Δ-$(-)_D$-*fac*-Co(CH_2=tah)$_3$·H_2O. The molecular structure is depicted in Figure 1b. The three ligands are planar. Least-squares planes through S, C, N, and N of each ligand have been calculated. The cobalt atom is only 0.066 Å out of the plane defined by S1, C11, N11, and N12 but 0.13 and 0.21 Å out of the planes defined by the two other ligands. The planes A, B, and C defined in this way form the angles A/B = 82.4°, A/C = 86.9°, and B/C = 78.0°. Both substituents of the chelate rings are displaced relative to the least-squares planes. The carbon atoms of the methylene groups show the largest distances, 0.11, −0.07, and −0.18 Å, respectively, for the three ligands. The pronounced deviation from 3-fold symmetry has been found to originate in the intermolecular interactions.

***fac*-Co(Htsc)$_3$Cl$_3$.** The cation is shown in Figure 1c. The packing arrangement for this compound is also determined by extensive hydrogen bonding between all the nitrogen-bound hydrogen atoms and chloride ions. The N–Cl distances are found to be between 3.1 and 3.5 Å. Hydrogen atoms on N32 and N21 form bifurcated hydrogen bonds to the chloride ions as formerly observed between $-NH_2$ groups and oxygen atoms.[19] The least-squares planes defined by the atoms S, C, N, and N of the three chelate backbones were calculated. The four atoms of the ligand in III have distances to the plane of −0.042, 0.095, and −0.103 Å, respectively, illustrating a small but significant puckering of this ligand. The two other ligands are planar, similar to what was observed in structures I and II. The difference between the ligand in Co(Htsc)$_3$Cl$_3$ and the other two is also reflected in the molecular dimensions of the ligand. The C3–N32 bond of 1.341 (2) Å is significantly longer than the two corresponding distances of 1.327 (2) and 1.325 (2) Å. The cobalt atom has distances to the three ligand planes varying between 0.46 and 0.51 Å. The angles for the three planes are calculated to be A/B = 82.7°, A/C = 61.6°, and B/C = 64.6°. It seems likely that the extensive hydrogen bonding is causing the irregularities of the coordination cation.

Discussion

Co(Htah)$_3$Cl$_3$ is the only compound of the three studied that possesses a 3-fold axis of symmetry in the crystal. In the two other structures the relative arrangement of the chelate rings does not show 3-fold symmetry, as demonstrated by the rather different angles between the planes defined by the backbone of each chelate. The packing arrangements in II and III are strongly influenced by hydrogen bonding, and this seems to be the plausible cause for the lack of 3-fold symmetry in these compounds. The molecular dimensions observed in the three independent chelate ligands of II and III do not differ grossly, and the averaged bond lengths and angles are listed in Table V.

In Co(Htah)$_3^{3+}$, S, C1, and N2 seem to participate in the π-bonding system and the C–S bond (1.694 (3) Å) has a value close to the distance of a C–S double bond.[20] In Co(CH_2=tah)$_3$, the chain of S, C1, N2, N1, and C3 forms the π-system, and consequently the C–S bond (1.727 (4) Å) is elongated compared to that of Co(Htah)$_3^{3+}$. The N1–N2 distance also reflects the effect of the conjugation, being longer (1.428 (3) Å) in I, where a pure single bond is expected, and shorter (1.418 (2) Å) in II, where the bond is participating in the conjugated system. In Co(Htsc)$_3^{3+}$ the conjugation is clearly dominated by the bond between the amide nitrogen and the carbon atom, as indicated by the long C–S bond length of 1.7222 (4) Å compared to the bond distance 1.688 (4) Å found for I.

The absolute configurations of the $(-)_D$-*fac*-tris(thioacethydrazide)cobalt(III) ion and of $(-)_D$-*fac*-tris(formaldehyde thioacethydrazonato)cobalt(III) have here been determined to be Δ, in agreement with an earlier assignment based on circular dichroism spectroscopy.[8] In the visible region $(-)_D$-Co(Htah)$_3^{3+}$ exhibits an absorption band at ca. 500 nm due to the lowest lying spin-allowed transition. In connection with this, a single circular dichroism band of negative sign is observed. This would imply the Δ absolute configuration according to an empirical correlation that, however, is known to have exceptions.[21] In the UV region these compounds exhibit a series of absorption bands with varying molar absorption coefficients up to 30 000 M^{-1} cm^{-1}. The allowed transitions giving rise to these bands are interpreted as ligand to metal charge-transfer and internal ligand π to π^* transitions. The latter transitions are expected to show exciton splitting of the absorption band combined with relatively intense Cotton effects. However, with unsymmetric bidentate chelates the symmetry allows extensive mixing of transitions and the spectroscopic determination of the absolute configuration becomes unreliable. The present determination of the absolute configurations is therefore in this case considered a necessity.

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Supplementary Material Available: For Δ-Co(Htah)$_3$Cl$_3$, listings of anisotropic thermal parameters (Table SI), hydrogen positions (Table SII), and possible hydrogen bonds (Table SIV), for Δ-Co(CH_2=tah)$_3$·H_2O, listings of anisotropic thermal parameters (Table SV), hydrogen positions and thermal parameters (Table SVI), bond lengths and angles (Table SVIII), and possible hydrogen bonds (Table SIX), and for *fac*-Co(Htsc)$_3$Cl$_3$, listings of anisotropic thermal parameters (Table SX), hydrogen positions and thermal parameters (Table SXI), bond lengths and angles (Table SXIII) and possible hydrogen bonds (Table SXIV) (10 pages); listings of observed and calculated structure amplitudes (Tables SIII, SVII, and SXII) (43 pages). Ordering information is given on any current masthead page.

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Molecular Dinitrogen Complexes of Ruthenium(II) Porphyrins

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Binding of dinitrogen at a ruthenium(II) porphyrin center was first noted by Hopf and Whitten,[3] but the reaction, monitored only by UV/visible spectral changes, involved surfactant species in monolayer assemblies. Subsequent to this, UV/visible studies suggested in situ formation of a dinitrogen complex following exposure of Ru(OEP)(DMF)$_2$ to N_2.[4,5] Later, the labile Ru(OEP)(THF)(N_2) complex was isolated ($\nu(N_2)$ = 2110 cm^{-1}).[6] The existence of such species was questioned at one time,[7] but recent work on Ru(TMP) systems has fully established the existence of both mono- and bis(dinitrogen) complexes.[8] Here we

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(4) OEP and TMP are dianions of 2,3,7,8,12,13,17,18-octaethylporphyrin and 5,10,15,20-tetramesitylporphyrin, respectively; DMF = dimethylformamide; THF = tetrahydrofuran; py = pyridine; en = ethylenediamine.

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Table I. ^{1}H NMR Chemical Shifts (δ) for the New Ru(TMP) Derivatives[a]

complex	pyrrole H	*m*-H	*p*-Me	*o*-Me
Ru(TMP)(DMF)(N_2)[b] (**4**)	8.77	7.25, 7.17	2.50	2.09, 2.08
Ru(TMP)(Et_3N)(N_2)[c] (**5**)	8.69	7.31, 7.08	2.57	2.46, 1.64
Ru(TMP)$(DMF)_2$[d]	8.43	7.28	2.52	2.28

[a] Measured at 300 MHz in C_6D_6 at ambient conditions; relative integrations for protons are consistent with the assignments (all singlets unless stated otherwise); residual benzene (δ 7.20) used as reference. [b] Ru–OCHNMe_2, δ 0.33, −0.16, $\nu(N_2)$ 2108 cm^{-1}, ν(DMF) 1644 cm^{-1}. [c] Ru–NCH_2CH_3, δ −1.39 t; –NCH_2–, 1.95 q; $\nu(N_2)$ 2147 cm^{-1}. [d] Ru–OCHNMe_2, δ +0.56, +0.06.

report some details on the TMP species, including an X-ray crystallographic study of Ru(TMP)(THF)(N_2).

Experimental Section

^{1}H NMR spectra were obtained on C_6D_6 solutions under 1 atm of N_2 with a Varian XL-300 spectrometer. Visible spectra were run on a Cary 17D spectrophotometer, and IR spectra on a Nicolet 5DX FT instrument. The THF was freshly distilled from CaH_2 and stored under Ar. A 450-W Hg vapor lamp with a Pyrex water-cooling jacket was used for photolysis. The Ar was purified by passing it successively through a Ridox column (Fisher Scientific) and activated molecular sieve to remove O_2 and moisture, respectively. Elemental analyses were performed by H. Malissa and G. Reuter (Analytische Laboratorien, Elback, FRG).

Ru(TMP)(THF)(N_2) (1). The carbonyl Ru(TMP)(CO) (80 mg, 0.09 mmol), prepared by a literature method,[9] was dissolved in 200 mL of THF and the solution subjected to photolysis for 17 h under an Ar purge. The solution was then cannulated onto an alumina column (20 mL, neutral, Activity I), and the resulting brownish red band front was eluted with 20 mL of THF. Removal of eluent by pumping yielded Ru(TMP)$(THF)_2$ in >90% yield as a copper brown microcrystalline solid. Evaporation of benzene solutions of this material under N_2 gives a quantitative yield of complex **1**. To grow a crystal of **1**, the bis(tetrahydrofuran) complex (5 mg, 0.005 mmol) was dissolved under vacuum in 2 mL of C_6D_6 in a sealed NMR tube, and the purity was checked by recording the ^{1}H NMR spectrum.[8] The tube was then opened in an N_2-filled glovebox; a darkening of the solution occurred with rapid formation of **1**, and slow evaporation of solvent within the glovebox (3 days) led to formation of dark red crystals suitable for X-ray analysis.

Ru(TMP)(L)(N_2) (L = N_2, 2; L = Et_2O, 3; L = DMF, 4; L = Et_3N, 5). The acetonitrile complex[10] Ru(TMP)$(MeCN)_2$ was made from Ru(TMP)(CO) by photolysis in MeCN, as described above for the $(THF)_2$ complex. Vacuum pyrolysis of Ru(TMP)$(MeCN)_2$ for 2 h at 225 °C and 2×10^{-5} Torr gives in quantitative yield the highly reactive brown Ru(TMP) species.[8] Anal. Calcd for $C_{56}H_{52}N_4Ru$: C, 76.25; H, 5.94; N, 6.35. Found: C, 75.92; H, 6.06; N, 6.21. On exposure to N_2 (e.g., in a glovebox), Ru(TMP) in the solid state instantly forms the red complex Ru(TMP)$(N_2)_2$ (**2**).[8] Anal. Calcd for $C_{56}H_{52}N_8Ru$: C, 71.70; H, 5.59; N, 11.94. Found: C, 71.21; H, 5.71; N, 11.24.

Complex **2** (1–2 mg) was dissolved in C_6D_6 (~1 mL) in an NMR tube in a glovebox under N_2; addition of 5–10 equiv of L (=Et_2O, DMF, Et_3N) generated in situ red solutions of the Ru(TMP)(L)(N_2) species, **3**–**5**. Complete removal of N_2 from the C_6D_6 solutions of **2** (at least five freeze–pump–thaw cycles) followed by corresponding addition of L (=Et_2O, DMF) generated in situ Ru(TMP)L_2 species; subsequent exposure to 1 atm of N_2 presented an alternative route to **3** and **4**. Evaporation of the solutions of **3**–**5** yielded sufficient solid material to obtain IR (Nujol) data. Table I provides some spectroscopic data.

X-ray Crystallographic Analysis of Ru(TMP)(THF)(N_2) (1). Some details of data collection are given in Table II. The compound was X-ray sensitive, even at −100 °C, and so the data were collected as fast as possible with no rescans of weak data. Three separate crystals of approximately the same size were used. Each data shell was corrected for decay of intensity standards: crystal **1**, 11%; crystal **2**, 15%; crystal **3**, 12%. After correction for absorption, the data sets were merged and used in the solution and refinement of the structure. The structure was solved by a conventional heavy-atom method,[11] the coordinates of the Ru, N(5), and O(1) atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms by direct methods (DIRDIF).[12]

Table II. Crystal Data and Data Collection Procedures for Ru(TMP)(THF)(N_2)[a]

formula	$C_{60}H_{56}N_6ORu$
fw	978.2
space group	C^5_{2h}-$P2_1/c$
a, Å	13.617 (6)
b, Å	17.021 (10)
c, Å	26.194 (10)
β, deg	94.15 (2)
Vol, Å^3	6056
Z	4
temp, °C	−100[b]
density (calcd), g/cm^3	1.073
cryst vol, mm^3	0.030
linear abs coeff, cm^{-1}	2.90
transmission factors	0.913–0.929
detector aperture	3 mm high × 2 mm wide, 17.3 mm from crystal
takeoff angle, deg	2.4
scan mode	ω
scan speed, deg/min	2 in ω
θ limits	$2 \le \theta \le 25$
scan range, deg	±0.8
bkgd counts	$^1/_4$ of scan on each side of rflcn
data collected	$+h,+k,\pm l$
no. of total unique data	10350
no. of total unique data with $F_o^2 > 3\sigma(F_o^2)$	5564
no. of variables	315
p factor for $\sigma(F_o^2)$	0.03
$R(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.093
$R_w(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.128
error in observn of unit wt, e	3.60

[a] Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation ($\lambda(K\alpha_1)$ = 0.7093 Å), graphite monochromator. [b] The low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. I. de Vic, 31320 Castanet-Tolosan, France. A temperature of −100 °C was used, as crystals of this material break up at ≅−150 °C.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) in Ru(TMP)(THF)(N_2)[a]

Distances			
Ru–N(5)	1.822 (13)	Ru–N(2)	2.047 (10)
Ru–O(1)	2.123 (9)	Ru–N(3)	2.057 (9)
N(5)–N(6)	1.074 (16)	Ru–N(4)	2.047 (10)
Ru–N(1)	2.058 (9)	av Ru–N	2.052 (10)
av N–C_a	1.365 (16)[b]	av C_m–C_{Ph}	1.578 (29)
av C_a–C_b	1.429 (27)	av C_{Ph}–C_{Ph}	1.377 (29)
av C_b–C_b	1.337 (26)	av C_{Ph}–C_{Me}	1.507 (37)
av C_a–C_m	1.391 (16)		

Angles[c]			
N(6)–N(5)–Ru	177.6 (16)	N(5)–Ru–O(1)	179.1 (5)
av N–Ru–N(N_2)	91.6 (12)[b]	av Ru–N–C_a	125.9 (10)
av N–Ru–O(1)	88.5 (7)		
av C_a–N–C_a	108.1 (11)	av C_a–C_m–C_{Ph}	117.2 (11)
av N–C_a–C_b	108.2 (11)	av C_m–C_{Ph}–C_{Ph}	120.0 (13)
av C_a–C_b–C_b	107.8 (15)	av C_{Ph}–C_{Ph}–C_{Ph}	120.0 (21)
av N–C_a–C_m	126.1 (12)	av C_{Ph}–C_{Ph}–C_{Me}	120.0 (19)
av C_a–C_m–C_a	125.6 (14)		
av Ru–O(1)–C	125.3 (10)	av C–C–C	105.0 (16)
av O(1)–C–C	108.5 (15)	C(57)–O(1)–C(60)	109.4 (13)

[a] Labeling: C_a and C_b refer to carbon atoms α and β to the pyrrole N, respectively; C_m, C_{Ph}, and C_{Me} refer to the meso, phenyl, and methyl carbon atoms, respectively; C refers to the carbon atoms of THF. [b] The error in the mean value is the larger of the unweighted estimated standard deviation of a single observation or the error estimated from the least-squares matrix. [c] N(pyrrole)–Ru–N(pyrrole) angles are close to 90° (within 0.8°).

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(10) This compound has been characterized by ^{1}H NMR and IR data[8] and by an X-ray structure determination; Camenzind, M. J.; Rettig, S. J.; James, B. R.; Dolphin, D., to be submitted for publication.

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Refinement was by full-matrix least-squares methods on F_o for the 5564 reflections having $F_o^2 > 3\sigma(F_o^2)$. In the last two refinements, atoms Ru, O(1), and N(1)–N(6) were refined anisotropically. Hydrogen atoms were located from a difference electron density synthesis; positions were idealized [C–H = 0.95 Å; $B(\mathrm{H}) = B(\mathrm{C}) + 1$ Å^2]. A final difference electron density map was essentially featureless. Analysis of $\sum w\Delta^2$ over ranges of θ, F_o, and Miller indices revealed no unusual trends. The high residual R index (0.093) presumably is the result of the instability of the compound.

Selected bond lengths and angles are given in Table III, and final positional and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table IV. Complete bond lengths and angles, displacements of atoms from the porphyrin plane, dihedral angles between the porphyrin core and pyrrole rings, positional parameters for the hydrogen atoms, anisotropic thermal parameters for atoms Ru, O(1), and N(1)–N(6), and structure amplitudes are included as supplementary material (Tables S1–S7).

Results and Discussion

The Ru(TMP)(L)(N_2) complexes (L = THF, **1**; Et_2O, **3**; DMF, **4**) can be prepared in benzene via the equilibria shown in eq 1.

$$\mathrm{Ru(TMP)L_2} \underset{\mathrm{L}}{\overset{\mathrm{N_2}}{\rightleftharpoons}} \mathrm{Ru(TMP)(L)N_2} \underset{\mathrm{L}}{\overset{\mathrm{N_2}}{\rightleftharpoons}} \mathrm{Ru(TMP)(N_2)_2} \tag{1}$$

The L = Et_3N species (**5**) was formed only via the $(N_2)_2$ complex. The Ru(TMP)$(THF)_2$ precursor complex is readily isolated following photolysis of Ru(TMP)(CO) in THF solution but was usually contaminated with small amounts of the carbonyl, which may be unreacted starting material or that formed via decarbonylation of THF.[13] The $(DMF)_2$ and $(Et_2O)_2$ complexes are not formed by the photolysis procedure; a photoinduced catalytic decarbonylation of DMF to dimethylamine[6,14] certainly prevents effective formation of Ru(TMP)$(DMF)_2$, and such decarbonylation may well be involved with Et_2O, but the organic products have not been identified. The $(DMF)_2$ and $(Et_2O)_2$, species were formed by addition of the appropriate solvent to benzene solutions of Ru(TMP).[8] The elemental analysis of Ru(TMP)$(N_2)_2$ (**2**) is satisfactory considering the labile nature of the trans-disposed π-acid N_2 ligands; the $\nu(N_2)$ value of 2203 cm^{-1} for **2** is the highest recorded to date for any isolated dinitrogen complex.[8] A mono(dinitrogen) species was not formed at 1 atm of N_2 with Ru(TMP)$(MeCN)_2$, presumably because of the instability of a trans arrangement of the π-acceptors N_2 and CH_3CN.

Complexes **1**–**3** and the $(THF)_2$ and $(Et_2O)_2$ species were characterized previously by ^{1}H NMR and IR data,[8] and the crystallographic data for **1** (see below) now fully confirm the existence of the mono(dinitrogen)(ether) species. The ^{1}H NMR data for **4** and **5** (Table I) are as expected for diamagnetic Ru(II) porphyrins, with lack of a porphyrin plane of symmetry leading to magnetically inequivalent *o*-CH_3 groups and meta protons of the TMP ligand.[15] Resonances of the axial ligands (THF, Et_2O, DMF, and NEt_3) are shifted upfield from those of the free ligands because of the porphyrin ring current.

The $\nu(N_2)$ stretches for the Ru(TMP)(L)(N_2) complexes are in the range 2108–2147 cm^{-1} (see ref 8 and footnotes *b* and *c* in Table I) and are comparable to that found for Ru(OEP)(THF)(N_2), 2110 cm^{-1}.[6] The values are similar to those found for $\mathrm{Ru(NH_3)_5(N_2)^{2+}}$ (2105–2167 cm^{-1})[16] and *trans*-$\mathrm{Ru(NH_3)_4(H_2O)(N_2)^{2+}}$ species (2088–2115 cm^{-1}).[17]

Table IV. Positional Parameters and B_{eq} (Å^2) for Ru(TMP)(THF)(N_2)

atom	*x*	*y*	*z*	*B*
Ru	0.585 053 (81)	0.138 349 (75)	0.298 994 (38)	2.31 (4)
O(1)	0.539 22 (63)	0.019 95 (53)	0.306 48 (33)	3.1 (3)
N(1)	0.517 36 (75)	0.163 83 (64)	0.364 75 (34)	2.7 (3)
N(2)	0.713 60 (80)	0.112 17 (65)	0.340 94 (36)	3.1 (3)
N(3)	0.649 77 (72)	0.106 34 (64)	0.233 53 (34)	2.5 (3)
N(4)	0.454 91 (71)	0.158 40 (53)	0.256 93 (34)	2.2 (3)
N(5)	0.625 76 (90)	0.239 50 (74)	0.291 90 (44)	2.9 (4)
N(6)	0.652 7 (13)	0.298 2 (10)	0.287 42 (60)	6.8 (6)
C(1)	0.422 85 (97)	0.186 53 (80)	0.367 95 (47)	2.5 (3)
C(2)	0.406 91 (97)	0.198 09 (82)	0.421 62 (48)	2.9 (3)
C(3)	0.489 5 (10)	0.179 39 (86)	0.447 99 (50)	3.4 (3)
C(4)	0.560 36 (93)	0.159 43 (75)	0.413 80 (46)	2.5 (3)
C(5)	0.658 73 (95)	0.139 46 (89)	0.426 80 (47)	3.0 (3)
C(6)	0.727 76 (97)	0.117 68 (79)	0.392 47 (50)	3.1 (3)
C(7)	0.830 7 (10)	0.096 00 (84)	0.406 64 (49)	3.2 (3)
C(8)	0.871 44 (99)	0.077 34 (84)	0.364 25 (49)	3.1 (3)
C(9)	0.800 1 (10)	0.087 80 (82)	0.321 96 (48)	2.8 (3)
C(10)	0.813 43 (97)	0.075 95 (82)	0.269 90 (48)	2.9 (3)
C(11)	0.744 76 (94)	0.088 13 (78)	0.229 59 (45)	2.4 (3)
C(12)	0.761 13 (96)	0.075 61 (81)	0.176 83 (47)	2.8 (3)
C(13)	0.673 74 (99)	0.087 08 (82)	0.150 64 (48)	3.0 (3)
C(14)	0.601 68 (90)	0.106 26 (75)	0.185 06 (45)	2.1 (3)
C(15)	0.502 89 (88)	0.121 59 (71)	0.172 77 (43)	2.1 (3)
C(16)	0.436 57 (82)	0.149 17 (74)	0.205 26 (44)	2.0 (3)
C(17)	0.338 86 (96)	0.169 40 (79)	0.191 26 (47)	2.7 (3)
C(18)	0.295 97 (96)	0.195 37 (82)	0.233 90 (48)	2.9 (3)
C(19)	0.370 38 (96)	0.186 00 (80)	0.275 94 (46)	2.6 (3)
C(20)	0.353 19 (94)	0.199 55 (78)	0.327 85 (46)	2.5 (3)
C(21)	0.694 97 (95)	0.148 32 (88)	0.484 27 (48)	3.1 (3)
C(22)	0.691 0 (10)	0.083 47 (89)	0.515 39 (51)	3.4 (3)
C(23)	0.726 4 (12)	0.094 1 (10)	0.566 58 (59)	4.9 (4)
C(24)	0.764 0 (11)	0.161 85 (95)	0.582 85 (57)	4.3 (4)
C(25)	0.767 9 (11)	0.223 79 (97)	0.551 86 (58)	4.3 (4)
C(26)	0.733 4 (10)	0.217 40 (87)	0.502 14 (50)	3.2 (3)
C(27)	0.653 4 (13)	0.007 5 (12)	0.497 62 (68)	6.4 (4)
C(28)	0.802 8 (15)	0.166 7 (12)	0.641 03 (74)	8.0 (6)
C(29)	0.734 9 (13)	0.286 9 (11)	0.469 18 (66)	6.6 (5)
C(30)	0.915 24 (98)	0.049 62 (84)	0.257 75 (47)	2.8 (3)
C(31)	0.979 5 (11)	0.104 49 (92)	0.237 89 (51)	3.7 (3)
C(32)	1.071 1 (12)	0.076 0 (10)	0.223 55 (57)	4.7 (4)
C(33)	1.097 7 (12)	−0.002 4 (10)	0.229 00 (56)	4.4 (4)
C(34)	1.033 7 (11)	−0.055 65 (95)	0.248 88 (55)	4.4 (4)
C(35)	0.942 3 (10)	−0.029 70 (86)	0.262 67 (48)	3.1 (3)
C(36)	0.954 9 (11)	0.190 82 (98)	0.234 39 (55)	4.8 (4)
C(37)	1.196 0 (14)	−0.030 1 (11)	0.212 45 (67)	6.7 (5)
C(38)	0.876 5 (12)	−0.089 3 (11)	0.281 59 (60)	5.5 (4)
C(39)	0.464 39 (93)	0.105 00 (80)	0.118 16 (47)	2.4 (3)
C(40)	0.467 1 (10)	0.161 32 (85)	0.080 38 (51)	3.4 (3)
C(41)	0.430 2 (11)	0.143 4 (11)	0.030 14 (56)	4.8 (4)
C(42)	0.392 1 (11)	0.071 11 (96)	0.018 87 (55)	4.0 (3)
C(43)	0.391 4 (11)	0.018 49 (90)	0.055 14 (54)	3.8 (3)
C(44)	0.427 04 (97)	0.032 28 (83)	0.105 26 (49)	3.0 (3)
C(45)	0.508 3 (12)	0.241 0 (11)	0.091 18 (59)	5.4 (4)
C(46)	0.353 1 (13)	0.054 3 (11)	−0.036 46 (65)	6.2 (5)
C(47)	0.427 1 (12)	−0.032 57 (96)	0.145 17 (57)	4.7 (4)
C(48)	0.256 32 (96)	0.231 82 (82)	0.340 45 (46)	2.7 (3)
C(49)	0.240 3 (10)	0.312 34 (86)	0.341 09 (49)	3.1 (3)
C(50)	0.149 4 (11)	0.344 91 (88)	0.352 39 (51)	3.8 (3)
C(51)	0.078 0 (12)	0.293 17 (97)	0.362 10 (54)	4.1 (3)
C(52)	0.089 2 (11)	0.213 14 (95)	0.362 79 (53)	3.9 (3)
C(53)	0.180 1 (10)	0.181 55 (90)	0.351 02 (49)	3.2 (3)
C(54)	0.323 2 (11)	0.365 5 (10)	0.329 65 (55)	4.7 (4)
C(55)	−0.023 5 (14)	0.324 9 (11)	0.375 68 (68)	6.9 (5)
C(56)	0.192 8 (12)	0.092 8 (11)	0.351 79 (60)	5.5 (4)
C(57)	0.444 9 (13)	−0.004 5 (11)	0.320 68 (64)	5.7 (4)
C(58)	0.444 1 (13)	−0.091 9 (11)	0.320 89 (62)	6.0 (4)
C(59)	0.538 1 (14)	−0.116 4 (11)	0.298 46 (65)	6.3 (5)
C(60)	0.598 9 (14)	−0.046 0 (12)	0.301 22 (68)	6.4 (5)

To our knowledge, outside of the (porphyrinato)ruthenium(II)–N_2 complexes, the only other isolated metalloporphyrin–N_2 complex reported is Os(OEP)(THF)(N_2), $\nu(N_2)$ = 2030 cm^{-1};[18] also, slow decomposition of a solution of an azido(porphyrinato)iron(III) complex has been shown to generate a species with an IR band at 2100 cm^{-1}, and this was tentatively assigned to

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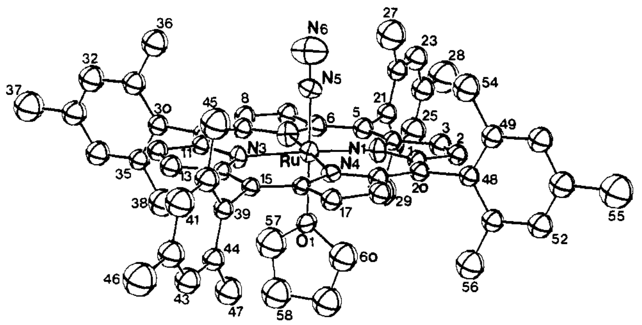

Figure 1. Drawing of the Ru(TMP)(THF)(N_2) molecule showing 50% probability ellipsoids and a partial labeling scheme. Hydrogen atoms have been omitted for the sake of clarity.

Fe(porp)(py)(N_2) where porp = the dianion of a protoporphyrin IX diester.[19] It is clear from the limited literature available[6,18-20] and our own more recent observations, that the N_2 ligand in the mono(dinitrogen) complexes is highly thermolabile and radiation labile (laboratory lighting and X-rays). The growing of a crystal of **1**, and its subsequent analysis by X-ray diffraction, were not trivial problems.

The structure of **1** is shown in Figure 1. The complex shows the typically linear Ru←N≡N arrangement with the metal being essentially in the plane (0.014 Å above the weighted least-squares plane of the 25-atom porphyrin skeleton). The Ru-N(5) distance of 1.822 (13) Å is slightly shorter than that found in the Ru(N_2)(N_3)(en)$_2^{2+}$ ion[21] (1.894 (9) Å). Other features of the Ru-N-N geometry are comparable in the two compounds and in the less accurately determined structures of two ruthenium dinitrogen hydrido phosphine complexes.[22,23] Other averaged bond lengths and angles for the metalloporphyrin moiety within **1** show no unusual features when compared with those of other monomeric, 6-coordinate Ru porphyrin complexes.[24-30]

The chemistry and redox properties of the Ru(II) porphyrin dinitrogen complexes, particularly the reactivity of the bound N_2, remain to be elucidated.

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Registry No. **1**, 106210-10-0; **2**, 106210-09-7; **3**, 106210-11-1; **4**, 115227-06-0; **5**, 115227-07-1; Ru(TMP)(CO), 92669-43-7; Ru(TMP)(THF)$_2$, 97877-73-1; Ru(TMP)(MeCN)$_2$, 97877-74-2; Ru(TMP), 79235-76-0.

Supplementary Material Available: Table S1 (bond distances), Table S2 (bond angles), Table S3 (displacements from the porphyrin plane), Table S4 (dihedral angles), Table S5 (hydrogen atom parameters), and Table S6 (anisotropic thermal parameters) (8 pages); Table S7 (structure amplitudes) (23 pages). Ordering information is given on any current masthead page.

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A Phosphido-Capped Tritungsten Alkoxide Cluster: $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ and Speculation upon the Existence of a Reactive $(t\text{-}BuCH_2O)_3W{\equiv}P$ Intermediate

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and James W. Pasterczyk

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Lappert and co-workers[1] ended "The Quest for Terminal Phosphinidene Complexes"[2] with their reported synthesis and structural characterizations of $(\eta^5\text{-}C_5H_5)_2M({=}PAr)$ where M = Mo (X-ray) and W and Ar = $C_6H_2(t\text{-}Bu)_3$-2,4,6. We wish to report here our synthesis and characterization of a novel[3] phosphido-capped tritungsten cluster supported by alkoxide ligands and further to speculate that its formation may involve the reactive intermediate of formula $(t\text{-}BuCH_2O)_3WP$ having a W-P triple bond.

The reaction between $W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2$[4] and white phosphorus, P_4, proceeds in hydrocarbon solvents according to the stoichiometry (as determined by ^1H NMR spectroscopy) shown in eq 1.[5]

$$2W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2 + P_4 \xrightarrow[\text{toluene}]{75°,\ 4\ h} (HNMe_2)(t\text{-}BuCH_2O)_3W(\eta^3\text{-}P_3) + W_3(P)(OCH_2\text{-}t\text{-}Bu)_9 + 3HNMe_2 \quad (1)$$

The compound $(HNMe_2)(t\text{-}BuCH_2O)_3W(\eta^3\text{-}P_3)$ was previously characterized[6] from reaction 1, but the nature of the major tungsten-containing compound $W_3(P)(OCH_2\text{-}t\text{-}Bu)_9$ was not readily established. The elemental analysis indicated an approximate empirical formula $W(OCH_2\text{-}t\text{-}Bu)_3$, and though the presence of phosphorus was indicated, none could initially be detected by ^{31}P NMR studies.[7] The compound $W_3(P)(OCH_2\text{-}t\text{-}Bu)_9$ is only sparingly soluble in hydrocarbon solvents though this allowed the observation by NMR spectroscopy of two types of OCH_2-*t*-Bu groups in the integral ratio 2:1, with the former having diastereotopic methylene protons.[7] Repeated attempts to obtain single crystals suitable for a single-crystal X-ray study failed until crystals appeared in an NMR tube in which the course of reaction 1 was being followed.[8]

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(3) Phosphorus-, arsenic-, and even bismuth-capped triangular carbonyl clusters are known for the later transition elements, e.g. $Co_3(\mu_3\text{-}Bi)(CO)_9$: Whitmire, K. H.; Leigh, J. S.; Gross, M. E. *J. Chem. Soc., Chem. Commun.* **1987**, 926. Martinengo, S.; Ciani, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1589. To our knowledge, however, no triangular phosphido-capped clusters are known for the early transition elements (groups 4-6) in oxidation states M^{x+} where $x = 3$ or 4. See: Herrmann, W. A. *Angew. Chem., Intl. Ed. Engl.* **1986**, *25*, 56 and references therein.
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(5) Note the use of dry and oxygen-free atmospheres (N_2) and solvents throughout. Anal. Calcd (found) for $W_3(P)(OCH_2\text{-}t\text{-}Bu)_9$: C, 39.54 (38.30); H, 7.30 (6.95); P, 2.27 (2.27).
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(7) Ultimately, the ^{31}P signal was found: $\delta = 274.8$ vs 85% H_3PO_4, flanked by satellites due to coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance, $^1J_{^{183}W-^{31}P} = 45$ Hz. ^1H NMR data are temperature invariant (+60 to −60 °C) in toluene: δ 1.03 (18 H), 1.08 (9 H), 4.14 (2 H), 4.23 (2 H), 4.39 (2 H) ($J_{AB} = 10.8$ Hz).
(8) Crystal data for $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ at −156 °C: $a = b = 23.55$ (8) Å, $c = 17.97$ (6) Å, $\gamma = 120°$, space group *R*3. Of the 5360 reflections collected (Mo Kα, $5° < 2\theta < 45°$), 2488 were unique and the 2325 having $F > 3\sigma(F)$ were used in the full-matrix least-squares refinement. All non-hydrogen atoms were refined using anisotropic thermal parameters. H atoms were located but placed in idealized fixed positions during the final refinements. The final residuals are $R(F) = 0.029$ and $R_w(F) = 0.029$.

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