1}H NMR ($CDCl_3$): δ 8.84 (s, 8 H, pyr-H), 8.13 (d, J 8 Hz, 4 H, *o*-H of ttp), 8.05 (d, J 8 Hz, 4 H, *o'*-H of ttp), 7.54 (app t, J 8/8 Hz, 8 H, *m*-H of ttp), 2.69 (s, 12 H, CH_3 of ttp), −6.74 (s, 3 H, Ru–Me)] is prepared similarly in *ca.* 35% isolated yield by the reaction of [Ru(ttp)(NO)Cl] with MgCl(Me) in thf. The ν_{NO} of this compound is at 1743 cm^{-1} and is 30 cm^{-1} lower than the aryl analogue, and the mass spectrum shows a parent peak at *m/z* 813. We have found that the product is sometimes obtained concurrently with the known [Ru(ttp)Me_2][14] (≤3% by ^{1}H NMR in the crystallized product) which was not readily separable from [Ru(ttp)(NO)Me] by crystallization or chromatography. This known [Ru(ttp)Me_2] compound is also obtained from the reaction of [Ru(ttp)(NO)Me] with excess Grignard reagent.

Reaction of a 97:3 mixture of [Ru(ttp)(NO)Me]–[Ru(ttp)Me_2] (0.020 g) with gaseous SO_2 in CH_2Cl_2 (15 ml) results in a quantitative shift of the ν_{NO} of the reaction mixture from 1743 to 1857 cm^{-1}. About half of the reaction mixture was filtered, and the solvent removed to give [Ru(ttp)(NO){OS(O)Me}] in 74% crude yield (corrected for the portion worked up). The ^{1}H NMR spectrum of the crude product

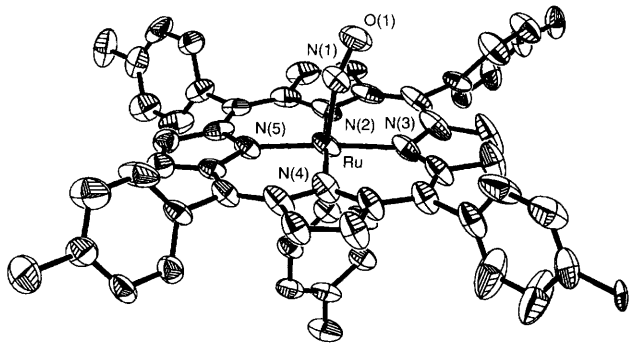

Fig. 1 Molecular structure of [Ru(ttp)(NO)(C_6H_4F-*p*)]. Hydrogen atoms have been omitted for clarity.

indicated the presence of [Ru(ttp)Me_2] (δ −2.74) indicating its relative lack of reactivity, suggesting that the NO ligand in [Ru(ttp)(NO)Me] activates the *trans* Ru–C bond towards insertion by SO_2. Authentic [Ru(ttp)Me_2] or [Ru(ttp)(NO)(C_6H_4F-*p*)] do not react with SO_2 under identical conditions. The [Ru(ttp)(NO){OS(O)Me}] insertion product is obtained pure (correct analysis for C, H, N, S) after recrystallization from benzene–hexanes in 50% isolated yield based on [Ru(ttp)(NO)Me]. The low-resolution mass spectrum (FAB^-) shows a parent peak at *m/z* 879. This product has a ν_{NO} of 1839 cm^{-1} (KBr), and the bands expected for ν_{SO_2}(s) and ν_{SO_2}(as) of an *O*-bound sulfinato group were obscured by the porphyrin bands.[19] No peaks appeared in the regions associated with an *S*-bound sulfinato group.[19] The methyl hydrogen resonance in the ^1H NMR spectrum shifts downfield from δ −6.74 (in $CDCl_3$) in the precursor methyl compound to δ −1.39 in the sulfinato product [^1H NMR ($CDCl_3$): δ 9.01 (s, 8 H, pyr-H), 8.12 (m, 8 H, *o*-H of ttp), 7.57 (m, 8 H, *m*-H of ttp), 2.71 (s, 12 H, CH_3 of ttp), -1.39 (s, 3 H, CH_3)]. A similar large deshielding of methyl protons has been observed for related reactions of indium porphyrins that produce *O*-bound sulfinato ligands.[20] To the best of our knowledge, [Ru(ttp)(NO){OS(O)Me}] is only the second metal nitrosyl sulfinato complex prepared to date from the insertion of SO_2 into a metal–carbon bond.[21]

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Footnotes

† For example, nitrosoalkanes (RNO) may add to metal complexes to form metal nitrosyl alkyls, R-metal–NO (refs. 2 and 8).

‡ Abbreviations: por = porphyrinato dianion, oep = octaethylporphyrinato dianion, ttp = *meso*-tetratolylporphyrinato dianion, tpp = *meso*-tetraphenylporphyrinato dianion, Np = neopentyl, Ph = phenyl, thf = tetrahydrofuran.

§ [Ru(ttp)(NO)Cl] was prepared in quantitative yield (by ^1H HMR and IR spectroscopy) and 57% isolated yield from the reaction of [Ru(tpp)(CO)] with ClNO[17c] in CH_2Cl_2. *Spectroscopic data*: IR (ν_{NO}, KBr) 1837 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.01 (s, 8 H, pyr-H), 8.17 (d *J* 7, 4 H, *o*-H of ttp), 8.13 (d, *J* 8, 4 H, *o'*-H of ttp), 7.57 (overlapping d, *J* 7/8, 8 H, *m*-H of ttp), 2.71 (s, 12 H, CH_3 of ttp). Low-resolution mass spectrum (FAB^+): *m/z* 835 [Ru(ttp)(NO)Cl]$^+$ 32, 800 [Ru(ttp)(NO)]$^+$ 93, 770 [Ru(ttp)]$^+$ 100%. Correct analyses for C, H, N, Cl (±0.3%) were obtained.

¶ X-Ray diffraction studies were performed at the University of Minnesota. Crystal data were collected on a Siemens SMART diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved using the SHELXTL V5.0 system and refined by full-matrix least squares on F^2 using all reflections. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. *Crystal data*: $C_{54}H_{40}FRuN_5O{\cdot}0.4CH_2Cl_2$, *M* = 929.13, triclinic, space group $P\bar{1}$ (no.2), *a* = 11.6696(2), *b* = 13.9427(3), *c* = 14.4519(1) Å, α = 80.049(1), β = 78.956(1), γ = 74.559(1)°, *U* = 2206.04(6) Å^3, *Z* = 2, D_c = 1.399 g cm^{-3}, *T* = 173(2) K. Final *R*1 = 0.0745 (*wR*2 = 0.1685, GOF = 1.033) for 4763 'observed' reflections with $I > 2\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/217.

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