559 Hz; **5b**). Elemental analysis (%): calcd for $C_{76}H_{110}O_{28}P_2BF_4Ag$ (1728.30): C 52.82, H 6.41; found: C 53.08, H 6.45; MS (FAB): *m/z* (%): 1657.4 (60) $[M^+ - BF_4 + O]$, 1641.4 (100) $[M^+ - BF_4]$.

**6**: $^1$H NMR (400.1 MHz, $CDCl_3/C_6H_5CN$, 25 °C; assignment by COSY): $\delta = 2.28$, 3.60 (AB, $^2J_{AB} = 10.2$ Hz, 4H; H-6$^{B,E \text{ or } C,F}$), 2.73 (s, 6H; $OCH_3$), 2.76, 3.30–3.35 (br AB (×2), 8H; H-6$^{A,D}$ and H-6$^{C,F \text{ or } B,E}$), 2.93 (s, 6H; $OCH_3$), 2.95 (t, 2H; H-3$^{B,E \text{ or } C,F}$), 2.95 (t, 2H; H-3$^{C,F \text{ or } B,E}$), 3.00 (d, 2H; H-2$^{C,F \text{ or } B,E}$), 3.03 (s, 6H; $OCH_3$), 3.05 (d, 2H; H-5$^{C,F \text{ or } B,E}$), 3.05 (d, 2H; H-2$^{B,E \text{ or } C,F}$), 3.32 (s, 6H; $OCH_3$), 3.35 (d, 2H; H-2$^{A,D}$), 3.37 (s, 6H; $OCH_3$), 3.40 (d, 2H; H-5$^{B,E \text{ or } C,F}$), 3.50 (s, 6H; $OCH_3$), 3.50 (br, 2H; H-4$^{A,D}$), 3.52 (s, 6H; $OCH_3$), 3.55 (d, 2H; H-4$^{B,E \text{ or } C,F}$), 3.65 (d, 2H; H-4$^{C,F \text{ or } B,E}$) 3.70 (s, 6H; $OCH_3$), 3.75 (t, 2H; H-3$^{A,D}$), 4.70 (m, 2H; H-5$^{A,D}$), 4.84 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.2$ Hz, 2H; H-1$^{C,F \text{ or } B,E}$), 4.88 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.6$ Hz, 2H; H-1$^{A,D}$), 5.16 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.3$ Hz, 2H; H-1$^{B,E \text{ or } C,F}$), 7.35–7.90 (m, 20H, arom. H); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3/C_6H_5CN$, 25 °C): $\delta = 8.7$ (2d, $^{107}J_{Ag,P} = 458$, $^{109}J_{Ag,P} = 529$ Hz); MS (ES): *m/z* (%): 1744.7 (22) $[M^+ - BF_4]$.

Crystal structure analysis of $\mathbf{4} \cdot H_2O \cdot 3CH_3CN$: crystals suitable for X-ray diffraction were obtained by slow diffusion of diisopropyl ether into a butanone–acetonitrile (100:1, v/v) solution of the complex; $M_r = 1910.56$, triclinic, space group $P\bar{1}$, $a = 13.7530(4)$, $b = 14.4944(6)$, $c = 15.0189(6)$ Å, $V = 2447.8(6)$ Å$^3$, $Z = 1$, $\rho = 1.30$ g cm$^{-3}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.321$ mm$^{-1}$. Data were collected on a Kappa CCD Enraf Nonius system at 173 K. The structure was solved by direct methods and refined on $F_o^2$ by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. The absolute structure was determined by refining Flack's *x* parameter. $R1 = 0.069$ and $\omega R2 = 0.089$ for 5753 data with $I > 3\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157445. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[23] Owing to $C_2$ symmetry, the B and C glucose units are equivalent to the E and F units, respectively.
[24] The whole variable-temperature NMR study required the use of two distinct solvents, $CD_2Cl_2$ (−40–20 °C) and $C_2D_2Cl_4$ (20–100 °C). The coalescence temperature for the two low-energy processes is close to the boiling point of $CD_2Cl_2$ and hence the corresponding activation barriers could not be determined accurately.
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## Ruthenium Nitrides: Redox Chemistry and Photolability of the Ru–Nitrido Group**

Lucia Bonomo, Euro Solari, Rosario Scopelliti, and Carlo Floriani*

The metal nitride[1] group plays a key role in nitrogen transfer to organic[2–4] and inorganic[5] substrates. Such reactivity exists when the nitrido group is associated with a labile metal, which generally displays catalytic properties. To this end we considered the ruthenium ion in *meso*-octamethylporphyrinogen,[6] which is related to porphyrin—the macrocycle par excellence in ruthenium chemistry. Ruthenium nitride chemistry[7] has received considerable attention in the recent past, and some major issues are considered here: 1) the formation of the Ru≡N group by cleavage of N–N bonds[7] which mimic the $N_2$ molecule; 2) the redox chemistry associated with the [Ru≡N] fragment, with the intent of tuning the nucleophilic–electrophilic properties of the nitrido group;[7a,b] 3) the relationship between the terminal [Ru≡N] and the bridging [Ru=N=Ru] groups; 4) the photolabilization of Ru–N bonds; and 5) the use of a tetrapyrrolic macrocycle related to porphyrin, a key ligand in Ru chemistry and one with which the Ru≡N group has so far not been associated.

[*] C. Floriani, L. Bonomo, E. Solari, R. Scopelliti
Institut de Chimie Minérale et Analytique
Université de Lausanne
BCH, 1015 Lausanne (Switzerland)
Fax: (+41) 21-692-3905
E-mail: carlo.floriani@icma.unil.ch

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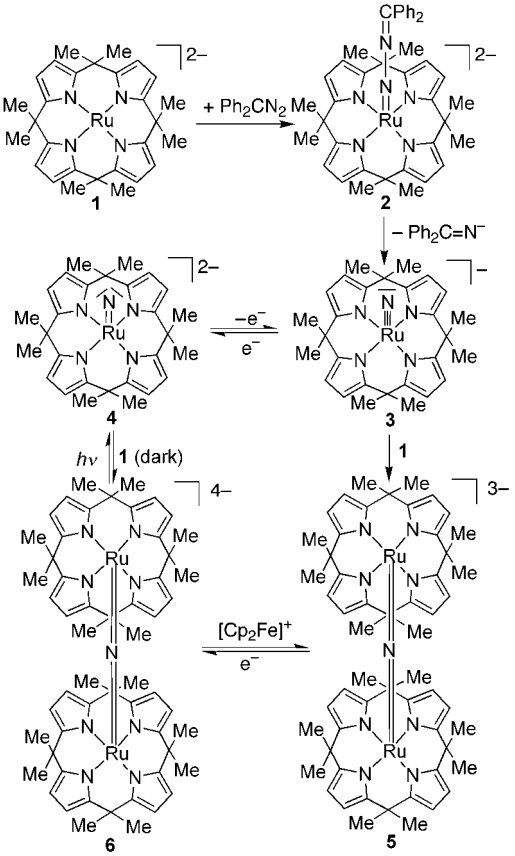
Ruthenium(II) *meso*-octamethylporphyrinogen (**1**)[8] (Scheme 1) was synthesized by the methodology that has been applied to a variety of metals.[6] The reaction of **1** with diphenyldiazomethane led to the terminal $Ru^{VI}$ nitrido complex **3** via the intermediate **2**. The reaction first forms the $Ru^{IV}$ diphenylhydrazone, which then spontaneously undergoes a reductive cleavage of the N–N single bond to give **3** and $Ph_2C{=}N^-$, both of which were identified.




Scheme 1. Formation of Ru≡N and Ru=N=Ru groups and their redox chemistry.

The terminal nitrido complex **3** undergoes a reversible one-electron reduction to the dianion **4**,[8] which contains a $Ru^V$ ion ($\mu = 1.84\,\mu_B$ at 293 K). The major structural difference between **3** and **4** is expected to be the Ru–N bond length[7] (1.569(6) Å in **3**).[9] The two structures are quite similar. Complex **3** occurs in an ion-separated form with a $[Na(dme)_3]^+$ countercation (dme = 1,2-dimethoxyethane). The anion shown in Figure 1[10] has $C_{2v}$ symmetry, and it exhibits the usual saddle conformation, with the metal atom –0.482(3) Å out of the $N_4$ mean plane.

The moderate electrophilicity of the nitrido nitrogen atom in **3** allowed the formation of the dimer **5**[8] when it was treated with an equimolar amount of the electron-rich **1**. Complex **5** is a diamagnetic, dinuclear $Ru^{IV}$ compound and is thermally and photochemically inert. It undergoes a reversible one-electron reduction to **6**, which contains an unpaired electron ($\mu = 1.60\,\mu_B$ at 293 K). The synthesis of **6** can be equally well performed by treating **4** with **1** in equimolar amounts in the dark. The two bridging nitrido complexes differ significantly, not only in their chemical behavior, but also in their structures. The Ru-N-Ru skeleton[7] is linear in both cases (**5**, 180°; **6**, 179.5(2)°), while the $Ru–N_{av}$ distance changes from 1.768(9) Å in **5**[8] to 1.826(3) Å in **6**. In **6**, the two Ru–porphyrinogen fragments sandwich two sodium ions and a nitrido group (Figure 2),[10] the two remaining $[Na(thf)_3]$ cations being weakly bonded to the periphery. The two Ru–porphyrinogen moieties display a structure similar to that of **3**, with a saddle conformation of the ligand and protrusion of Ru1 and Ru2 by 0.506(1) and –0.510(1) Å, respectively, from their $N_4$ planes. The sodium cations Na1 and Na2 are $\eta^5$ bonded to two pyrrolyl anions (Na1–$\eta^5$-Pyr 2.385(2) Å, 2.380(2) Å; Na2–$\eta^5$-Pyr 2.376(2) Å, 2.378(2) Å) and they experience a short contact with the nitrido anion (Na1 ··· N9 3.032(3) Å, Na2 ··· N9 3.102(3) Å).

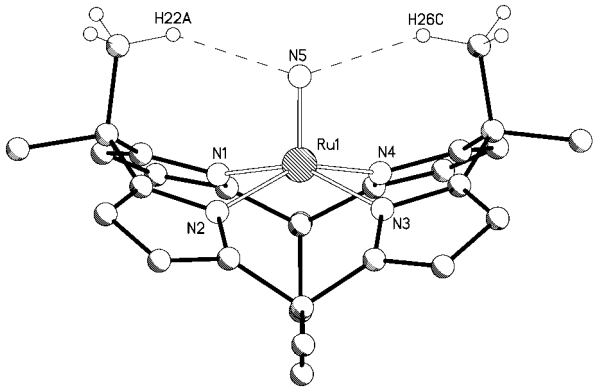



Figure 1. Ball-and-stick diagram for **3** ($[Na(dme)_3]^+$, free DME molecule, and hydrogen atoms omitted for clarity). Selected bond lengths [Å]: Ru1-N5 1.569(6), Ru1-N1 1.996(6), Ru1-N2 2.042(7), Ru1-N3 2.009(7), Ru1-N4 1.971(7).

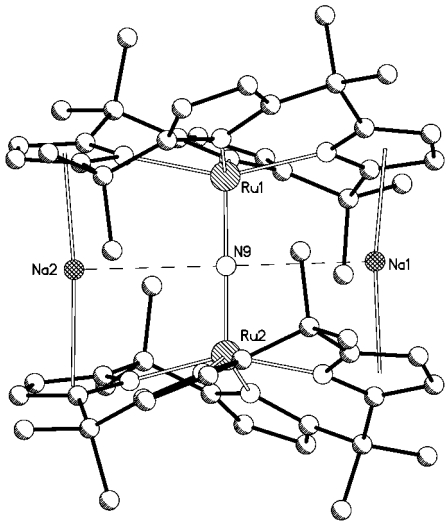



Figure 2. Ball-and-stick representation of **6** ($[Na(thf)_3]^+$, $Na^+$, and hydrogen atoms omitted for clarity). Selected bond lengths [Å]: Ru1-$N_{av}$ 2.099(2), Ru1-N9 1.827(3), Ru2-$N_{av}$ 2.097(2), Ru2-N9 1.825(3).

The above results suggest: 1) how a metal–nitrido functionality can be synthesized from dinitrogen or related organic groups; 2) how to tune the nature and hence the

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reactivity of the Ru nitrido group; 3) how to make homo- or heterodinuclear nitrido complexes;[11] and 4) how to labilize the [Ru=N] group.

## *Experimental Section*

**1**: $[RuCl_2(cod)]$ (cod = 1,5-cyclooctadiene; 6.19 g, 22.0 mmol) was added to a solution of $[Me_8N_4Na_4(thf)_4]$ (17.8 g, 22.0 mmol) in DME (300 mL). The reaction mixture was refluxed for 24 h, and the NaCl was filtered off. The resulting solution was allowed to stand at $-20\,^{\circ}C$, and the resulting orange crystalline product was collected and dried in vacuo (11 g, 45%). Crystals suitable for X-ray diffraction were grown from DME. $^1H$ NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 5.74$ (s, 8H, $C_4H_2N$), 3.41 (s, 24H, DME), 3.23 (s, 36H, DME), 1.43 (s, 24H, $CH_3$); $^{13}C$ NMR (400 MHz, [D$_6$]DMSO, 25 °C): $\delta = 146.1$, 100.1, 71.0, 58.0, 39.1, 36.9; elemental analysis (%) calcd for $\mathbf{1}\cdot 6\,C_4H_{10}O_2$, $C_{52}H_{92}N_4Na_2O_{12}Ru$ ($M_r = 1112.4$): C 56.15, H 8.34, N 5.04; found: C 55.91, H 8.40, N 4.96.

**3**: Compound **1** (19.0 g, 17.1 mmol) was added to a solution of diphenyldiazomethane (3.32 g, 17.1 mmol) in THF (600 mL) at $-40\,^{\circ}C$. The reaction mixture was slowly warmed to room temperature and stirred overnight. The resultant dark amber solution was concentrated, and then $Et_2O$ (200 mL) was added. An amber microcrystalline solid was isolated (10.6 g, 74.6%). $Ph_2CNH$ was detected by gas-chromatography and characterized by mass spectroscopy from a hydrolyzed sample of the mother liquor. Crystals suitable for X-ray diffraction were grown from DME. $^1H$ NMR (400 MHz, [D$_6$]benzene/[D$_8$]THF, 298 K, TMS): $\delta = 6.33$ (s, 8H, $C_4H_2N$), 3.22 (s, 12H, DME), 3.05 (s, 18H, DME), 1.88 (s, 12H, $CH_3$), 1.54 (br s, 12H, $CH_3$); elemental analysis (%) calcd for **3**, $C_{40}H_{62}N_5NaO_6Ru$ ($M_r$ = 833.01): C 57.67, H 7.50, N 8.41; found: C 57.41, H 7.45, N 8.22.

**6**: Method A: Sodium (38.0 mg, 1.64 mmol) and a catalytic amount of naphthalene were added to a suspension of **5** (1.38 g, 1.64 mmol) in THF (80 mL) at room temperature. The reaction mixture was stirred for 36 h, after which a green solid formed (0.98 g, 80%). Crystals suitable for X-ray diffraction were grown from THF/$Et_2O$. Elemental analysis (%) calcd for **6**, $C_{72}H_{96}N_9Na_4O_4Ru_2$ ($M_r = 1445.68$): C 59.82, H 6.69, N 8.72; found: C 59.98, H 6.75, N 8.52; $\mu_{eff} = 1.60\,\mu_B$ at 293 K; UV/Vis (THF/DME): $\lambda_{max}$ [nm] ($\varepsilon$ [mol$^{-1}$ dm$^3$ cm$^{-1}$]) = 286 (35898), 338 (18114), 486 (2676), 582 (698), 674 (973).

**6**: Method B: An equimolar mixture of **1** (1.42 g, 1.28 mmol) and **4** (1.05 g, 1.28 mmol) in THF (100 mL) was allowed to stand in the dark for 2 h. The resulting green suspension was concentrated to 30 mL, and $Et_2O$ (100 mL) was added. The bright green crystalline solid that precipitated was collected and then dried in vacuo (1.64 g, 89%). Crystals suitable for X-ray diffraction were grown from THF.

Photolysis of **6**: A green solution of **6** in THF/DME was irradiated with visible light. The resulting yellow solution reverted to the initial green one on allowing it to stand in the dark. When the yellow solution was cooled to $-40\,^{\circ}C$ under continuous irradiation, orange crystals of **1** were isolated. The presence of **1** in solution was further supported by the $^1H$ NMR spectrum.

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[9] The Ru=N group in **4** is affected by disorder. After solving this problem, 1.74(1) and 1.78(3) Å were obtained as the bond lengths for the two different sites A and B (occupancy factor for A: 0.51(1)).

[10] Crystal structure analysis of **3**: $[C_{28}H_{32}N_5Ru][Na(C_4H_{10}O_2)_3]\cdot(C_4H_{10}O_2)$, $M_r = 923.13$, orthorhombic, space group $Pca2_1$, $a = 31.587(6)$, $b = 11.802(2)$, $c = 12.986(3)$ Å, $V = 4841.0(17)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.267$ g cm$^{-3}$, $F(000) = 1960$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), $\mu(Mo_{K\alpha}) = 0.385$ mm$^{-1}$; $x = 0.06(5)$; crystal dimensions $0.24 \times 0.20 \times 0.14$ mm$^3$. Diffraction data were collected on a mar345 Imaging Plate at 143 K. For 4071 observed reflections ($I > 2\sigma(I)$) and 533 parameters, the conventional $R$ factor was 0.0525 ($wR2 = 0.1390$ for 6730 independent reflections). Crystal structure analysis of **6**: $[C_{56}H_{64}N_9Ru_2][Na]_2[Na(C_4H_8O)_3]_2$, $M_r = 1589.89$, monoclinic, space group $P2_1$, $a = 13.8984(8)$, $b = 15.7887(8)$, $c = 17.5436(9)$ Å, $\beta = 95.929(5)^{\circ}$, $V = 3829.1(4)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.379$ g cm$^{-3}$, $F(000) = 1670$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 0.476$ mm$^{-1}$; $x = 0.025(14)$; crystal dimensions $0.34 \times 0.30 \times 0.20$ mm. Diffraction data were collected on a Kuma diffractometer with a $\kappa$ geometry and equipped with a CCD detector at 143 K. For 16324 observed reflections ($I > 2\sigma(I)$) and 910 parameters, the conventional $R$ value was 0.0277 ($wR2 = 0.0665$ for 16674 independent reflections). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-158333 (**3**) and CCDC-158334 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] The phthalocyanine (Pc) bis-ruthenium $\mu$-nitrido species, [(Pc)Ru–N–Ru(Pc)] and the mixed-ligand heterobimetallic analogue [(tpp)Fe$^{IV}$–N–Ru$^{III}$(Pc)] (tpp = tetraphenylporphyrin) have been previously reported: a) G. Rossi, M. Gardini, G. Pennesi, C. Ercolani, V. L. Goedken, *J. Chem. Soc. Dalton Trans.* **1989**, 183; b) C. Ercolani, J. Jubb, G. Pennesi, U. Russo, G. Trigiante, *Inorg. Chem.* **1995**, *34*, 2535.


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