

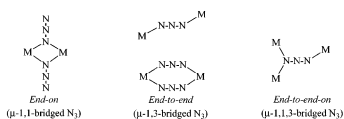
## Multiple Mixed-Valence Behavior in *trans,trans*-[(*tpy*)(Cl)<sub>2</sub>Os<sup>III</sup>(μ-1,3-N<sub>3</sub>)Os<sup>III</sup>(Cl)<sub>2</sub>(*tpy*)]<sup>+</sup>. An Azido Bridge from the Reaction between *trans*-[Os<sup>VI</sup>(*tpy*)(Cl)<sub>2</sub>(N)]<sup>+</sup> and NH<sub>3</sub>

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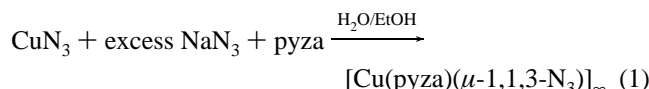
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There is an extensive chemistry of N<sub>3</sub><sup>-</sup> as a bridging ligand with μ-1,1-N<sub>3</sub> (end-on), μ-1,3-N<sub>3</sub> (end-to-end), and μ-1,1,3-N<sub>3</sub> (end-to-end-on) modes of coordination as illustrated below.<sup>1</sup>



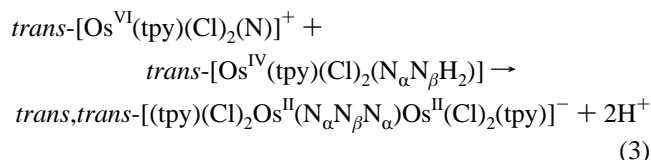
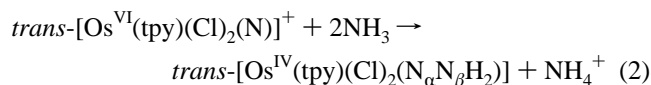
Syntheses are typically based on ligand substitution reactions, that is, eq 1.<sup>1b</sup>



where pyza = pyrazinecarboxamide.

We report here the synthesis of the μ-1,3-N<sub>3</sub> Os dimer, *trans,trans*-[(*tpy*)(Cl)<sub>2</sub>Os<sup>III</sup>(μ-1,3-N<sub>α</sub>N<sub>β</sub>N<sub>α</sub>)Os<sup>III</sup>(Cl)<sub>2</sub>(*tpy*)]<sup>+</sup> ([Os<sup>III</sup>-N<sub>3</sub>-Os<sup>III</sup>]<sup>+</sup>), which contains a single N<sub>3</sub><sup>-</sup> bridge. It was prepared by the reaction between *trans*-[Os<sup>VI</sup>(*tpy*)(Cl)<sub>2</sub>(N)]PF<sub>6</sub> ([Os<sup>VI</sup>≡N]<sup>+</sup>) (*tpy* = 2,2':6',2''-terpyridine) and ammonia (NH<sub>3</sub>) under N<sub>2</sub> in dry CH<sub>3</sub>CN to give the [Os<sup>II</sup>-N<sub>3</sub>-Os<sup>II</sup>]<sup>-</sup> precursor followed by air oxidation to give [Os<sup>III</sup>-N<sub>3</sub>-Os<sup>III</sup>]<sup>+</sup>. The synthetic procedure is remarkable because of the flexibility in introducing <sup>15</sup>N into the resulting μ-1,3-N<sub>3</sub> bridge and the complex for the rich mixed-valence properties supported by the bridge.<sup>2</sup>

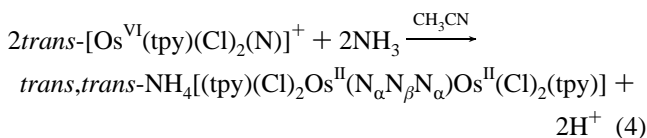
The reaction with NH<sub>3</sub> presumably occurs similarly to that with secondary amine,<sup>3</sup> but in this case, it occurs with [Os<sup>VI</sup>≡N]<sup>+</sup> attack on N<sub>β</sub> of an initial Os(IV)-hydrazido intermediate, eqs 2 and 3.



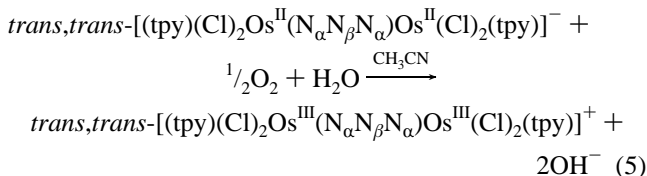
The overall reaction, eq 4, is remarkable in that there is a net 8-electron transfer from the three N atoms to two [Os<sup>VI</sup>≡N]<sup>+</sup> units accompanied by the formation of a μ-1,3-N<sub>3</sub><sup>-</sup> bridge.

**Table 1.** Selected Infrared Data (±1 cm<sup>-1</sup>) for *trans,trans*-[(*tpy*)(Cl)<sub>2</sub>Os<sup>III</sup>(μ-1,3-N<sub>α</sub>N<sub>β</sub>N<sub>α</sub>)Os<sup>III</sup>(Cl)<sub>2</sub>(*tpy*)]PF<sub>6</sub> and Its <sup>15</sup>N-Labeled Analogues in Nujol Mulls

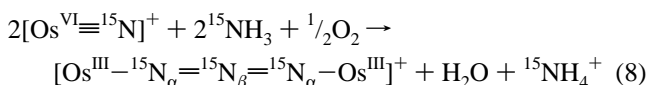
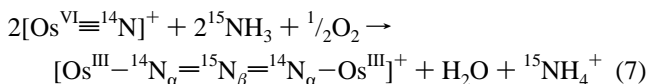
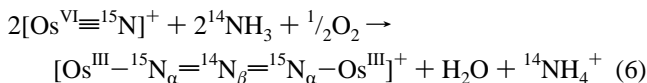
complex	ν <sub>asym</sub> (N <sub>3</sub> <sup>-</sup> ), cm <sup>-1</sup>	Δν <sub>asym</sub> (N <sub>3</sub> <sup>-</sup> ), cm <sup>-1</sup>
[Os <sup>III</sup> - <sup>14</sup> N= <sup>14</sup> N= <sup>14</sup> N-Os <sup>III</sup> ] <sup>+</sup> (1)	2039	(1) - (2) = 30
[Os <sup>III</sup> - <sup>14</sup> N= <sup>15</sup> N= <sup>14</sup> N-Os <sup>III</sup> ] <sup>+</sup> (2)	2009	(2) - (3) = 32
[Os <sup>III</sup> - <sup>15</sup> N= <sup>14</sup> N= <sup>15</sup> N-Os <sup>III</sup> ] <sup>+</sup> (3)	1977	(1) - (3) = 62
[Os <sup>III</sup> - <sup>15</sup> N= <sup>15</sup> N= <sup>15</sup> N-Os <sup>III</sup> ] <sup>+</sup> (4)	1944	(1) - (4) = 95



The [Os<sup>II</sup>-N<sub>3</sub>-Os<sup>II</sup>]<sup>-</sup> product is reducing and air sensitive. In the presence of air, it rapidly undergoes air oxidation to the [Os<sup>III</sup>-N<sub>3</sub>-Os<sup>III</sup>]<sup>+</sup> analogue, *trans,trans*-[(*tpy*)(Cl)<sub>2</sub>Os<sup>III</sup>(μ-1,3-N<sub>3</sub>)Os<sup>III</sup>(Cl)<sub>2</sub>(*tpy*)]<sup>+</sup>, eq 5, which was isolated and characterized as its PF<sub>6</sub><sup>-</sup> salt.



Validation of the mechanism in eqs 2 and 3 comes from the results of <sup>15</sup>N labeling. When [Os<sup>VI</sup>≡<sup>15</sup>N]<sup>+</sup> is allowed to react with <sup>14</sup>NH<sub>3</sub>, the oxidized product is [Os<sup>III</sup>-<sup>15</sup>N=<sup>14</sup>N=<sup>15</sup>N-Os<sup>III</sup>]<sup>+</sup>, eq 6. Similarly, the reaction between [Os<sup>VI</sup>≡<sup>14</sup>N]<sup>+</sup> and <sup>15</sup>NH<sub>3</sub> gives [Os<sup>III</sup>-<sup>14</sup>N=<sup>15</sup>N=<sup>14</sup>N-Os<sup>III</sup>]<sup>+</sup>, eq 7, and the fully μ-1,3-<sup>15</sup>N<sub>3</sub><sup>-</sup> bridged Os product, [Os<sup>III</sup>-<sup>15</sup>N=<sup>15</sup>N=<sup>15</sup>N-Os<sup>III</sup>]<sup>+</sup>, is formed from the reaction between [Os<sup>VI</sup>≡<sup>15</sup>N]<sup>+</sup> and <sup>15</sup>NH<sub>3</sub>, eq 8.



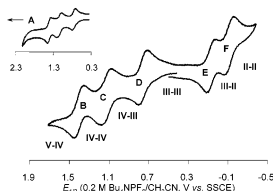
The formulation of the three <sup>15</sup>N-labeled forms of [Os<sup>III</sup>-N<sub>3</sub>-Os<sup>III</sup>]<sup>+</sup> is supported by the IR data in Table 1 which summarizes

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**Figure 1.** Cyclic voltammogram of *trans,trans*-[(*tpy*)(Cl)<sub>2</sub>Os<sup>III</sup>( $\mu$ -1,3-N<sub>3</sub>)-Os<sup>III</sup>(Cl)<sub>2</sub>(*tpy*)]PF<sub>6</sub> in 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN, V versus SSCE.

**Table 2.** Cyclic Voltammetric Data for *trans,trans*-[(*tpy*)(Cl)<sub>2</sub>Os<sup>III</sup>(N<sub>3</sub>)Os<sup>III</sup>(Cl)<sub>2</sub>(*tpy*)]PF<sub>6</sub> in 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN

waves	couples	$E_{1/2}$ (V vs SSCE)	$\Delta E_{1/2}$ (V vs SSCE)
A	V–V/V–IV	> 2.10	(A–B) > 0.71
B	V–IV/IV–IV	+1.40	
C	IV–IV/IV–III	+1.28	(C–D) = 0.52
D	IV–III/III–III	+0.76	
E	III–III/III–II	+0.07	(E–F) = 0.19
F	III–II/II–II	–0.12	

shifts in  $\nu_{\text{asym}}(\text{N}_3^-)$  with <sup>15</sup>N substituted for <sup>14</sup>N. As can be seen by the band energies in entries 1 and 2, substitution of <sup>15</sup>N in the  $\beta$ -position results in a shift of 30 cm<sup>-1</sup> which is in agreement with the value predicted by Hook's Law approximation. On the basis of the band energies from entries 1 and 3, the introduction of two <sup>15</sup>N's in the  $\alpha$ -positions gives rise to the expected shift of ~60 cm<sup>-1</sup> (62 cm<sup>-1</sup>). From entries 1 and 4, the replacement of all three <sup>15</sup>N's in the two  $\alpha$ -positions and  $\beta$ -position causes a shift of 95 cm<sup>-1</sup>, consistent with the fully labeled N<sub>3</sub><sup>-</sup> bridged ligand.

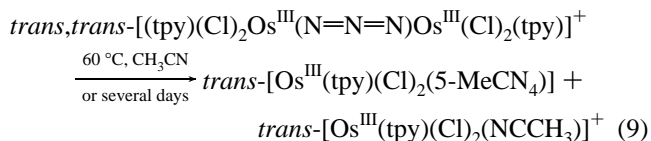
The proposed  $\mu$ -1,3-N<sub>3</sub><sup>-</sup> bridged structure is confirmed by <sup>15</sup>N NMR measurements in deuterated DMSO on [Os<sup>III</sup>-<sup>15</sup>N=<sup>15</sup>N=<sup>15</sup>N-Os<sup>III</sup>]PF<sub>6</sub>.<sup>4</sup> The singlet resonance for [Os<sup>VI</sup>=<sup>15</sup>N]<sup>+</sup> at 1185 ppm becomes a doublet at -400.0 ppm (<sup>1</sup>J(<sup>15</sup>N-<sup>15</sup>N) = 2.4 Hz) in [Os<sup>III</sup>-<sup>15</sup>N <sub>$\alpha$</sub> =<sup>15</sup>N <sub>$\beta$</sub> =<sup>15</sup>N <sub>$\alpha$</sub> -Os<sup>III</sup>]<sup>+</sup> due to the two <sup>15</sup>N <sub>$\alpha$</sub> 's. A triplet at -350.3 ppm can be assigned to <sup>15</sup>N <sub>$\beta$</sub>  (<sup>1</sup>J(<sup>15</sup>N-<sup>15</sup>N) = 2.4 and 2.4 Hz). The [<sup>15</sup>N=<sup>15</sup>N=<sup>15</sup>N]<sup>-</sup> one-bond coupling constants of 2.4 Hz are much smaller than those for other <sup>15</sup>N-labeled azide compounds.<sup>5a-e</sup> They span the range from 5.9 Hz for [Me<sub>2</sub>AlN<sub>3</sub>]<sub>3</sub> in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub><sup>5d</sup> to 24.0 Hz for ClN<sub>3</sub> (in CD<sub>2</sub>Cl<sub>2</sub>).<sup>5a</sup> This is the first example of a transition metal complex containing the fully labeled <sup>15</sup>N<sub>3</sub> ligand.

Formulation of [Os<sup>III</sup>-N<sub>3</sub>-Os<sup>III</sup>]<sup>+</sup> as a symmetrical, diamagnetic d<sup>5</sup>-d<sup>5</sup> dimer with retention of the *trans*-geometry is consistent with its spectroscopic properties. In its <sup>1</sup>H NMR spectrum, the expected aromatic resonances for *tpy* appear from 8.35 to 7.20 ppm, in pattern similar to those for the parent *trans*-[Os<sup>VI</sup>(*tpy*)(Cl)<sub>3</sub>(N)]PF<sub>6</sub> complex. The diamagnetism shows that there is strong magnetic coupling across the bridge. The pattern of bands in the visible with  $\lambda_{\text{max}}$  = 466, 556, 642, and 720 nm in CH<sub>3</sub>CN is analogous to that of bands at 455, 485, 540, and 608 nm for *trans*-[Os<sup>III</sup>(*tpy*)(Cl)<sub>2</sub>(CH<sub>3</sub>CN)]<sup>+</sup>.

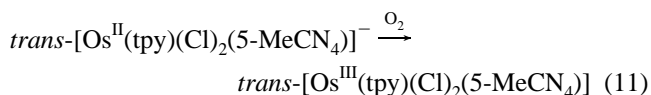
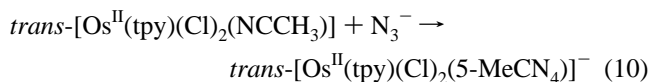
A cyclic voltammogram of [Os<sup>III</sup>-N<sub>3</sub>-Os<sup>III</sup>]<sup>+</sup> in 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN is shown in Figure 1. It reveals the appearance of a series of chemically reversible waves from -0.12 to 1.40 V arising from couples that range from Os<sup>V</sup>-Os<sup>IV</sup>/Os<sup>IV</sup>-Os<sup>IV</sup> at 1.40 V to Os<sup>III</sup>-Os<sup>II</sup>/Os<sup>II</sup>-Os<sup>II</sup> at -0.12 V, versus SSCE (SSCE = 0.236 V versus NHE or  $E_{1/2}(\text{FcCp}_2^{\text{O}+/}) = 0.39$  V versus SSCE). The peak-to-peak splitting values between the waves adjacent to the three mixed-valence forms are summarized in Table 2. The Os<sup>V</sup>-Os<sup>V</sup>/Os<sup>V</sup>-Os<sup>IV</sup> couple is beyond the solvent limit with  $E_{1/2} > 2.10$  V.

We have not yet investigated the spectroscopic properties of the three mixed-valence forms, but the variations in  $\Delta E_{1/2}$  values in Table 2 point to increasingly enhanced M–M coupling in the higher oxidation states.<sup>6,7</sup>

There is also a reactivity chemistry at the  $\mu$ -1,3 N<sub>3</sub><sup>-</sup> bridged ligand. When [Os<sup>III</sup>-N<sub>3</sub>-Os<sup>III</sup>]<sup>+</sup> was heated, it undergoes a [2 + 3] cycloaddition reaction with CH<sub>3</sub>CN followed by a solvolysis to give *trans*-[Os<sup>III</sup>(*tpy*)(Cl)<sub>2</sub>(5-MeCN<sub>4</sub>)]<sup>8a</sup> and *trans*-[Os<sup>III</sup>(*tpy*)(Cl)<sub>2</sub>(NCCH<sub>3</sub>)]<sup>+</sup>,<sup>8b</sup> eq 9.



The former was isolated and structurally characterized, Supporting Information Figure 1. It contains the Os<sup>III</sup>-5-Me-tetrazolate ring structure which was reported earlier as the product of the reaction between *trans*-[Os<sup>II</sup>(*tpy*)(Cl)<sub>2</sub>(NCCH<sub>3</sub>)] and N<sub>3</sub><sup>-</sup> in the presence of air,<sup>8a</sup> eqs 10 and 11.



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**Supporting Information Available:** Crystallographic information (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (a) *trans,trans*-[(*tpy*)(Cl)<sub>2</sub>Os<sup>III</sup>( $\mu$ -1,3-N<sub>3</sub>Na<sub>3</sub>Os<sup>III</sup>(Cl)<sub>2</sub>(*tpy*)]PF<sub>6</sub>: (a) Anal. Calcd for Os<sub>2</sub>C<sub>30</sub>H<sub>22</sub>N<sub>9</sub>Cl<sub>4</sub>PF<sub>6</sub>: C, 30.65; H, 1.89; N, 10.72. Found: C, 30.72; H, 1.92; N, 10.86. (b)  $\lambda_{\text{max}}$  (nm),  $\epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>): 720 (2.46 × 10<sup>3</sup>); 642 (3.54 × 10<sup>3</sup>); 556 (5.91 × 10<sup>3</sup>); 466 (9.39 × 10<sup>3</sup>); 330 (2.24 × 10<sup>4</sup>); and 276 (2.38 × 10<sup>4</sup>). (c) IR (cm<sup>-1</sup>, Nujol):  $\nu_{\text{asym}}(\text{N}_3^-) = 2039$  cm<sup>-1</sup> and  $\nu(\text{tpy}) = 1469, 1458, \text{ and } 1378$  cm<sup>-1</sup>.
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- (a) 30 MHz <sup>15</sup>N NMR measurements were conducted by using a Varian Unity series spectrometer. All <sup>15</sup>N chemical shifts are reported relative to the resonance for a saturated solution of <sup>15</sup>NH<sub>4</sub>Cl in D<sub>2</sub>O at +353.0 ppm, referred to a neat nitromethane external standard. (b) Witanowski, M.; Stefaniak, L. In *Annual Reports on NMR Spectroscopy: Nitrogen NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1983; Vol. 15, p 138.
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