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Electron-Rich Nitrido-Bridged Complexes. Structure and Bonding in Triosmium Dinitrido Compounds

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Triosmium dinitrido-bridged compounds $Os_3(N)_2Cl_8L_6$ (L = 3-picoline, 4-ethylpyridine, 4-*tert*-butylpyridine) have been prepared via the thermolysis of the terminal nitrido complexes $Os(N)Cl_3L_2$. X-ray structural studies of $Os_3(N)_2Cl_8(4\text{-Etpy})_6$ and $Os_3(N)_2Cl_8(4\text{-}t\text{-Bupy})_6$ reveal a linear $Os_3(N)_2$ unit with multiple bonding significantly localized in the outer osmium−nitrogen bonds in $Os^{V}\equiv N-Os^{IV}-N\equiv Os^{V}$. A simple model of bonding and electronic structure consistent with the solid-state structures is discussed.

Introduction

An enormous variety of high oxidation state transition-metal nitrido compounds are known.[1−4] In comparison, there are fewer electron-rich metallonitrides, that is, nitrido compounds incorporating metal centers with d-electron counts greater that d^2. This can be viewed as a straightforward consequence of the need for empty d-orbitals for productive metal−nitrogen multiple bonding, especially in terminal metal nitrido complexes, $L_nM\equiv N$. However, a situation in which electron-rich transition metals circumvent this constraint is in polynuclear nitrido-bridged species. General classes of such compounds can be identified: (1) hetero- and homometallic μ_2-nitrido complexes including a high oxidation state transition metal center capable of multiply bonding with the nitrido ligand[5−20] (e.g., **A** in Figure 1); (2) cluster complexes in which μ_n-nitrido ligands ($n \geq 3$) have access to empty cluster orbitals[21−23] (e.g., **B** in Figure 1); (3) μ_2-metallonitrides with readily populated nonbonding (π_n and n_d) molecular orbitals[24−54] (e.g., **C** in Figure 1).

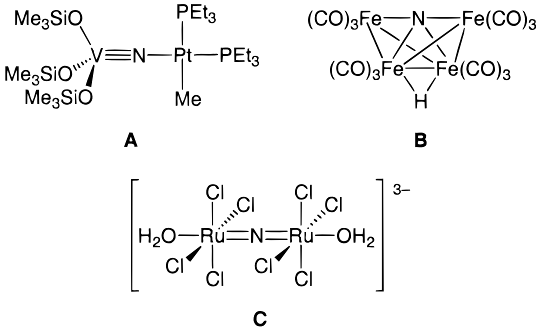

Figure 1. Examples from general classes of electronic-rich ($d^n > d^2$) metal nitrido complexes (see text).

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The latter type of compound is intriguing because of the analogy between polynuclear metallonitrides and conjugated organic polyenes such as polyacetylene.[55] Interesting predictions about geometric and electronic structure have been put forward for electron-rich metallonitrides. For example, calculations suggest that metallonitride polymers with $d^n > d^2$ will adopt symmetrically bridged structures[56] rather than the very asymmetrically bridged structures found to date for structurally characterized linear chain metallonitrides.[57−65] More generally, control over the nature of M(N)M interactions should be possible via control of the metal electron count and electronic structure. These ideas, plus our longstanding interest in the nitrido ligand as a bridging group to link transition metals in polynuclear, oligomeric, and polymeric species,[5−7,65−68] sparked our interest in the study of electron-rich polynuclear metallonitrides.

Our initial focus has been on new and known ruthenium and osmium nitrido-bridged compounds. We are interested in using M_2N and M_3N_2 species as both models and building blocks for larger electron-rich metallonitride oligomers and polymers. In a 1991 report on N−N coupling by osmium(VI) nitrido compounds, Ware and Taube showed that thermolysis of Os(N)Cl_3(4-Mepy)$_2$[69] (**1a**) in a noncoordinating solvent resulted in formation of $Os_3(N)_2Cl_8$(4-Mepy)$_6$[39] (**2a**). This $[Os_3(N)_2]^{8+}$ compound is related to species such as $Cs_3[Os_3(N)_2Cl_{11}(NH_3)_3]$ and “Claus’ salt” $Os_3(N)_2(NH_3)_4(OH)_8(OH_2)_2$ studied by Griffith and co-workers in the 1970’s.[30,31] Spectroscopic and analytical data support formulation of such compounds as dinitrido-bridged trimetallic complexes. However, there is a noticeable lack of structural confirmation of this formulation and minimal information on the bonding and electronic structure. We report herein our initial studies of the pyridine-substituted triosmium dinitrido system and provide, for the first time, details on the structures and bonding of electron-rich M_3N_2 compounds.

Experimental Section

General Considerations. All experiments were performed under standard anhydrous and anaerobic conditions using appropriately dried reagent-grade solvents and chemicals.[70,71] $NBu_4[Os(N)Cl_4]$ was prepared according to a literature procedure.[30] 3-Picoline, 4-ethylpyridine, and 4-*tert*-butylpyridine were purchased from Aldrich. ^{1}H NMR spectra were obtained at 500.13, 500.06, or 300.15 MHz at ambient temperature in CD_2Cl_2; chemical shifts are reported in ppm relative to $SiMe_4$. Infrared spectra were recorded as KBr pellets or as Nujol mulls on NaCl or CsI plates and are reported in cm^{-1}. Mass spectra were obtained by FAB in the positive mode from a standard 3-nitrobenzyl alcohol matrix.

Syntheses. $Os(N)Cl_3L_2$. Starting with Ware and Taube’s procedure for Os(N)Cl_3(4-Mepy)$_2$ (**1a**)[69] and Os(N)Cl_3(4-*t*-Bupy)$_2$ (**1d**),[69] we have found a range of conditions produce **1** in good yield. Generally, a solution of $NBu_4[Os(N)Cl_4]$ in methanol is added via cannula to a solution of the substituted pyridine in THF at room temperature. The resulting mixture is stirred either at room temperature for 20 h or while heating at reflux for 2−3 h and then cooled to room temperature. The solvent volume is reduced until purple solids begin to appear, the mixture is cooled to −30 °C for several hours, and the resulting purple solid $Os(N)Cl_3L_2$ is collected by filtration, washed with cold methanol, and dried under vacuum.

Os(N)Cl_3(3-Mepy)$_2$ (1b). $NBu_4[Os(N)Cl_4]$ (600 mg, 1.02 mmol) in 10 mL of methanol and 3-picoline (218 mg, 2.34 mmol) in 30 mL of THF afforded 265 mg of **1b** (52%). ^{1}H NMR: δ 9.19 (d, $J = 6$, 2 H), 9.18 (s, 2 H), 7.87 (d, $J = 7$, 2 H), 7.54 (dd, $J = 6$ and 7, 2 H), 2.48 (s, 6 H). IR (Nujol): 1609, 1575, 1252, 1195, 1127, 1101, 1063, 791, 689, 663. MS: *m/z* 462 $(OsNCl_2L_2)^+$.

Os(N)Cl_3(4-Etpy)$_2$ (1c). $NBu_4[Os(N)Cl_4]$ (1.00 g, 1.70 mmol) in 15 mL of methanol and 4-ethylpyridine (418 mg, 3.90 mmol) in 30 mL of THF afforded 400 mg of **1c** (45%). ^{1}H NMR: δ 9.21 (d, $J = 7$, 4 H), 7.48 (d, $J = 7$, 4 H), 2.93 (q, $J = 8$, 4 H), 1.34 (t, $J = 8$, 6 H). IR (KBr): 1621, 1552, 1501, 1453, 1436, 1416, 1349, 1308, 1223, 1194, 1067, 1039, 834, 788, 542, 502. MS: *m/z* 490 $(OsNCl_2L_2)^+$. Anal. Calcd for $C_{14}H_{18}Cl_3N_3Os$: C, 32.04; H, 3.46; N, 8.01. Found: C, 32.40; H, 3.46; N, 7.94.

$Os_3(N)_2Cl_6L_6$. Following Ware and Taube’s procedure for $Os_3(N)_2Cl_8$(4-Mepy)$_6$ (**2a**),[39] a Fischer−Porter bottle is charged with Os(N)-

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Cl_3L_2 dissolved in dichloromethane (20−60 mL), the vessel is pressurized to 45 psi with argon, and the mixture is heated with stirring. (**Caution!** *Appropriate safety precautions should be taken working with glass apparatus under pressure*.) After the time indicated, the solution is allowed to cool to room temperature and depressurized, and the volume reduced under vacuum (to ca. 3 mL). In a slight modification of the reported purification procedures, any yellow solid $OsCl_4L_2$,[39,72] present is removed by filtration, and the resulting dark orange-brown solution is loaded onto a silica gel column (20 × 2 cm) prepared in dichloromethane for **2b** or **2d** or in dichloromethane/1% methanol for **2c**. Elution with this solvent initially produces a yellow band containing any additional $OsCl_4L_2$.[39,72] Further elution under N_2 pressure with dichloromethane/10% acetone for **2b**, dichloromethane/1% methanol for **2c**, and dichloromethane for **2d** produces a red-brown band that, upon removal of solvent and recrystallization from dichloromethane/diethyl ether or dichloromethane/toluene, affords pure $Os_3(N)_2Cl_8L_6$.

$Os_3(N)_2Cl_8$(3-Mepy)$_6$ (2b). Compound **1b** (380 mg, 0.765 mmol) afforded 135 mg of **1b** (37% of starting Os, 49% yield based on eq 2 below) after 1 d at 100 °C. ^1H NMR: δ 9.09 (s, 4 H), 8.93 (d, $J = 6$, 4 H), 8.90 (s, 2 H), 8.72 (d, $J = 6$, 2 H), 7.34 (d, $J = 8$, 4 H), 7.11 (dd, $J = 6$ and 8, 4 H), 7.04 (d, $J = 8$, 2 H), 6.62 (dd, $J = 6$ and 8, 2 H), 2.08 (s, 12 H), 2.03 (s, 6 H). IR (Nujol): 1610, 1580, 1246, 1201, 1112, 1070, 1036, 974, 919, 875, 827, 795, 722, 694, 663 498, 425, 376, 323, 277. MS: *m/z* 1440 $(Os_3N_2Cl_8L_6)^+$, 1405 $(Os_3N_2Cl_7L_6)^+$, 1312 $(Os_3N_2Cl_7L_5)^+$, 1279 $(Os_3N_2Cl_6L_5)^+$, 1221 $(Os_3N_2Cl_7L_4)^+$, 1183 $(Os_3N_2Cl_6L_4)^+$, 1091 $(Os_3N_2Cl_6L_3)^+$, 1001 $(Os_2NCl_4L_5)^+$, 945 $(Os_2NCl_5L_4)^+$, 908 $(Os_2NCl_4L_4)^+$, 460 $(OsNCl_2L_2)^+$. Anal. Calcd for $C_{36}H_{42}Cl_8N_8Os_3$: C, 30.01; H, 2.94; N, 7.78. Found: C, 30.14; H, 3.02; N, 7.56.

$Os_3(N)_2Cl_8$(4-Etpy)$_6$ (2c). Compound **1c** (504 mg, 0.714 mmol) afforded 120 mg of **2c** (45% of starting Os, 60% yield based on eq 2 below) after 14 h at 95 °C. ^1H NMR: δ 9.09 (d, $J = 6$, 8 H), 8.90 (d, $J = 6$, 4 H), 7.06 (d, $J = 6$, 8 H), 6.69 (d, $J = 6$, 4 H), 2.74 (q, $J = 8$, 8 H), 2.53 (q, $J = 8$, 4 H), 1.24 (t, $J = 8$, 12 H), 1.14 (t, $J = 8$, 6 H). IR (KBr): 1622, 1506, 1436, 1232, 1063, 1038, 971, 834. MS: *m/z* 1524 $(Os_3N_2Cl_8L_6)^+$, 1489 $(Os_3N_2Cl_7L_6)^+$, 1382 $(Os_3N_2Cl_7L_5)^+$, 1348 $(Os_3N_2Cl_6L_5)^+$, 1277 $(Os_3N_2Cl_7L_4)^+$, 1240 $(Os_3N_2Cl_6L_4)^+$, 1133 $(Os_3N_2Cl_6L_3)^+$, 1073 $(Os_2NCl_4L_5)^+$, 1001 $(Os_2NCl_5L_4)^+$, 966 $(Os_2NCl_4L_4)^+$, 490 $(OsNCl_2L_2)^+$. Anal. Calcd for $C_{42}H_{54}Cl_8N_8Os_3$: C, 33.08; H, 3.57; N, 7.35. Found: C, 32.97; H, 3.52; N, 7.27.

$Os_3(N)_2Cl_8$(4-*t*-Bupy)$_6$ (2d). Compound **1d** (250 mg, 0.430 mmol) afforded 35 mg of **2d** (14% of starting Os, 19% yield based on eq 2 below) after 6 d at 80 °C. ^1H NMR: δ 9.12 (d, $J = 7$, 8 H), 9.09 (d, $J = 7$, 4 H), 7.21 (d, $J = 7$, 8 H), 6.91 (d, $J = 7$, 4 H), 1.24 (s, 36 H), 1.08 (s, 18 H). MS: *m/z* 1694 $(Os_3N_2Cl_8L_6)^+$, 1657 $(Os_3N_2Cl_7L_6)^+$, 1522 $(Os_3N_2Cl_7L_5)^+$, 1489 $(Os_3N_2Cl_6L_5)^+$, 1389 $(Os_3N_2Cl_7L_4)^+$, 1352 $(Os_3N_2Cl_6L_4)^+$, 1217 $(Os_3N_2Cl_6L_3)^+$ and $(Os_2NCl_4L_5)^+$, 1113 $(Os_2NCl_5L_4)^+$, 1078 $(Os_2NCl_4L_4)^+$, 546 $(OsNCl_2L_2)^+$. Anal. Calcd for $C_{54}H_{78}Cl_8N_8Os_3$: C, 38.30; H, 4.64; N, 6.62. Found: C, 38.63; H, 4.72; N, 6.24.

X-ray Diffraction Studies. Crystals were oil-mounted on a glass fiber under a stream of cold N_2.[73] Determinations of Laue symmetries, crystal classes, unit cell parameters, and the crystal orientation matrixes were carried out according to standard techniques.[74] Intensity data were collected using a $2\theta/\omega$ scan technique with Mo Kα radiation. The raw data were processed with a local version of CARESS;[75] subsequent calculations were carried out using the SHELXTL program.[76] All data were corrected for absorption and Lorentz and polarization effects and were placed on an approximately absolute scale. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analyses.[77] Crystallographic data are summarized in Table 1; selected metrical data are given in Table 2.

Table 1. Crystallographic Data for $Os_3(N)_2Cl_8$(4-Etpy)$_6$ (**2c**) and $Os_3(N)_2Cl_8$(4-*t*-Bupy)$_6$ (**2d**)

	2c·2tol	**2d**·2tol•2CH_2Cl_2
chem formula	$C_{56}H_{70}Cl_8N_8Os_3$	$C_{70}H_{98}Cl_{12}N_8Os_3$
fw	1709.40	2047.56
space group	*C*2/*c*	*I*4$_1$222
a, Å	31.374(3)	17.4716(13)
b, Å	12.1153(12)	17.4716(13)
c, Å	21.252(2)	26.435(4)
β, deg	130.958(5)	90
V, Å^3	6100.4(10)	8069.5(16)
Z	4	4
T, K	158	158
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.861	1.685
μ, mm^{-1}	6.627	5.153
transm coeff	0.6016−0.6976	0.1976−0.2369
wR2[a]	0.0580	0.0850
R1[b]	0.0274	0.0325

[a] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Os_3(N)_2Cl_8$(4-Etpy)$_6$ (**2c**) and $Os_3(N)_2Cl_8$(4-*t*-Bupy)$_6$ (**2d**)

	2c	**2d**
$Os_{outer}-N_{nitrido}$	1.719(3)	1.702(9)
$Os_{inner}-N_{nitrido}$	1.895(3)	1.911(9)
$Os_{outer}-N_{pyridine}$	2.107(3), 2.102(3)	2.112(7)
$Os_{inner}-N_{pyridine}$	2.104(3)	2.118(8)
$Os_{outer}-Cl_{cis}$	2.3730(10), 2.3605(10)	2.368(2)
$Os_{inner}-Cl_{cis}$	2.3900(12), 2.3886(12)	2.394(3)
$Os_{outer}-Cl_{trans}$	2.4176(9)	2.431(3)
$Os_{outer}-N_{nitrido}-Os_{inner}$	179.43(13)	180
$N_{nitrido}-Os_{inner}-N_{nitrido}$	177.6(2)	180
$N_{nitrido}-Os_{outer}-N_{pyridine}$	92.46(12), 91.56(12)	91.7(2)
$N_{nitrido}-Os_{outer}-Cl_{cis}$	94.60(10), 94.06(10)	95.29(6)
$N_{nitrido}-Os_{outer}-Cl_{trans}$	178.38(10)	180
$N_{nitrido}-Os_{inner}-N_{pyridine}$	90.13(11), 89.91(11)	90
$N_{nitrido}-Os_{inner}-Cl_{cis}$	88.80(9), 91.20(9)	90

$Os_3(N)_2Cl_8$(4-Etpy)$_6$·2tol (2c·2tol) (tol = Toluene). Yellow crystals were obtained by cooling a dichloromethane solution of **2c** to which toluene had been added. Data were collected on a Siemens P4 rotating anode diffractometer. The diffraction symmetry was 2/*m* with systematic absences *hkl* for $h + k = 2n + 1$ and *h*0*l* for $l = 2n + 1$. The two possible monoclinic space groups are *Cc* and *C*2/*c*; it was later determined that the centrosymmetric space group *C*2/*c* was correct. The molecule is located on a 2-fold rotation axis. Hydrogen atoms were located from a difference-Fourier map and included with isotropic thermal parameters, except for those on the ethyl carbons of the N(3) pyridine ring which were included using a riding model. There are two molecules of toluene solvent present per formula unit. At convergence, wR2 = 0.0580 and GOF = 1.031 for 460 variables refined against all 8898 unique data. (As a comparison for refinement on *F*, R1 = 0.0274 for those 6920 data with $F_o > 4.0\sigma(F_o)$.)

$Os_3(N)_2Cl_8$(4-*t*-Bupy)$_6$·2tol·2CH_2Cl_2 (2d·2tol·2CH_2Cl_2). Red-orange crystals were obtained by cooling a dichloromethane solution of **2d** to which toluene had been added. Data were collected on a Siemens P4 diffractometer. The noncentrosymmetric tetragonal space group *I*4$_1$222 was chosen and later determined to be correct. The molecule is located on a site of 222 symmetry. There are two molecules of dichloromethane and two molecules of toluene solvent present per formula unit; each is located on a 2-fold axis. The toluene is disordered as are the three methyl carbons of the *tert*-butyl group on the N(2) pyridine ring; all disordered atoms were included with partial site occupancies. Hydrogen atoms associated with disordered carbons were

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not included in the refinement; the remaining hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0850 and GOF = 1.119 for 224 variables refined against all 2634 unique data. (As a comparison for refinement on F, R1 = 0.0325 for those 2344 data with $F_o > 4.0\sigma(F_o)$.)

Results

Compounds of formula $\mathrm{Os(N)Cl_3L_2}$ (L = nitrogen donor ligand) have been known for some time.[69,78−80] Ware and Taube reported the synthesis of $\mathrm{Os(N)Cl_3(4\text{-}Mepy)_2}$ (**1a**) and $\mathrm{Os(N)Cl_3(4\text{-}}t\mathrm{\text{-}Bupy)_2{\cdot}THF}$ (**1d·**THF) from $\mathrm{NBu_4[Os(N)Cl_4]}$ and the substituted pyridine.[69] Using their method, we have extended the series of $\mathrm{Os(N)Cl_3L_2}$ compounds to L = 3-picoline (**1b**) and 4-ethylpyridine (**1c**) (eq 1). The reactions proceed smoothly

$$\begin{array}{lcl} \mathrm{NBu_4[Os(N)Cl_4] + 2L} \rightarrow & \mathrm{Os(N)Cl_3L_2} & + \mathrm{NBu_4Cl} \\ & \mathbf{1a}\ (\mathrm{L = 4\text{-}Mepy}) & \\ & \mathbf{1b}\ (\mathrm{L = 3\text{-}Mepy}) & \\ & \mathbf{1c}\ (\mathrm{L = 4\text{-}Etpy}) & \\ & \mathbf{1d}\ (\mathrm{L = 4\text{-}}t\mathrm{\text{-}Bupy}) & \end{array} \qquad (1)$$

to produce the osmium(VI) nitrido complexes in decent purified yields. Compounds **1a**−**d** are readily identified and characterized by ^{1}H NMR and IR spectroscopy and by mass spectrometry. In our hands, samples of **1d**, previously reported as a THF adduct $\mathrm{Os(N)Cl_3(4\text{-}}t\mathrm{\text{-}Bupy)_2{\cdot}THF}$,[69] contain variable fractional amounts of THF (typically 0.2−0.5 equiv).

Ware and Taube reported the thermolysis of **1a** to yield $\mathrm{Os_3(N)_2Cl_8(4\text{-}Mepy)_6}$ (**2a**) accompanied by formation of $\mathrm{N_2}$ and $\mathrm{OsCl_4(4\text{-}Mepy)_2}$ with the stoichiometry shown in eq 2.[39] Starting

$$\begin{array}{lcl} 4\ \mathrm{Os(N)Cl_3L_2} \rightarrow & \mathrm{Os_3(N)_2Cl_8L_6} & + \mathrm{OsCl_4L_2} + \mathrm{N_2} \\ \mathbf{1a} & \mathbf{2a}\ (\mathrm{L = 4\text{-}Mepy}) & \\ \mathbf{1b} & \mathbf{2b}\ (\mathrm{L = 3\text{-}Mepy}) & \\ \mathbf{1c} & \mathbf{2c}\ (\mathrm{L = 4\text{-}Etpy}) & \\ \mathbf{1d} & \mathbf{2d}\ (\mathrm{L = 4\text{-}}t\mathrm{\text{-}Bupy}) & \end{array} \qquad (2)$$

from **1b**−**d**, we have likewise used thermolysis to prepare $\mathrm{Os_3(N)_2Cl_8L_6}$, where L is 3-picoline (**2b**), 4-ethylpyridine (**2c**), or 4-*tert*-butylpyridine (**2d**) (eq 2). Compounds **2b**−**d** are readily identified and characterized by ^{1}H NMR spectroscopy, by mass spectrometry, and by elemental analysis.

Details of the conversion of **1** to **2** merit comment. Ware and Taube report performing the thermolysis of **1a** producing **2a** in dichloromethane solution under argon pressure. This is presumably to increase the reflux temperature of this otherwise low-boiling solvent. We have found that formation of **2** proceeds under a variety of conditions, vacuum through pressure, from room temperature through heating to 120 °C, producing **2** in yields that vary from poor to excellent depending on the system and conditions. Additionally, we note that the reaction is sensitive to the presence of various reagents and impurities.[72] The best yields are obtained for L = 4-picoline due to an advantageous combination of stability, solubility, and chromatographic properties. Low solubility in the L = 3-picoline system limits conversion and yields. Decreasing thermal stability of reaction mixtures for L = 4-ethylpyridine and, especially, 4-*tert*-butylpyridine leads to competitive decomposition. Also for L = 4-*tert*-butylpyridine, chromatographic separation of products is less straightforward, decreasing isolated yields.

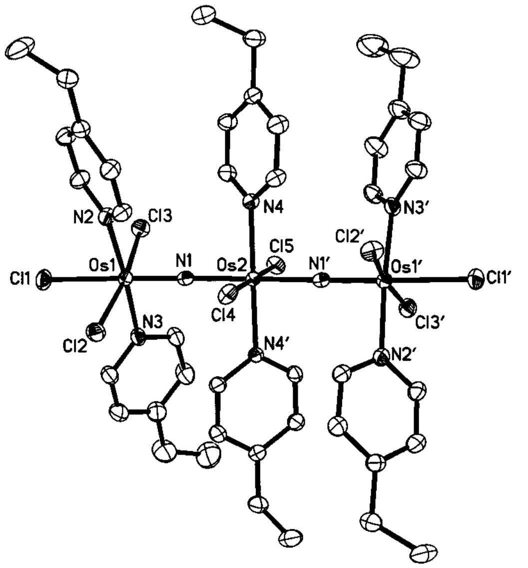

Figure 2. Drawing of $\mathrm{Os_3(N)_2Cl_8(4\text{-}Etpy)_6}$ (**2c**) with 50% probability thermal ellipsoids for non-hydrogen atoms.

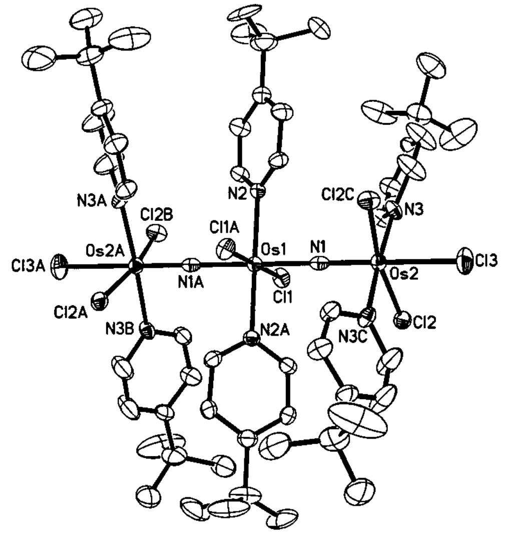

Figure 3. Drawing of $\mathrm{Os_3(N)_2Cl_8(4\text{-}}t\mathrm{\text{-}Bupy)_6}$ (**2d**) with 50% probability thermal ellipsoids for non-hydrogen atoms.

Compounds **2b**−**d** exhibit normal ^{1}H NMR spectra consistent with diamagnetic compounds having two pyridine ligands coordinated to each of two equivalent outer osmium atoms and one unique inner osmium atom, as proposed by Ware and Taube. FAB mass spectra for **2b**−**d** support this formulation showing two series of peaks with appropriate isotope envelopes for triosmium dinitrido $(\mathrm{Os_3N_2Cl}_x\mathrm{L}_y)^+$ and diosmium nitrido $(\mathrm{Os_2NCl}_x\mathrm{L}_y)^+$ fragments, plus the monoosmium nitrido fragment $(\mathrm{OsNCl_2L_2})^+$ that is also observed as the major peak in the FAB mass spectra of **1**. X-ray crystal structures of **2c**·2tol and **2d**·2tol·$2\mathrm{CH_2Cl_2}$ confirm this formulation and provide further details of the structure and bonding.

The molecular structures of **2c**,**d** (Figures 2 and 3, Table 2) are very similar. Each molecule contains three octahedral osmium centers connected in an essentially linear $\mathrm{Os_3(N)_2}$ structure. The pyridine and chloride ligands on adjacent osmium atoms are closer to eclipsed than staggered (dihedral angles: $\mathrm{N_{py}{-}Os{-}Os{-}N_{py}}$ = 27.4, 29.6 ° in **2c**, 35.6 ° in **2d**; Cl−Os−Os−Cl = 27.2, 28.2 ° in **2c**, 34.6 ° in **2d**). This imparts a helical twist to the ligand sets about the three osmium atoms. The pyridine ligands adopt a common arrangement found at octa-

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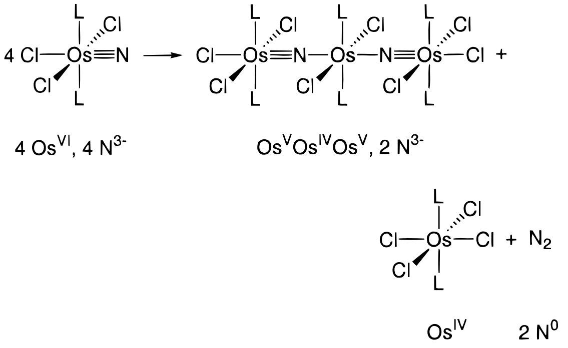
hedral metal centers, trans to each other, with their rings twisted almost perpendicular to each other and staggered relative to the other metal−ligand bonds.

The bond distances (Table 2) suggest that the multiple bonding is significantly localized in the outer osmium−nitrido bonds. The $Os_{outer}-N_{nitrido}$ distances suggest a triple bond, albeit at the long end of the range of reported terminal Os≡N complexes (1.525−1.703 Å, average 1.631 Å).[81] Consistent with $Os_{outer}-N_{nitrido}$ multiple bonding, typical distortions are observed to the ligand set about the outer osmium atoms in **2c**,**d**: there is a statistically significant lengthening of the Os−Cl bonds trans to the nitrido ligands versus the other Os−Cl bonds, and the pyridine and chloride ligands on the outer osmium atoms are bent away from the nitrido ligand (Table 2). The $Os_{inner}-N_{nitrido}$ bond distances are short for single bonds (cf. the $Os-N_{py}$ distances in **2c**,**d**) but longer than the Os=N=Os distances in $Os_2(N)(S_2CNMe_2)_5$ (1.752, 1.763 Å),[37,38] likely reflecting a small degree of $Os_{inner}-N_{nitrido}$ multiple-bond character.

Discussion

Formation of the triosmium dinitrido-bridged compounds $Os_3(N)_2Cl_8L_6$ (**2a**−**d**) from the terminal nitrido compounds $Os(N)Cl_3L_2$ (**1a**−**d**) is a general reaction for several alkylpyridine ligands. Thus, Ware and Taube's chemistry provides a synthetic route to a family of electron-rich polynuclear metallonitrides.

The reaction requires formal reduction of osmium(VI) in **1** to produce **2** plus osmium(IV) in $OsCl_4L_2$, accompanied by oxidation of nitrido ions to dinitrogen (eq 3).[39] The oxidation states in **2a** were given as $Os^VOs^{IV}Os^V$ by Ware and Taube[39] on the basis of earlier assignments by Griffith and co-workers for related compounds.[30,31] This assignment is consistent with the molecular structures reported here according to simple bonding models. Possible valence structures for **2** that balance the anionic (3−) charge of the nitrido ligand with various combinations of osmium oxidation states are illustrated in Figure 4. For example, valence structure **a** shows two molecules of the osmium(VI) nitrido compound **1** forming dative bonds to a central osmium(II) center. Our interpretation of the structure of **2** as involving localized multiple bonding of the nitrido ligand to the outer osmium atoms plus a small degree of multiple-bond character to the inner osmium atom is best represented by a combination of the $Os^VOs^{IV}Os^V$ valence structures **b** and **c** in Figure 4, weighted much more heavily toward **b**. Note that early reports of $[Os_3(N)_2]^{n+}$ (n = 6−8) and $[Ru_3(N)_2]^{8+}$ complexes have usually depicted the multiple bonding as delocalized (variations on **c** and **d**).[30,31]



(3)

The localization of π-bonding in **2** can also be understood using the model of electronic structure put forward by Wheeler, Hoffman, and Strähle involving the analogy between transition-metal nitrides and organic polyenes.[55] Their model for bonding in M_3N_2 complexes can be illustrated as follows. For linear $M_3(N)_2L_{14}$ (idealized D_{4h} symmetry), metal−nitrogen π-bonding between the p_π orbitals on the nitrogen atoms (p_x and p_y on each N) and the d_π orbitals on the metal atoms (d_{xz} and d_{yz} on each M) produces five pairs of degenerate perpendicular π-symmetry molecular orbitals with the nodal patterns shown in Figure 5 and associated energy ordering. Note that there are also three n_d orbitals (d_{xy}) (symmetry-adapted combinations in D_{4h} not shown in Figure 5) perpendicular to the M_3N_2 axis. Each of the nitrido ions contributes two pairs of π-electrons to the bonding picture, effectively filling the four π-bonding molecular orbitals as shown in Figure 5. The node at the inner metal atom in two of the four occupied π-orbitals is required by symmetry and leads to a concentration of π-bonding in the outer metal−nitrogen bonds, comparable to the localization of π-bonding in the pentadienyl cation.[82] This picture fits the structurally characterized complex $[W_3(N)_2Cl_{14}]^{2-}$, which has three octahedral d^0 tungsten(VI) centers connected in a linear fashion via bridging nitrido ligands and adopts a structure with π-bonding localized in the outer bonds ($W_{outer}-N_{nitrido}$ = 1.81, 1.86 Å vs $W_{inner}-N_{nitrido}$ = 2.01, 2.12 Å).[83] Wheeler, Hoffman, and Strähle report overlap populations from extended Hückel calculations on $[W_3(N)_2Cl_{14}]^{2-}$ consistent with the pentadienyl analogy.[55] Similarly, the one other structurally characterized homometallic M_3N_2 compound, $[Mo_3(N)_2(S_2CNEt_2)_9](PF_6)_3$,

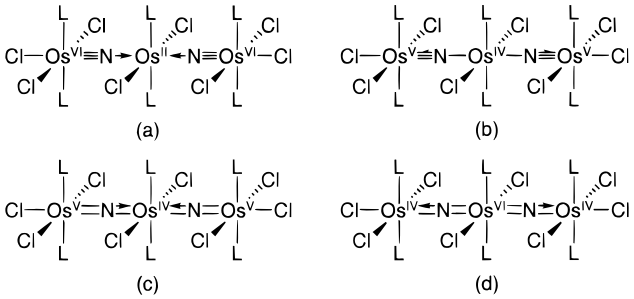


Figure 4. Possible valence structures and associated metal oxidation states for **2**.

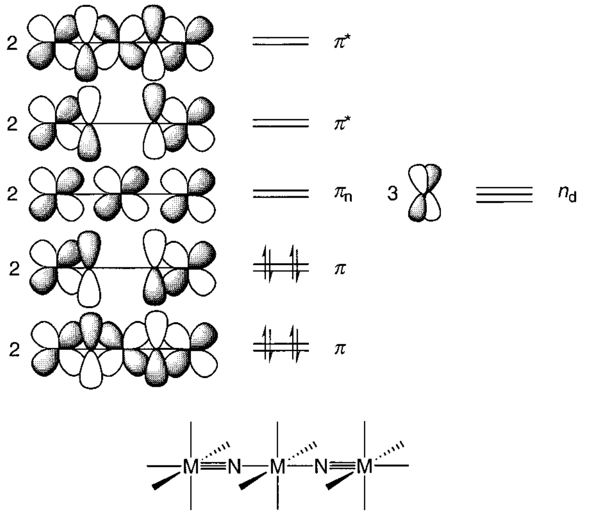


Figure 5. Qualitative depiction of π-symmetry and nonbonding d orbitals of $M_3(N)_2L_{14}$.

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[81] From the Cambridge Structure Database, April 1998 release: Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 1 and 33−37.

[82] Truong, T.; Gordon, M. S.; Boudjouk, P. *Organometallics* **1984**, *3*, 484−487.

[83] Godemeyer, T.; Dehnicke, K.; Fenske, D. *Z. Naturforsch.* **1985**, *40B*, 1005−1009.

also involves three d^0 metal centers and follows the same structural pattern ($Mo_{outer}-N_{nitrido} = 1.65, 1.66$ Å vs $Mo_{inner}-N_{nitrido} = 2.12, 2.14$ Å) to an even greater extreme.[84]

With application of this model to **2**, there are five nonbonding metal d-orbitals (the two empty π_n and three empty n_d orbitals in Figure 5) that can accommodate ten d-electrons, as is the case for **2**. Completely filling these sets of nonbonding orbitals should not effect a structural change, maintaining localization of the π-bonding in the outer Os−N bonds based on the nature of the filled π-bonding orbitals. Note that if these five nonbonding metal d-orbitals had equal contributions from the three osmium atoms, then each metal would formally have $3^1/_3$ d electrons. However, from the pentadienyl analogy,[55,82] the two π_n orbitals of $M_3(N)_2L_{14}$ should have a somewhat greater contribution from the inner metal atom than from an outer metal atom (this is not shown in Figure 5). Applying this idea to **2** places more nonbonding d-electron density from the filled π_n on Os_{inner} than Os_{outer} consistent with the $d^3-d^4-d^3$ electron count associated with $Os^VOs^{IV}Os^V$.

It is interesting to consider the general relationship between electron-rich di- and triruthenium and -osmium nitrido-bridged compounds $d^3-d^4-d^3$ $[M_3(N)_2]^{8+}$ and d^4-d^4 $[M_2(N)]^{5+}$. The former can be thought of as being formed from the latter upon coordination of a terminal d^2 $[M(N)]^{3+}$ unit plus partial electron transfer. Coordination of terminal metal nitrido compounds to other metal centers forming nitrido-bridged species is well established,[8−13,67,85−89] and partial electron transfer between metal centers in such nitrido-bridged compounds is known.[10] These ideas offer the intriguing possibility that electron-rich polynuclear metallonitrides (e.g., **2**) might be prepared by addition of d^2 terminal metallonitrides (e.g., **1**) to appropriate starting complexes (e.g., $Os_2(N)Cl_5L_5$[72]), an area we are now actively pursuing.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grants CHE 93-21196 and 97-12775). C.N. thanks the Fulbright Scholar Program for partial support.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $Os_3(N)_2Cl_8(4\text{-Etpy})_6\cdot 2tol$ (**2c**·2tol) and $Os_3(N)_2Cl_8(4\text{-}t\text{-Bupy})_6\cdot 2tol\cdot 2CH_2Cl_2$ (**2d**·2tol·2CH$_2$Cl$_2$). This material is available free of charge via the Internet at http://pubs.acs.org.

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