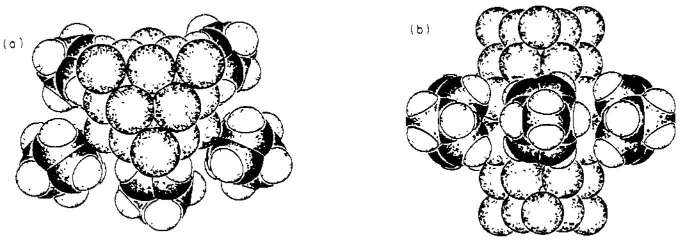

Figure 3. SCHAKAL[7] space-filling drawings of the $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion viewed along the same axes employed in Figures 1 and 2. The following atomic radii (Å) were employed: C, 1.7;[9] H, 1.2;[9] O, 1.4;[9] and for metals, 0.0.

sites labeled M in Figure 1 are 67% niobium and 33% tungsten while those labeled W are 100% tungsten. Refinement of occupancies for atoms in the $(C_7H_8)Rh^+$ moieties indicated full occupancy for Rh_1 units and $^2/_3$ occupancy for Rh_2 units resulting from the 3-fold disorder about the crystallographic C_3 axis passing through O_A. The structure of a single, nondisordered $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion is proposed in Figure 2. This structure is derived from the structure shown in Figure 1 by first removing a $(C_7H_8)Rh^+$ unit, shaded in Figure 1, and then assigning the Nb atoms to four of the M sites such that C_{2v} anion symmetry is obtained. This assignment is based on the assumption that Nb^V terminal oxygens will be utilized preferentially over W^{VI} terminal oxygens for binding $(C_7H_8)Rh^+$ cations. In this structure, each Rh^I center is bound to only oxygens that are bonded to at least one Nb^V center and completely avoids oxygens bonded only to the W^{VI} centers.

Although the $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ structure is unprecedented, all of its structural features are consistent with well-established inorganic and organometallic structural patterns. The 38 oxygen atoms form six close-packed layers in an ABCCBA sequence. The niobium and tungsten atoms occupy approximately octahedral sites between those layers. Each of the five rhodium atoms is a square-planar, d^8, 16-electron metal center with one pair of cis coordination sites occupied by olefinic C═C bonds and the other pair occupied by oxygen atoms.[8] The $(C_7H_8)Rh^+$ units are oriented relative to the $Nb_2W_4O_{19}^{4-}$ ions in such a fashion that effective Rh–O bonding is obtained with minimal weakening of Nb–O and W–O bonds. The 167 (3)° Rh_2–O_H–M angle reflects approximate sp hybridization at O_H and thus minimal interference of Rh_2–O_H bonding with Nb–O_H σ and π bonding. Similarly, the 121 (2)° Rh_1–O_B–M and 117 (2)° M–O_B–M angles reflect approximate sp^2 hybridization at O_B and minimal interference of Rh_1–O_B bonding with M–O_B σ and π bonding. From the viewpoint of nonbonding interactions, the $\{[(C_7H_8)Rh]_5(Nb_2W_2O_{19})_2\}^{3-}$ structure displays a remarkably compact structure (see Figure 3), particularly with regard to contacts between the Rh_1 norbornadiene units and adjacent $Nb_2W_4O_{19}^{4-}$ surface oxygens. The potential for realizing shape-selective chemistry at Rh_1 centers is evident.

Acknowledgment. W.G.K. acknowledges the National Science Foundation for support of this research.

Registry No. 1, 83248-21-8; $[(C_7H_8)Rh(NCCH_3)_2](PF_6)$, 83232-01-3; $(cis\text{-}Nb_2W_4O_{19})[n\text{-}(C_4H_9)_4N]_4$, 75005-92-4.

Supplementary Material Available: Table of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(8) The Rh atom, midpoints of the two olefinic bonds, and two oxygen atoms of each Rh coordination sphere are coplanar to within 0.05 Å; the O–Rh–O angles are 91 (1) and 92 (2)° for Rh_1 and Rh_2, respectively, and the Rh_1–O_B and Rh_2–O_H distances are 2.14 (3) and 2.06 (5) Å, respectively. These parameters are similar to those observed in the analogous $[(C_7H_8)Rh(CH_3CO_2)]_2$ structure: Reis, A. H.; Willi, C.; Siegel, S.; Tani, B. *Inorg. Chem.* **1979**, *18*, 1859.

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Reversible Iron–Nitrogen Migration of Alkyl, Aryl, or Vinyl Groups in Iron Porphyrins: A Possible Passage between σ Fe^{III}(porphyrin)(R) and Fe^{II}(*N*-R)(porphyrin) Complexes

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Evidence has been provided for the formation of cytochrome P-450 complexes involving an iron–carbon bond upon metabolic reduction of polyhalogenated compounds[1] and oxidation of 1,3-benzodioxole derivatives.[2] Analogous iron–porphyrin complexes involving either an iron(II)–carbene bond[2,3] or a σ-alkyl–iron(III) bond[4] have been isolated and, most often, fully characterized. It was shown recently that the oxidation of vinylidene carbene–iron porphyrin complexes could lead to *N*-vinyl- and *cis-N,N*-vinylideneporphyrins.[5,6]

The following results are concerned with the reactivity of σ-methyl- (or -vinyl- or -phenyl-) iron(III) porphyrin complexes, and show that their oxidation by $FeCl_3$ leads to the corresponding iron(II) *N*-alkylporphyrin complexes. Moreover, they show that the reverse transfer of the alkyl group from a pyrrole nitrogen atom to the iron, leading from Fe(*N*-R)(porphyrin)(Cl) to Fe(porphyrin)(R) complexes, can be easily obtained upon sodium dithionite reduction of the iron *N*-alkylporphyrin complexes.

Very recently, similar reversible metal–nitrogen migrations of ethyl, ethoxycarbonyl, and phenyl groups in cobalt porphyrins have been described, and their mechanisms have been established.[7] Moreover, transfers of an alkyl group, R, from nitrogen to metal have been reported in the cobalt (R = CH_3[8a] and CH_2COOEt[8b]),

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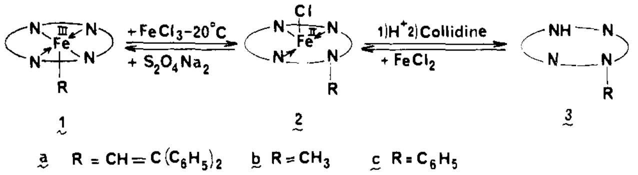
iridium (R = CH_3[9]), and rhodium (CH_3[10] and C_2H_5[10b,c]) porphyrin series, as well as the transfer of a vinyl group from cobalt to nitrogen upon acidic treatment of a σ-vinylcobalt(III) (porphyrin) complex.[11] However, to our knowledge, this communication is the first report on the reversible metal–nitrogen migration of alkyl, vinyl, or phenyl groups in iron porphyrins.



The three σ complexes $\mathrm{Fe^{III}(TPP)(R)}$(TPP = 5,10,15,20-tetraphenylporphyrinato) (**1a**, R = $CH{=}C(C_6H_5)_2$; **b**, R = CH_3; **c**, R = C_6H_5)[12] have been synthesized by reaction of $\mathrm{Fe^{III}}$(TPP)(Cl) with the corresponding Grignard reagents RMgX, a method previously used for the preparation of $\mathrm{Fe^{III}}$(porphyrin)(R) complexes.[4a,b,d,h,i] Under anaerobic conditions, the addition of a few equivalents of $FeCl_3$ (in CH_3CN) to a toluene solution of complex **1a**, at -20 °C, leads to the formation of a new complex **2a** characterized in visible spectroscopy by peaks at 452, 566, 618, and 663 nm. Upon warming complex **2a** solution up to 20 °C or addition of an excess of $FeCl_3$ and further addition of a base such as collidine, one observes the formation of compound **3a**,[13] which displays electronic and ^{1}H NMR spectra characteristic of a N-substituted porphyrin.[14] In a preparative experiment performed at -20 °C under argon, 2 equiv of $FeCl_3$ are progressively added within 2 h to 0.21 g (2.5×10^{-4} mol) of complex **1a** (5×10^{-4} M in toluene); compound **3a** is obtained as purple crystals (60% yield) after demetalation by HCl, washing with water in presence of collidine, purification by column chromatography (aluminum oxide, 9:1 CH_2Cl_2–CH_3COCH_3 as eluent), and recrystallization from CH_2Cl_2–pentane. Its spectra[13] are similar to those of the previously described[6] N—CH=CAr$_2$—TPP with (Ar = *p*-ClC_6H_4), indicating a similar structure for compound **3a**, in full agreement with its mass spectrum.[13] The corresponding ferrous complex, Fe(N—CH=CPh$_2$TPP)(Cl), **2a**, was prepared by treatment of **3a** with $FeCl_2$ in THF.[14c] Its visible spectrum is superimposable on that of the complex observed during reaction of complex **1a** with $FeCl_3$. Complex **2a**, which was further characterized by its mass spectrum,[15] loses its ferrous ion readily in the presence of trace amounts of acid and particularly in the presence of $FeCl_3$, at room temperature. However, it is only slowly demetalated at -20 °C in the presence of few equivalents of $FeCl_3$, explaining why its clean formation from complex **1a** was observed at this temperature.

When treated by a reducing agent such as sodium dithionite (in a biphasic toluene–H_2O mixture), complex **2a** quantitatively reverts to the σ complex **1a** within 30 min.

The same reactions were observed with complexes **1b** and **1c**. Authentic samples of compounds **2b**[14c] and **3b**[14b] were prepared as described previously and found identical with the compounds formed upon reaction of complex **1b** with $FeCl_3$ by visible and ^{1}H NMR spectroscopy[16] (and thin-layer chromatography for **3b**). The characteristics of compounds **2c** and **3c**,[16] obtained from reaction of complex **1c** with $FeCl_3$, are in agreement with their proposed structure derived from *N*-C_6H_5-TPP.

The main differences observed between the reactions of the three complexes **1** are the following: (i) oxidation of complex **1** performed at -20 °C (1 mM $FeCl_3$, 0.5 mM complex **1**) gives the N-substituted porphyrin **3** with 60% yield when R = $CH{=}C(C_6H_5)_2$ but only 30% and 5% yield when R = C_6H_5 and CH_3, respectively; the other main product observed in these reactions of complexes **1** with $FeCl_3$ is $\mathrm{Fe^{III}}$(TPP)(Cl); (ii) complex **2c** and to a lesser extent complex **2b** are much less easily demetalated by acids than complex **2a**, so that reaction of complex **1c**, even with 10 equiv of $FeCl_3$ at 20 °C, leads to complex **2c**, which is demetalated only after treatment by an excess of CF_3COOH; (iii) the rate of reduction of complexes **2** into complexes **1** by $Na_2S_2O_4$ in toluene–water mixtures decreases in the order R = $CH{=}CPh_2$ $\gtrsim$ CH_3 > C_6H_5; complex **1** formation (from 0.15 mM **2** and 10 mM $Na_2S_2O_4$) is complete within 30 min for R = vinyl and methyl and 1 day for R = phenyl.

The aforementioned results show a new reaction[20] in iron porphyrin chemistry, the reversible transfer of a group between iron and nitrogen upon redox activation of σ-Fe(III) or N-substituted Fe(II) porphyrin complexes, and suggest that this reaction could be general since it was already observed with groups as different as methyl, vinyl, and phenyl. The transfer of the R group from iron to nitrogen by treatment of $\mathrm{Fe^{III}}$(TPP)(R) complexes with $FeCl_3$ competes with the irreversible dissociation of their Fe–R bond leading to $\mathrm{Fe^{III}}$(TPP)(Cl). This competition is mainly in favor of the iron–nitrogen group migration when R = vinyl but of $\mathrm{Fe^{III}}$(TPP)(Cl) formation when R = CH_3. From the point of view of stoichiometry, the formation of complex **2** from complex **1** requires a one-electron oxidation of the starting molecule together with a Cl^- transfer; both reactions are afforded by $FeCl_3$. We have also observed the transfer of the vinyl group of complex **1a** from iron to nitrogen in the conditions of a resonance Raman study of this complex (10^{-4} M in benzene, irradiation frequency of the laser 514.5 nm), indicating that a photochemical activation of its iron–carbon bond can also lead to the corresponding *N*-substituted porphyrin **3a**.

Since σ-alkyliron–cytochrome P-450 complexes have been invoked as intermediates in substrates hydroxylation by this cytochrome,[17] it seems interesting to check whether *N*-alkylporphyrins

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(12) Spectral data of complexes **1** are almost identical with those previously described:[4d,c,h] Mass spectra (*m*/*e* (EI) 70 eV, 220 °C) **1a** 847 (M^+), 668; **1b** 683 (M^+), 668; **1c** 745 (M^+), 668. UV–visible (C_6H_6, 27 °C) λ **1a** 411 nm, 522, 549; **1b** 390, 413, 518, 546; **1c** 393, 412, 521, 547. ^{1}H NMR ($CDCl_3$, 20 °C, Cameca TSN 250 operating at 250 MHz) δ (Me_4Si) assignments were made by comparison with $\mathrm{Fe^{III}}$(tetrakis(pentadeuteriophenyl)porphyrin)(R) complexes: **1a** (TPP), -14.00 (8 H) s, 6.44 (6 H), 5.52 (12 H), 4.60 (2 H); (R), 18.40 (2 H), 6.44 (2 H), 6.00 (2 H), -2.16 (1 H), -2.56 (1 H), -10.64 (2 H); **1b** (TPP), -19.5 (8 H) s, 5.61 (4 H), 4.73 (4 H), 4.57 (4 H), 3.60 (4 H), 2.50 (4 H); **1c** (TPP), -17.48 (8 H) s, 5.60 (4 H), 4.92 (4 H), 4.68 (4 H), 4.44 (4 H), 2.84 (4 H); (R), 13.36 (2 H), -25.68 (1 H). We were not able to detect any signal for the vinylic, methyl, or *o*-phenyl protons of the ligand R because of their close proximity to the paramagnetic center.[4e,4h]

(13) **3a**: mass spectrum (*m*/*e*, 70 eV, 220 °C) 792 (M^+), 715 ($M^+ - C_6H_5$), 638 ($M^+ - 2C_6H_5$); UV–visible (C_6H_6, 27 °C) 435, 532, 570, 620, 683; ^{1}H NMR (CD_2Cl_2, δ (Me_4Si) *J* in Hz) (TPP) 8.99 (2 H) s, 8.66 (2 H) d (5), 8.49 (2 H) d (5), 7.61 (2 H) s, 8.30 (4 H) m, 7.93 (4 H) m, 7.81 (12 H) m; (R) 7.56 (1 H) t (8), 7.30 (2 H) t (8), 6.24 (1 H) t (8), 5.81 (2 H) d (8), 5.77 (2 H) t (8), 3.05 (2 H) d (8), -1.99 (1 H) s.

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(15) **2a**: mass spectrum (*m*/*e*, 70 eV, 200 °C) 882 (M^+), 847 ($M^+ - Cl$), 703 ($M^+ - CH{=}CPh_2$), 668.

(16) **2b**: UV–vis (C_6H_6, 27 °C) 447, 459, 563, 613, 661. **3b**: UV–vis 428, 530, 570, 616, 678; ^{1}H NMR ($CDCl_3$) (TPP) 8.86 (2 H) s, 8.60 (2 H) d (5), 8.52 (2 H) d (5), 7.48 (2 H) s, 8.40 (4 H) m, 8.24 (4 H) m, 7.80 (12 H) m; (R), -4.16 (3 H) s; *m*/*e* 628 (M^+), 551 ($M^+ - C_6H_5$). **2c**: UV–vis 454, 466, 569, 630, 682; *m*/*e* 745 ($M^+ - Cl$), 703 ($M^+ - C_6H_5$), 668. **3c**: UV–vis 444, 549, 596, 636, 704; ^{1}H NMR ($CDCl_3$) (TPP) 8.70 (2 H) s, 8.33 (2 H) d (5), 8.16 (2 H) d (5), 7.35 (2 H) s; 8.32 (4 H) m, 8.25 (4 H) m, 7.69 (12 H) m; (R) 5.67 (1 H) t (8), 5.20 (2 H) t (8), 2.99 (2 H) d (8); *m*/*e* 690 (M^+), 613 ($M^+ - C_6H_5$).

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("green pigments") could be formed by such a transfer mechanism.[18]

Registry No. 1a, 83219-57-2; **1b**, 79197-95-8; **1c**, 70936-44-6; **2a**, 83219-58-3; **2b**, 83219-60-7; **2c**, 83219-61-8; **3a**, 83219-59-4; **3b**, 51552-53-5; **3c**, 81856-91-9; $Fe^{III}(TPP)(Cl)$, 16456-81-8.

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[18] So far, most *N*-alkylporphyrins found in vivo as "green pigments" in the liver were derived from the oxidative activation of exogenous compounds containing an easily accessible double or triple carbon–carbon bond.[19]

[19] (a) Ortiz de Montellano, R. E.; Kunze, K. L.; Mico, B. A. *Mol. Pharmacol.* **1980**, *18*, 602. (b) Ortiz de Montellano, R. E.; Mico, B. A. *Ibid.* **1980**, *18*, 128. (c) Ortiz de Montallano, R. E.; Beilan, H. S.; Kunze, K. L.; Mico, B. A. *J. Biol. Chem.* **1981**, *256*, 4395.

[20] **Note Added in Proof**: During the submission of this paper, a paper appeared describing the transfer of the phenyl group of Fe(TPP)(Ph) from iron to nitrogen upon treatment of this complex by O_2 and acids: Ortiz de Montellano, R. E.; Kunze, K. L.; Augusto, O. *J. Am. Chem. Soc.* **1982**, *104*, 3545.

Osmium(IV)-Mediated Oxidative Dehydrogenation of Coordinated Amines: Crystal and Molecular Structures of *cis*-1,2-Ethanediaminebis(1,2-ethanediaminato(1–))osmium(IV) Dibromide

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The Os(IV) complexes $[Os(en)(en\text{-}H)_2]^{2+}$ and $[Os(en)_2(en\text{-}H)]^{3+}$ were originally prepared by Dwyer and Hogarth[3,4] and formulated as diamagnetic Os(IV) 1,2-ethanediamine complexes deprotonated at the N centers. An alternative interpretation would have been diamagnetic osmium(II) imine complexes. This reinvestigation stemmed from the recognition by Basolo et al.[5] that the complex formulated[6] as $[Ru(en\text{-}H)_2(en\text{-}2H)]^{2+}$ was in fact the Ru(II) complex $[Ru(en)_2(diim)]^{2+}$. An X-ray crystallographic study of the complex $[Os(en)(en\text{-}H)_2]Br_2$[7] (Figure 1) has now substantiated the original interpretation.[4] The complex cation has an octahedrally distorted $Os^{IV}N_6$ core, with two mononegative aminate ions (on different ligands) occupying a cis configuration. The short Os–N (aminate) bonds (1.90 Å), as compared to the Os–N (amine) bonds, 2.11 Å (cis) and 2.19 Å (trans), are attributed to donation of electron density from filled p_z orbitals of the ligands to empty d orbitals on Os(IV), giving effectively two Os–N double bonds. The conclusion is supported by the increase in angle between the double bonds (110°) and the consequent narrowed N–Os–N angle (76°) for the en chelate trans to the cis aminate ions, together with the location and refinement in (x, y, z) of all hydrogen atoms (Tables I and II).

Table I. Atomic Coordinates for *cis*-$[Os(en)(en\text{-}H)_2]Br_2$

atom	x	y	z
		Cation	
Os	0.00000 (–)	0.21515 (6)	0.25000 (–)
		Axial Ligand	
N	–0.0950 (5)	–0.0134 (9)	0.1973 (6)
H_N(A)	–0.132 (8)	–0.017 (15)	0.106 (12)
H_N(B)	–0.143 (11)	0.039 (24)	0.200 (16)
C	–0.0407 (6)	–0.1772 (11)	0.2568 (9)
H_C(A)	–0.079 (6)	–0.284 (12)	0.221 (9)
H_C(B)	–0.005 (7)	–0.187 (14)	0.369 (10)
		Other Ligand	
N	0.1120 (5)	0.3588 (10)	0.3319 (7)
H_N	0.146 (5)	0.372 (10)	0.310 (7)
C	0.1601 (6)	0.4129 (11)	0.4687 (8)
H_C(A)	0.218 (6)	0.329 (13)	0.529 (9)
H_C(B)	0.180 (7)	0.543 (15)	0.467 (10)
C′	0.0866 (6)	0.4007 (12)	0.4947 (8)
$H_{C'}$(A)	0.121 (6)	0.411 (12)	0.579 (8)
$H_{C'}$(B)	0.033 (6)	0.507 (12)	0.449 (9)
N′	0.0324 (5)	0.2335 (10)	0.4371 (6)
$H_{N'}$(A)	0.072 (7)	0.138 (16)	0.489 (10)
$H_{N'}$(B)	–0.012 (6)	0.224 (11)	0.448 (8)
		Anion	
Br	0.18660 (6)	0.11325 (13)	0.12672 (8)

Table II. Cation Geometry[a]

(a) Osmium Coordination Environment[b]

	$r_{Os\text{-}N}$	N	N′	N_{ax}	N	N'
N_{ax}	2.194 (7)	161.7 (3)	92.5 (3)	76.0 (3)	87.4 (3)	93.5 (3)
N	1.896 (7)		81.0 (4)	87.4 (3)	110.0 (3)	94.6 (3)
N′	2.113 (9)			93.5 (3)	94.6 (3)	172.5 (3)

(b) Ligand Geometries

ligand	"axial"	"equatorial"
	Distances (Å)	
N–C	1.46 (1)	1.48 (1)
N′–C′		1.48 (1)
$\text{C–}\underset{\sim}{\text{C}}(1)$	1.52 (2)	1.49 (2)
	Angles (deg)	
Os–N–C	112.3 (5)	118.6 (7)
Os–N′–C′		106.3 (7)
$\text{N–C–}\underset{\sim}{\text{C}}(1)$	106.8 (9)	107.2 (6)
$\text{N'–C'}\overset{\sim}{–}\text{C}$		108.0 (9)

[a] Atoms generated by the 2-fold rotor are italicized. [b] r is the metal ligand distances (Å). Other entries in the matrix are the angles subtended at the osmium by the relevant atoms.

Stable Os(IV) ammine complexes are rare,[8] and the stabilization in this instance apparently arises from the donation of electron density to the Os(IV) center. The effect is seen dramatically in the redox potentials for the singly (+0.29V vs. Ag/AgCl/saturated LiCl (acetone) electrode in acetone) and double deprotonated (~–1.2 V) ions. The difference of >1 V cannot be attributed to just the change in charge. Comparable effects for Co(III) amine complexes lead to redox potential differences in the range 0.1–0.2 V.[9] Similar large stabilizations of M(IV) species have been noted by deprotonation of amines coordinated to Pt(IV),[9] but here the ability of d^6 Pt(IV) to accept electrons from the ligand is more questionable and needs to be observed structurally. The large effects are consistent, however, with the sets of lone pairs of electrons donating charge to the Os(IV) ion in a very substantial

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[3] Ligand abbreviations: en = 1,2-ethanediamine; en-H = 1,2-ethanediaminate(1–); en-2H = 1,2-ethanediaminate(2–); im = 2-aminoethanimine; diim = ethanediimine; Me_2diim = 2,3-butanediimine; bpy = 2,2′-dipyridine; ampy = 2-(aminomethyl)pyridine; impy = 2-(iminomethyl)pyridine; hepy = 2-(1-hydroxyethyl)pyridine.

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[7] Anal. for $C_6H_{22}Br_2N_6Os$, C, H, Br, N.[24] ^{13}C NMR (D_2O) –23.8 ppm vs. dioxane as internal reference.

[8] Stable complexes of Os(IV) with an N_4X_2 chromophore have been isolated previously, but $[Os^{IV}(NH_3)_5L]^{n+}$ and $[Os(NH_3)_6]^{4+}$ were reported to be very unstable. Buhr, J. D.; Winkler, J. R.; Taube, H. *Inorg. Chem.* **1980**, *19*, 2416–2425.

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