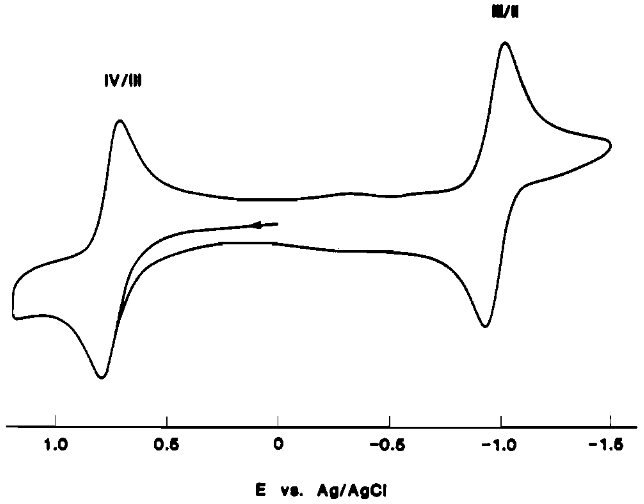

Figure 4. Cyclic voltammogram of $Os(NH_3)Cl_3(py)_2$ (**12**) in acetonitrile (0.1 M TEAP; platinum disk working electrode; Ag/AgCl reference electrode; scan rate 500 $mV{\cdot}s^{-1}$).

is observed at $E_{1/2} = -0.93$ V. This separation ($\Delta E_{1/2} = 1.70$ V) between the Os(IV/III) and Os(III/II) couple is comparable to that ($\Delta E_{1/2} = 1.55$ V) observed for *mer*-$OsCl_3(py)_3$, measured under the same conditions.[21] The quasi-reversible Os(III/II) couple for $[Os(NH_3)Cl_2(\eta^3\text{-terpy})]^+$ (**14**) appears at $E_{1/2} = -0.32$ V, and an irreversible Os(IV/III) couple is observed at $E_p = 0.90$ V (vs Ag/AgCl).

Attempts were made to prepare **12** directly from $K_2[Os(NH_3)Cl_5]$ by substitution of Cl^- in neat pyridine solution. After the mixture was stirred in air at ambient temperature for 2 days, a purple solid had formed on the walls of the flask. This material was found by IR and UV–visible spectroscopy to be the nitrido complex *trans*-$OsNCl_3(py)_2$ (**6**). The formation of **6** may be due to the disproportionation of a pyridine-substituted derivative of $[Os(NH_3)Cl_5]^{2+}$ induced by deprotonation of the ammine in the basic solvent.[22]

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Registry No. **1**, 42531-46-4; **2**, 136576-11-9; **3**, 136656-56-9; **4**, 136656-57-0; **5**, 136576-12-0; **6**, 136599-31-0; **7**, 136538-69-7; **8**, 136538-71-1; **9**, 136538-70-0; **10**, 136576-13-1; **11a**, 127571-46-4; **11b**, 127571-48-6; **11c**, 136576-14-2; **12**, 136576-15-3; **13**, 136576-16-4; **14a**, 136576-17-5; **14b**, 127571-51-1; N, 18851-77-9.

Supplementary Material Available: Non-hydrogen atom coordinates and anisotropic thermal parameters (cation and anion) (Table S1), hydrogen atom coordinates and isotropic thermal parameters (Table S2), weighted least-squares planes (Table S3), and crystallographic data (Table S4) (4 pages); a listing of observed and calculated structure factors (Table S5) (28 pages). Ordering information is given on any current masthead page.

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(21) Taube, H.; Ware, D. C. Unpublished results.

(22) Buhr, J. Ph.D. Thesis, Stanford University, 1978.

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Substitution-Induced N-N Coupling for Nitride Coordinated to Osmium(VI)

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In this paper are described several manifestations of the increase in the tendency of the nitrido ligand in pentachloronitridoosmium(VI) to couple, forming N_2, when pyridyl groups enter the coordination sphere of the metal. Thus, when *trans*-$[OsNCl_3(py)_2]$ is heated at 100 °C in pyridine for several hours, N_2 is liberated in good yield and $[OsCl_3(py)_3]$ (*mer* isomer) is formed. Experiments with substituted pyridines show that the coupling reaction is triggered by entry of a pyridine into the position trans to the nitrido group. Coupling with elimination of N_2 also occurs when *trans*-$[OsNCl_3(pic)_2]$ is heated in CH_3CN, *mer*-$[OsCl_3(pic)_2(CH_3CN)]$ being formed as product. In this case the structure of the osmium-containing product was established by X-ray diffraction. The *mer* isomer is the product expected if the configuration about osmium is retained, and CH_3CN assumes the position vacated by N_2. For $[OsNCl_2(terpy)]^+$ coupling is facile, so much so that it interferes with the preparation of the complex. The tendency to couple is reduced as solutions become more dilute. Coupling at room temperature takes place also when $[n\text{-}Bu_4N][OsNCl_4]$ is dissolved in deoxygenated 4-picoline, a variety of products being formed. The only pure product recovered from the mixture (~10% yield) is a μ-N_2 mixed-valence species, which, on the basis of the intensity of the N≡N stretch, and on the basis of the NMR spectrum of the reduced species, we conclude is unsymmetrically substituted (Cl^-, picoline). The activation of the coupling reaction by ligand exchange is discussed with reference to the MO diagram published for $[RuNCl_5]^-$.[17]

Introduction

In a separate publication,[1] the synthesis and characterization of a series of nitridoosmium(VI) complexes derived from tetrachloronitridoosmium(VI) by stepwise replacement of chloride by pyridyl and polypyridyl ligands is described. Certain of these species have been observed to undergo a coupling reaction to form molecules in which a dinitrogen ligand bridges two reduced osmium centers. A reaction of this kind has precedent in earlier work in which it was shown that $\{[Os(NH_3)_4(CO)]_2(N_2)\}^{4+}$ is formed in high yield when $[Os(NH_3)_5(CO)]^{2+}$ is oxidized by Ce(IV).[2] A point of special interest in the present work is the activation of the osmium nitrido moiety for the coupling reaction by partial replacement of Cl^- by pyridyl groups. Both studies are significant in relation to attempts to reduce N_2 to NH_3 by the action of metal ions. The production of NH_3 when bis(dinitrogen) complexes of W(0) are treated with strong acid has been reported.[3] In this case a single metal center supplies the reducing power. In principle, reduction in a binuclear complex, as indicated in eq 1, is also possible.[4] The earlier,[2] and the present work in which the reverse of eq 1 is observed, demonstrate that a path of this kind is not excluded kinetically.

$$[M(N{\equiv}N)M] = 2[M{\equiv}N] \tag{1}$$

Apart from its intrinsic interest and its possible relevance to the reduction of dinitrogen, the coupling reactions in the systems we are describing provide a useful route for certain syntheses, some

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(1) Ware, D. C.; Taube, H. *Inorg. Chem.*, preceding paper in this issue.

(2) Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208.

(3) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature* **1975**, *259*, 39.

(4) Creutz, C.; Taube, H. *Inorg. Chem.* **1971**, *10*, 2664.

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examples of which will be described.

Experimental Section

Glossary of numbered species: *trans*-[$OsNCl_3(py)_2$] (**1**); *mer*-[$OsCl_3(py)_3$] (**2**); *trans*-[$OsNCl_3(t\text{-Bu-py})_2$] (**3**); *trans*-[$OsNCl_2(t\text{-Bu-py})_2(py\text{-}d_5)]^+$ (**4**); *mer*-[$OsNCl_3(bpy)$] (**5**); *trans*-[$OsNCl_3(pic)_2$] (**6**); *mer*-[$OsCl_3(pic)_2(CH_3CN)$] (**7**); *trans*-[$OsCl_4(pic)_2$] (**8**); see Figure 1 for **9**; *trans*-[$OsNCl_2(terpy)]^+$ (**10**); [$OsCl_2(OH_2)(terpy)]^+$ (**11**); [$(pic)_2Cl_3OsN{\equiv}NOsCl(pic)_4$]Cl (**12**); **12a**, cation of **12**. Abbreviations: py, pyridine; pic, 4-picoline; *t*-Bu-py, 4-*tert*-butylpyridine; bpy, 2,2′-bipyridine; terpy, 2,2′:6′,2″-terpyridine.

Equipment. UV–vis spectra were recorded on a Beckman Model 5270 spectrophotometer and are reported as λ_{max} values in nanometers. ^1H NMR data were obtained on either a Varian XL-100 (100 MHz) or on a Nicolet NMC-300 (300 MHz) spectrometer. Chemical shifts are reported in ppm downfield from TMS. Infrared spectra were recorded on a Perkin-Elmer Model 621 or Nicolet Model 7199 FT-IR spectrophotometer as KBr or CsI pellets or as a Nujol mull on a KBr disk; spectra are reported as wavenumbers in reciprocal centimeters. Elemental analyses were performed by the Stanford Microanalytical Laboratory or by the UC Berkeley Microanalytical Laboratory.

Cyclic voltammetry and controlled-potential electrolysis were performed on a Princeton Applied Research potentiostat/digital coulometer equipped with a Model 175 universal programmer. A solvent-saturated argon purge and a three-electrode configuration were used throughout. The working electrode was either glassy carbon or platinum. A platinum coil was used as the counter electrode. The reference electrode was Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN). Controlled-potential electrolysis was conducted at a platinum gauze working electrode with the auxiliary electrode chamber separated by a glass frit. Reagent grade acetonitrile was dried by distillation from P_2O_5 and stored over 3-Å molecular seives. The electrolyte (0.1 M) was either tetra-*n*-butylammonium tetrafluoroborate (TBAB) or tetraethylammonium perchlorate (TEAP). Ferrocene was added as an internal potential standard and was measured at +0.05 V vs Ag/Ag^+.

Materials. Argon (high purity) was deoxygenated (Cr^{2+}) and dried (H_2SO_4) prior to use. All solvents were reagent grade or better and were used without further purification unless otherwise noted. Reagent grade pyridine and 4-methylpyridine were stored over KOH pellets and then distilled from barium oxide and stored over molecular sieves (4 Å). Trifluoromethanesulfonic acid (3M) was vacuum distilled prior to use. [$n\text{-}Bu_4N$][$OsNCl_4$], $OsNCl_3(py)_2$, $OsNCl_3(pic)_2$, $OsNCl_3(t\text{-Bu-py})_2$, $OsNCl_3(bpy)$, $OsNCl_3(\eta^2\text{-terpy})$, and [$OsNCl_2(\eta^3\text{-terpy})]^+$ were prepared as detailed in the preceding paper.[1] ^{15}N-labeled nitrido complexes were prepared by starting from K[$OsO_3{}^{15}N$] that had been prepared from $^{15}NH_4Cl$ (95 atom %, Merck). Cation-exchange resin was either Bio-Rad AG50W or Sephadex SP-C25 from Pharmacia Fine chemicals. These were preswelled in H_2O, and the columns were poured and then washed with acid followed by distilled H_2O.

Syntheses. *mer*-Trichlorotris(pyridine)osmium(III) (2). $OsNCl_3(py)_2$ (50 mg, 0.10 mmol) was ground to a fine power and suspended in 5 mL of dried pyridine. The solution was deoxygenated and then heated to 100 °C for 16 h. After the reaction proceeded the purple suspended $OsNCl_3(py)_2$ was filtered off and the filtrate evaporated to dryness in vacuo. The red crystalline residue was recrystallized from hot CH_2Cl_2/MeOH to yield red-brown plates that were filtered out, washed with ice-cold MeOH, and dried in vacuo. Yield = 46 mg, 0.086 mmol (81%). Anal. Calcd for [$C_{15}H_{15}N_3Cl_3Os$]: C, 33.75; H, 2.83; N, 7.87; Cl, 19.92. Found: C, 33.64; H, 2.94; N, 7.50; Cl, 20.18.

Trichloro(acetonitrile)bis(4-methylpyridine)osmium(III) (7). [$OsNCl_3(pic)_2$] (100 mg, 0.201 mmol) was suspended in 5 mL of dried CH_3CN. The solution was deoxygenated by bubbling with argon for 10 min and then heated to reflux with stirring. After 10 h the solution was cooled to room temperature and kept for 12 h. It was filtered, and the precipitate (light tan) was washed once with ice-cold CH_3CN and thrice with Et_2O. The solid was dried in vacuo. Yield = 51 mg, 0.0973 mmol (48.4%). The compound can be purified by flash chromatography on silica gel. A CH_2Cl_2 solution of the solid was loaded onto a silica gel column prepared in CH_2Cl_2. Elution was begun with 7% acetone/CH_2CL_2. A light yellow compound (**8**) eluted first and then, closely spaced, a dark red compound (**9**) and a pale yellow band containing product (**7**). This latter fraction was evaporated to dryness to give a beige powder. Recrystallization from CH_2Cl_2 by addition of toluene or by slow evaporation afforded large orange crystals. Anal. Calcd for [$C_{14}H_{17}N_3Cl_3Os$]: C, 32.10, H, 3.27; N, 8.02. Found: C, 31.61; H, 3.04; N, 7.76. UV–vis (CH_3CN) [λ_{max}, nm (log ϵ)]: 237 (3.91), 320 (3.99). NMR (DMSO-d_6, 300 MHz): spectrum not observed because product is paramagnetic.

***trans*-Tetrachlorobis(4-methylpyridine)osmium(IV) (8).** [$OsNCl_3(pic)_2$] (140 mg, 0.281 mmol) was dissolved in 20 mL of dried CH_2Cl_2 in a Fisher–Porter bottle. The solution was deoxygenated by bubbling with argon, pressurized under argon to 45 psi, and heated in an oil bath with stirring. As the bath temperature reached approximately 80 °C, the solution began to darken rapidly. Heating was continued, and after 2 h at 100 °C the bath temperature was lowered and kept at 80 °C for 8 h. The solution was allowed to reach ambient temperature and pressure, and its volume was reduced on the rotovap. The concentrated solution was loaded onto a silica gel column that had been prepared in CH_2Cl_2. The product was eluted from the column with CH_2Cl_2 as a light yellow band moving almost with the solvent front. The solvent was removed from this fraction in vacuo to give 16 mg, 0.031 mmol (44%), of the yellow microcrystalline product. Recrystallization from hot 1,2-dichloroethane afforded yellow crystals (**8**). UV–vis (CH_3CN) (λ_{max}, nm): 252, 350, 386. NMR (CD_2Cl_2, 300 MHz): H_o 13.29 (d, 4 H), CH_3 12.84 (s, 6 H), H_m 5.78 ppm (d, 4 H). $^3J(H_o,H_m)$ = 6 Hz.

Octachlorobis(μ-nitrido)hexakis(4-methylpyridine)triosmium(V,IV,V) (9). After **8** is eluted from the silica gel column with CH_2Cl_2, the eluant is changed to ~5–10% acetone/CH_2Cl_2 and a dark red band begins to elute. Collection of this band and evaporation of the solvent in vacuo yields 45 mg, 0.032 mmol (46%), of dark red microcrystalline product. This material may be recrystallized from CH_2Cl_2 by addition of toluene and cooling or slow evaporation of the solvent to yield fine needles (**9**). Anal. Calcd for [$C_{36}H_{46}N_8O_2Cl_8Os_3$]: C, 29.27; H, 3.14; N, 7.59; Cl, 19.20. Found: C, 29.10; H, 3.15; N, 7.33; Cl, 19.26. UV–vis (CH_3CN/CH_2Cl_2 1%) (λ_{max}, nm): 253, 297, 470, 550. NMR (CD_2Cl_2, 300 MHz): H_o 8.92 (d, 8 H), H_m 6.91 (d 8 H), H_o' 6.70 (d, 4 H), H_m' 6.56 (d, 4 H) [$^3J(H_oH_m)$ = 6.5 Hz], CH_3 2.37 (s, 12 H), CH_3' 2.20 ppm (s, 6 H). IR (KBr): $\nu(py)_{ring}$ 1618 (s), $\nu(Os{-}N{-}Os)_{asym}$ 970 cm^{-1} (vs).

***trans*-Dichloroaqua(η^3-2,2′:6′,2″-terpyridine)osmium(III) Trifluoromethanesulfonate (11).** [$OsNCl_3(\eta^2\text{-terpy})$] (100 mg, 0.201 mmol) was suspended in 20 mL of H_2O and the solution stirred. After 10 min the yellow solution was filtered and 2 mL of 0.1 M $HOSO_2CF_3$ was added. A 1.24-equiv amount (16 mg, 0.25 mmol) of NaN_3 dissolved in 2 mL of H_2O was then added slowly over a period of 30 min. The solution darkened immediately upon addition, and bubbles were observed to form on the walls of the flask. The solution was warmed briefly and stirred and then diluted with an equal volume of H_2O. A Sephadex SP cation-exchange column was prepared in the H^+ form. The solution was loaded onto the column, which was then washed with H_2O. Elution was begun with 0.1 M $HOSO_2CF_3$, which slowly moved a yellow band. This band was recovered by elution with 0.2 M $HOSO_2CF_3$, leaving much colored material on the column. The yellow band was concentrated on the rotovap to give a yellow-green microcrystalline solid that was separated by filtration and triturated five times with Et_2O. The solid, dried in vacuo, yielded 20 mg, 0.031 mmol (15.2%). Anal. Calcd for [$C_{16}H_{13}N_3O_4Cl_2F_3SOs$]: C, 29.05; H, 1.98; N, 6.35; S, 4.85. Found: C, 29.18; H, 1.89; N, 10.63; S, 4.76. UV–vis (0.02 M $HOSO_2CF_3$) [λ_{max}, nm (log ϵ)]: 271 (4.35), 297 (4.42), 316 (4.20), 331 (4.29), 387 (3.45), 446 (3.66), 630 (2.90). UV–vis (0.1 M NaOH) [λ_{max}, nm (log ϵ)]: 272 (4.30), 277 (4.29), 311 (4.47), 405 (3.49), 476 (3.64).

Tetrachloro(μ-dinitrogen)hexakis(4-methylpyridine)diosmium(II,III) Chloride, [$(pic)_2Cl_3OsN{\equiv}NOsCl(pic)_4$]Cl (12). [$n\text{-}Bu_4N$][$OsNCl_4$] (0.20 g) is dissolved in neat deoxygenated 4-picoline (5–10 mL). A color change from purple to orange-brown and finally to dark green takes place over 24 h. TLC of the reaction mixture (silica gel, 1:1 CH_3CN/CH_2Cl_2) shows that a number of species are present, many of which are dark green or blue in color. The major component was separated by chromatography on silica gel using CH_3CN/CH_2Cl_2 or acetone/CH_2Cl_2 as eluents. The center of the broad band corresponding to the product was collected and rechromatographed on glass beads, a much milder support, as decomposition on silica gel was suspected. The product was isolated as a dark blue green compound in ca. 10% yield. UV–vis (CH_3CN) [λ_{max}, nm (log ϵ)]: 690 nm (4.3). IR (KBr): $\nu(N{\equiv}N)$ 1965 (vs), $\nu(^{15}N{\equiv}^{15}N)$ 1895 cm^{-1} (vs).

Results

Coupling of Bis(pyridyl Complexes with Elimination of N_2. Compound **1**, [*trans*-$OsNCl_3py_2$], is only sparingly soluble in pyridine at room temperature, but when a suspension is heated, the solid slowly dissolves, yielding a solution from which $OsCl_3(py)_3$ (**2**) can be recovered in good yield. A compound of this composition had previously been prepared by heating K_2OsCl_6 with pyridine in DMF and had been characterized. Elemental analysis and comparison of the IR spectrum with that of **2** show that the products are identical. Although *fac* geometry had been assigned to the complex,[5] it has more recently been reformulated as the

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(5) Buckingham, D. A.; Dwyer, F. P.; Goodwin, H. A.; Sargeson, A. M. *Aust. J. Chem.* **1969**, *17*, 315.

mer isomer.[6] Gas is produced in the reaction we have carried out. It was quantitatively transferred by using a Toepler pump to a known volume and was shown by mass spectrometric analysis to be dinitrogen. Not all the starting material is consumed, and this in large part accounts for the fact that only 77% of the yield of N_2 expected on the basis of the stoichiometry of reaction 2 was found.

$$2OsNCl_3(py)_2 + 2py = 2OsCl_3(py)_3 + N_2 \qquad (2)$$

It is a matter of interest to learn whether the third pyridine is added to each osmium before coupling occurs or at some later stage. Accordingly, an experiment was undertaken in which the more soluble $[OsNCl_3(t\text{-Bu-py})_2]$ (**3**) was used as a substrate and the course of the reaction was followed by NMR spectroscopy. A pyridine-d_5 solution 6.3 × 10^{-3} M in **3** and containing a known amount of C_6Me_6 as internal reference was sealed under vacuum in an NMR tube, which was then heated at 95 °C in an oil bath, the NMR measurements being made periodically after the tube was cooled to room temperature.

In the first stage of the reaction the resonances arising from the *tert*-butylpyridine ligands (on the basis of work reported separately,[1] we take these to be mutually trans) are observed to shift, but the new values do not correspond to free ligand. We infer that the shifts are the result of entry of pyridine-d_5 into the coordination sphere and, because of the known facile addition at the site trans to nitride,[1] that it enters there. After coupling, and elimination of μ-N_2, the known final geometry would result without requiring further rearrangement of the other five groups. The formation of the intermediate *trans*-$[OsNCl_2(t\text{-Bu-py})_2(py\text{-}d_5)]^+$ (**4**) follows a first-order course, governed by a specific rate of 2.8 × 10^{-4} s^{-1} at 95 °C and is substantially complete before the second, much slower stage, has contributed significantly to reaction. In the second stage there is a loss of the resonances of the intermediate, without new peaks appearing, as expected for a reaction producing a paramagnetic osmium(III) complex.

No detectible coupling took place when *mer*-$[OsNCl_3(bpy)]$ (**5**) was heated in neat pyridine, at 100 °C for 4 h. Compound **5** was recovered unchanged. When *trans*-$[OsNCl_3(pic)_2]$ (**6**) is heated in CH_3CN, coupling occurs with loss of N_2. The main osmium-containing product (recovered in 50% yield) is *mer*-$[OsCl_3(pic)_2(CH_3CN)]$ (**7**), which has been characterized by a crystal structure determination by X-ray diffraction.[7a] The IR spectrum, as a guide to composition, is misleading because it shows no sign of the C≡N stretching frequency ascribable to the nitrile. The intensities of this band vary widely with the nature of the metal ion, a subject that is treated in detail elsewhere.[7b]

In CH_3CN, compounds *trans*-$[OsCl_4(pic)_2]$ (**8**) and the μ-nitrido trinuclear species **9** are minor products of the coupling reaction, but in the noncoordinating solvent CH_2Cl_2, they become the major osmium-containing products that can be recovered. In a noncoordinating solvent such as CH_2Cl_2, if dinitrogen loss on coupling occurs, the osmium must complete its coordination sphere from ligands brought in from the reactant osmium complex, and this in turn requires that in the products some of the ligands bridge metal centers. The investigation of the structure of the products **8** and **9** bears out this expectation.

The NMR spectrum of **9** (Figure 1) shows that picoline resonances are split into two sets in the ratio 2:1. The simplest structure consistent with the NMR data, the analyses, and the fact that the normal NMR shifts observed for the picoline protons show the complex to be diamagnetic is represented in Figure 1.

There is an element of arbitrariness in assigning oxidation states in a trinuclear species such as this. There are other known cases,[8] $K_4[Os_3N_2(CN)_8(OH)_4(OH_2)_2]$ and $Cs[N_2X_{11}(NH_3)_3{\cdot}2H_2O]$ (X = Cl^-, Br^-), in which the sum of the metal oxidation states is 14+; for these, as well as for **9**, the assignment as [(V)(IV)(V)] seems reasonable. Compound **9** shows a strong band at 970 cm^{-1} in the IR spectrum, in the same energy region as is observed for the literature compounds, which we assign to the $\nu(Os_3N_2)_{asym}$ mode.

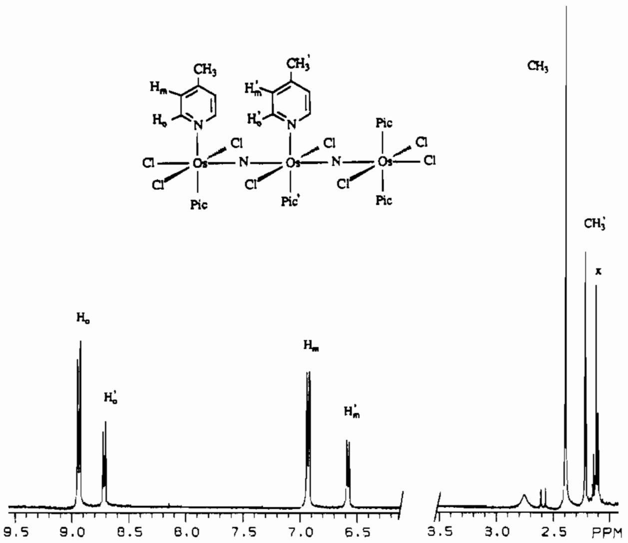

Figure 1. ^1H NMR spectrum of **9** (300 MHz, CD_2Cl_2).

The characterization of compound **8** rests primarily on its proton NMR spectrum, which shows only resonances in the ratio expected for picoline. The shifts however are large compared to those observed when the ligand is bound in a diamagnetic complex but are sharp (~1 Hz) compared to those observed for a paramagnetic species. This behavior has previously been observed[9] for a number of paramagnetic *trans*-bis(phosphine) derivatives of tetrachlorosmium(IV). The paramagnetism in question here is of the second-order type (TIP). Spin–orbit coupling, which is quite large for Os(IV) (~4 × 10^3 cm^{-1}) leads to a splitting of the $^3T_{1g}$ level and gives rise to a diamagnetic ground state ($J = 0$). In a magnetic field a second-order Zeeman effect mixes the higher $J = 1$ state into the ground state. The IR spectrum of **8** shows no sign of ν(Os≡N) but does show the usual pattern of ring ligand modes seen for the trans arrangement of two picoline molecules. The NMR data strongly suggest the 4+ oxidation state, and the fact that the complex is neutral then requires that four Cl^- ions are present. The NMR spectrum in particular shows that the sample of compound **8** is rather pure. When taken together with the other evidence, we believe that the conclusion that it is *trans*-$[OsCl_4(pic)_2]$ is reasonably well established.

If the compositions for **8** and **9** are as we believe them to be, the overall reaction can be written as shown in eq 3. This can be considered to be the sum of the two disproportionation reactions (eqs 4 and 5).

$$4[OsNCl_3(pic)_2] = [OsCl_4(pic)_2] + \{[OsNCl_3(pic)_2]_2OsCl_2(pic)_2\} \qquad (3)$$

$$2[Os^{VI}NCl_3(pic)_2] = 2[Os^{III}Cl_3(pic)_2] + N_2 \qquad (4)$$

$$2[Os^{III}Cl_3(pic)_2] + 2[Os^{VI}NCl_3(pic)_2] = [Os^{IV}Cl_4(pic)_2] + \{[Os^{V}NCl_3(pic)_2]_2Os^{IV}Cl_2(pic)_2\} \qquad (5)$$

In a strongly nucleophilic solvent such as pyridine, the intermediate $[Os^{III}Cl_3(pic)_2]$ is quenched by reaction with the solvent leading to quantitative formation of an Os(III) product. Acetonitrile apparently lies between pyridine and CH_2Cl_2 in nucleophilic power in giving mainly **7** as product, together with some **8** and **9**.

Coupling in Tris(pyridyl) Complexes with Elimination of N_2. As can be inferred from what has gone before, the reactivity for coupling is increased when Cl^- is replaced by a pyridyl group. It is no surprise then to learn that for certain of the tris(pyridyl)

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(6) Scheffler, A.; Preetz, W. *Z. Naturforsch.* **1976**, *31*, 1099.

(7) (a) Bino, A.; Cohen, S. Unpublished results. (b) Johnson, A.; Taube, H. *J. Indian Chem. Soc.* **1989**, 503.

(8) (a) Hall, J. P.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2410. (b) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315.

(9) (a) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Randall, E. W.; Shaw, D. *J. Chem. Soc., Chem. Commun.* **1968**, 419. (b) Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867.

complexes the coupling reaction is more facile than for bis(pyridyl) complexes. The coupling of $[OsNCl_2(terpy)]^+$ (**10**) proceeds at room temperature and is so facile that it interferes with the preparation of the species.[1] Coupling is favored as the concentration rises, as expected for a second-order process. Carrying out the preparation under dilute conditions enables **10** to be isolated in good yield free of Os(III) impurities. Although no attempt was made to observe the evolution of N_2, the oxidation state change and the detection of no other species containing osmium are indicative of the coupling reaction.

In aqueous solution, the only product of coupling of **10** to be detected is $[OsCl_2(OH_2)(terpy)]^+$ (**11**). This species was identified by comparison of its UV–visible spectrum with that of an authentic sample which was prepared by an alternative route. The analytical results alone do not prove that H_2O is coordinated to osmium, but this is shown by the reversible changes in the spectrum that result from changes in the acidity. It is suggested also by the observation that **11** in water undergoes a slow reaction leading to a blue product (λ_{max} ~650 nm), which, in analogy to the behavior reported[10] for $[Os(OH_2)(bpy)(terpy)]^{3+}$, we take to be the μ-oxo species $\{[OsCl_2(terpy)]_2O\}$. Coupling of **10** also occurs in nonaqueous solvents, as evidenced by darkening of the solutions. In attempts made with such solvents we failed to isolate pure products.

Coupling To Produce μ-Dinitrogen Species. It is likely that μ-dinitrogen species are produced prior to the loss of dinitrogen but that these intermediates are so unstable under the experimental conditions that they have not been detected in the work thus far outlined. We have been able to characterize at least one μ-dinitrogen complex as the product of the coupling reaction. When $[n\text{-}Bu_4N][OsNCl_4]$ is dissolved in neat deoxygenated 4-picoline, the major product, which after considerable difficulty we succeeded in isolating in pure form, is a dark blue-green compound. On the basis of evidence adduced, we formulate it as the chloride salt **12** of $[(pic)_2Cl_3OsN{\equiv}NOsCl(pic)_4]^+$ (**12a**), a binuclear Os(III)/Os(II) μ-dinitrogen species with unsymmetrical substitution. Isolated yields were low (~10% by weight) due to the diversity of products formed and the drawn out scheme necessary for isolation in pure form. An analogous reaction takes place when pyridine is used in place of 4-picoline, but in this case yields are significantly lower due to precipitation of the sparingly soluble bis(pyridine complex) **1**, which is an intermediate in the reaction. This is in fact why 4-picoline was used, and in the following discussion reference is made only to the complexes formed with 4-picoline as ligand. Yields are also reduced if the reaction is carried out in more dilute solution or when oxygen is not excluded.

Compound **12** dissolves in a wide range of organic solvents, including CH_2Cl_2, CH_3CN, acetone, DMSO, and alcohols, to give deep blue-green solutions. It is slightly soluble in water, especially if it is first "wetted" with a small amount of CH_3CN or MeOH. Upon addition of base to an aqueous solution of **12** the blue color bleaches to yellow. TLC of solutions kept for a few days or of a solution of the solid kept for 1–2 weeks demonstrated that **12** is unstable in solution or in the solid state even in the absence of air. Decomposition occurs by cleavage of the osmium–dinitrogen bond, resulting in loss of the binuclear structure and the intense blue color.

That the blue component of **12** is cationic is shown by the rapid precipitation of the dark blue PF_6^- salt from aqueous solution on addition of $AgPF_6$ or KPF_6. In addition, AgCl is rapidly formed upon treatment of an aqueous solution of **12** with $AgNO_3$; the NO_3^- salt is soluble in H_2O and remains in solution. Remarkably though, cation-exchange resin (Sephadex SP or Bio-rad H^+ form) does not retain **12a** and the blue species passes through unhindered.

Strong evidence for the formation of dinitrogen in this system and its ligation to osmium is given by the IR spectrum of **12**, shown in Figure 2. The strong absorption at 1965 cm^{-1} is assigned to the $\nu(N{\equiv}N)$ mode of the μ-dinitrogen moiety in this complex. This is confirmed by the observation of the $\nu(^{15}N{\equiv}^{15}N)$ mode at 1895 cm^{-1} (observed $\Delta\nu$ = 70 cm^{-1}, calculated $\Delta\nu$ = 67 cm^{-1} in the ^{15}N-labeled analogue of **12** obtained from $[n\text{-}Bu_4N][Os^{15}NCl_4]$). The good agreement between the experimental and calculated shift in $\nu(N{\equiv}N)$ disposes of the possibility that only one nitrogen is present in the diatom giving rise to the band at 1965 cm^{-1}, as would be the case for a nitrosyl complex. For a symmetrical μ-N_2 complex the $\nu(N{\equiv}N)$ mode is IR forbidden but Raman allowed. For noncentrosymmetric complexes this mode becomes IR active, the intensity being roughly in proportion to the extent the molecule is made unsymmetrical. The effect of asymmetry is enhanced in a mixed-valence molecule because it leads to partial valence trapping of the normally delocalized μ-N_2 mixed-valence complex. The very high intensity of the $\nu(N{\equiv}N)$ band for **12** is consistent with both the mixed-valence formulation and asymmetric nature of the complex. The rest of the bands in the IR spectrum of **12** are due primarily to vibration modes of the 4-picoline ligand, the pattern being quite similar to that seen for the bis(picoline) nitrido complex **6** and the bis(picoline)osmium(IV) complex **8**.

The intense blue color of **12a** is due to a band at 690 nm with an extinction coefficient of 2.2×10^4 M^{-1} cm^{-1}. Absorption with these properties is characteristic of μ-N_2 mixed-valence complexes in particular.[11] The NMR spectrum of **12a** shows broadened peaks in the aromatic region (7.13–7.66 ppm) for the H_o and H_m protons of the picoline ligands, which is indicative of a paramagnetic species. When a deoxygenated solution of **12a** in CD_3CN is reduced by stirring with Na/Hg for 15 min, the

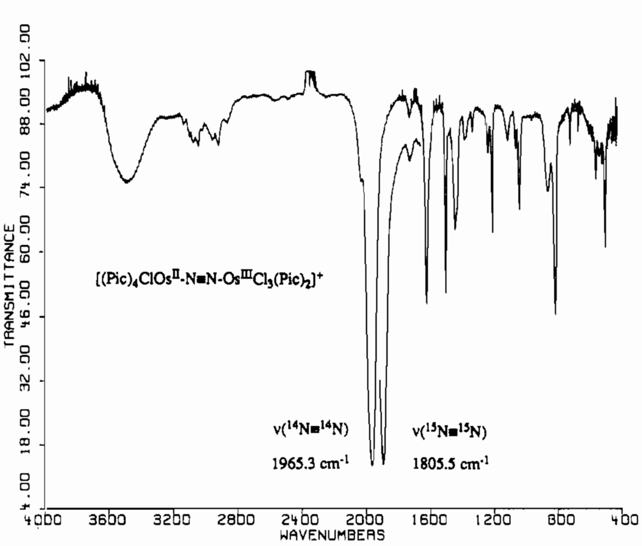

Figure 2. FTIR spectrum of $[(pic)_2Cl_3OsN{\equiv}NOsCl(pic)_4]Cl$ (**12**) (KBr disk).

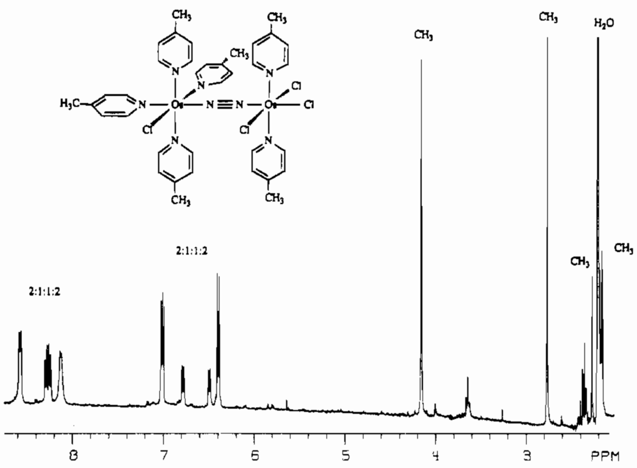

Figure 3. ^1H NMR spectrum of $[(pic)_2Cl_3OsN{\equiv}NOsCl(pic)_4]$ (300 MHz, CD_3CN).

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[10] Buckingham, D. A.; Dwyer, F. P.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 622.

[11] Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1972**, *94*, 7213.

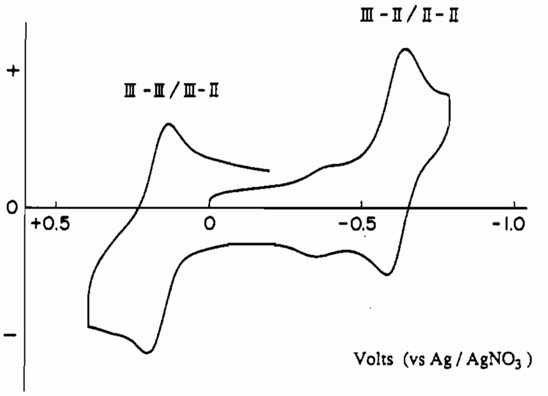

Figure 4. Electrochemical properties of **12a** from cyclovoltammetry in 0.1 M TEAP/CH_3CN (room temperature; sweep rate 100 mV s^{-1}; Pt working electrode; reference electrode Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN).

blue-green color is rapidly changed to the red-brown of the (II,II) species. The NMR spectrum of this reduced complex is shown in Figure 3.

Sharp peaks are observed for all resonances of the picoline ligand. In the aromatic region two well-separated groups of doublets of equal intensity are assigned to the ortho and meta protons of the coordinated picoline ligands. Within each group a pattern of four doublets in a 2:1:1:2 ratio appears at 8.56, 8.28, 8.23, and 8.12 ppm for the ortho protons and at 7.00, 6.77, 6.48, and 6.38 ppm for the meta protons. This is consistent with a minimum of six picoline ligands in four distinct environments in the complex. The methyl group resonances support this, as there are four singlets also in a ratio of 2:2:1:1. These appear at 4.15, 2.76, 2.26, and 2.15 ppm and have intensities relative to the ring protons of 3:2 as expected.

The presence of six picoline ligands in a ratio of 2:1:1:2 could arise from three different isomers of $[(pic)_3Cl_2OsN{\equiv}NOsCl_2(pic)_3]$ (two *fac–mer* and one *mer–mer* with respect to the $Os(pic)_3$ fragments) and one isomer of $[(pic)_4ClOsN{\equiv}NOsCl_3(pic)_2]$, as shown in Figure 3. The latter formulation is favored first because the relatively large chemical shift difference of the picoline CH_3 groups is indicative of two rather chemically different Os centers. Second and most important, the intensities of both the very strong $\nu(N{\equiv}N)$ stretch in the IR spectrum of **12** (Figure 2) and the strong stretch ($\nu(N{\equiv}N) = 2029\ cm^{-1}$) in the IR spectrum of the diamagnetic reduced derivative of **12** suggest a markedly unsymmetrical species, in terms of both ligand substitution and charge distribution.

Cyclic voltammetric measurements demonstrate that three distinct oxidation states are accessible in complex **12a**. The cyclic voltammogram as measured in CH_3CN at a platinum electrode is shown in Figure 4. The $E_{1/2}$ values determined from this trace for the half-reactions (III,III)/(III,II) and (III,II)/(II,II) couples are +0.16 and –0.62 V vs $Ag/AgNO_3$, respectively. The potential separations between the anodic and cathodic peaks of each couple were, in both cases, 60 mV. This is close to the theoretical value of 59 mV found for reversible one-electron processes.[12]

As mentioned previously, it is possible to reduce the binuclear complex with either Zn or Na amalgam. The resulting (II,II) yellow-brown complex is air sensitive and is rapidly reoxidized to the mixed valence form upon exposure to air. When the reduction is carried out in CH_3CN, the reoxidation takes place cleanly, as seen from the UV-vis spectrum of the solution after exposure to air. In MeOH the process is not so simple, the formation of other products being revealed by the IR spectrum of the product.

For a symmetrically substituted binuclear complex, the difference $\Delta E_{1/2}$ in potential for the two stages of oxidation, after correction for electrostatic contributions (small even in the present case), provides a measure of energy effects arising from delocalization. These include destabilization of the isovalent forms (shown to be great for (μ-dinitrogen)osmium species[11]) and stabilization of the mixed-valence forms ascribable to electron delocalization. Compositional asymmetry itself makes a contribution to $\Delta E_{1/2}$, which in the absence of any communication would simply be the difference in the III/II redox potential for the two different sites. For the substitutions $[Os(terpy)_2] \rightarrow [Os(terpy)(bpy)_2Cl] \rightarrow Os(bpy)_2Cl_2$ the value of $E_{1/2}$ for the Os(III)/Os(II) couple decreases by 0.53 and 0.48 V, respectively.[13,14] The change from one type of pyridyl ligand to another has only a small effect on potentials, as shown by the comparison of the values of $E_{1/2}$ for $[Os(bpy)_3]^{3+/2+}$ and $[Os(terpy)_2]^{3+/2+}$ reported as being identical within 0.01 V.[15] The changes are ascribable mainly to the replacement of a pyridyl group (which as a π-acid ligand tends to stabilize the lower oxidation state) by the electron-releasing ligand, which, acting solely as electron donor, stabilizes the higher oxidation state. Compositional asymmetry could therefore fully account for the observed value of $\Delta E_{1/2}$ if stabilization by delocalization was not a factor. The similarity of the absorption spectrum of **12a** compared to that of a substitutionally symmetrical μ-N_2 complex however shows that **12a** is delocalized; i.e., much of the observed $\Delta E_{1/2}$ is accounted for by electronic effects. The system provides a dramatic illustration of the point already made in the literature[16] that, for a delocalized system, the effects on $\Delta E_{1/2}$ of substitutional asymmetry and of delocalization are not simply additive.

Electrochemical experiments, now to be described, suggest that coupling is much more efficient when Os(VI) is reduced, the first product of the reduction presumably being Os(V). In Figure 5a are shown cyclic voltammograms registered for **10** in CH_3CN as a solvent, the solid line showing the trace for the first cycle, and the broken line, that for the fifth continuous cycle. The irreversible reduction at $E_{pc} = -0.74$ V (all values referenced to $Ag/AgNO_3$) is assigned to reduction of Os(VI) to Os(V). Evident is the development of an oxidation peak at $E_{pa} = -0.23$ V and a couple at $E_{1/2} = 0.42$ V. The trace for the fifth scan is shown as a broken line. The wave for the reduction of Os(VI) has diminished significantly in amplitude, and two rather prominent couples, $E_{1/2} = -0.28$ V and $E_{1/2} = 0.42$ V, have appeared. Also appearing is a weak feature at an intermediate value of E, which appears more prominently in the trace of Figure 5b. This trace was obtained from a solution of **10** in CH_3CN that had been subjected to controlled-potential reduction at –1.0 V (vs $Ag/AgNO_3$). It shows that the main electroactive component is that which gives rise to the two couples at $E_{1/2} = 0.42$ and –0.28 V. Because the two waves appear to be of nearly equal amplitude, and because the separation, 0.70 V, corresponds rather closely to that observed for (μ-dinitrogen)osmium species based on the 3+/2+ couple, rather than a separation of ca. 1.5 V that characterizes the sequence Os(IV)–Os(III)–Os(II) in mononuclear polypyridine species,[1] we attribute the behavior to the formation of a dinitrogen-bridged species. In contrast to the coupling that takes place by disproportionation of $[OsNCl_4]^-$, the chemistry by the partial reduction route appears to be rather clean. The only recognizable impurity is the species giving rise to the feature at $E_{1/2} = 0.13$ V. We ascribe it to the $[Os(NCCH_3)Cl_2(terpy)]^{+/0}$ couple, which, it is reasonable to suppose, arises from cleavage of the fully oxidized μ-N_2 species.

Discussion

The foregoing work has shown (a) that the coupling reaction is greatly facilitated when pyridyl groups or CH_3CN replace Cl^- in the chloronitridoosmium(VI) complex; (b) that, in the activation of a *trans*-bis(pyridyl) derivative, an additional substitution by a π-acid ligand takes place prior to coupling, and (c) that this

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[12] Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460.

[13] Kober, E. M.; Marshall, J. L.; Dressik, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755.

[14] Balzani, V.; Juris, A.; Barigellette, F.; Belser, P.; Von Zelewsky, N. *Sci. Pap. Inst. Phys. Chem. Res.* (*Jpn.*) **1984**, *78*, 78.

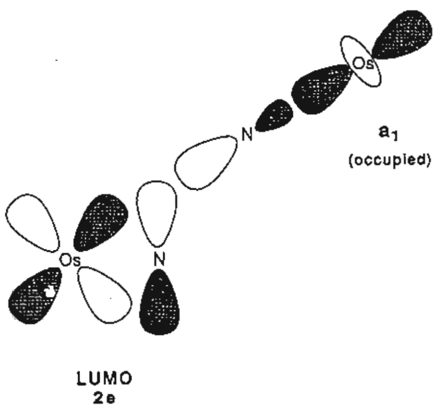
[15] Kober, E. M. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC, 1981.

[16] Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.* **1988**, *27*, 2364.

substitution is in the position trans to the nitrido group. The last stated conclusion is supported by the observation that the complex with terpyridyl as ligand, in which the position trans to the nitrido group is occupied by a pyridyl nitrogen, is sensitive to coupling without additional activation, as well as by the observation that the coupling of $OsNCl_3(bpy)$ in pyridine is very slow. In this complex, the labile trans position is occupied by a pyridyl group. Substitution of chloride by pyridine is expected to be extremely slow, because it would take place in a position cis to the nitrido ligand. Such substitution is inherently much slower than in a trans position; moreover the rate is reduced because of the electron-withdrawing effects of the pyridyl groups already in place. These arguments suggest that some of the complexes we have prepared have not necessarily adopted their most stable geometrical structures but rather those dictated by kinetic influences. Thus, the structure we haved assigned to $OsNCl_3(bpy)$ is that expected to be the first to form (a configuration in which a labile and a substitution-inert site are occupied will form more readily than one in which both sites are of the second type) though it may not be the more stable.

The MO diagram for $[OsNCl_5]^-$, in respect to the relative ordering of the orbitals, is likely to be the same as that of the Ru analogue, and the discussion that follows is based on the figure published by Dubois and Hoffmann,[17] where d_{xy}, d_{xz}, d_{yz}, and d_{z^2} together with the three p orbitals of N^{3-} lead to the ranking 1e, $1a_1$, b_2, 2e, and 2a, in order of decreasing stability, b_2 being the HOMO.

When the nitrido ligands are brought together, a colinear approach is not a favorable geometry. The interaction most favoring bonding would be that of a filled 1e orbital of one partner with an unoccupied 2e orbital of another, but this would take effect only at short distances, where repulsions arising from the interaction of electrons in the filled $1a_1$ orbitals would be severe. A more favorable approach is indicated in the following sketch where now a filled $1a_1$ orbital can overlap with a 2e orbital, without suffering antibonding interactions to the same extent as in a colinear approach:



It is to be noted that the $1a_1$ orbitals are higher in energy than the 1e to begin with, and the bonding interactions already existing in the chloro complex are improved when Cl^- is partially replaced by pyridyl groups. The interaction of the π^* orbitals of the pyridyl ligands cis to the nitride will lower the energy of one of the 2e orbitals. Moreover, to the extent that the ligand trans to nitride is a good electron donor, the energy of the $1a_1$ orbitals is raised. What this analysis suggests is that in activating $[OsNCl_3(pic)_2]$ by replacing Cl^- in the trans position NH_3 or alkoxide ion would be more effective than a pyridyl group, a possibility that unfortunately was not tested.

The MO rationalization can also be employed to account for the more facile coupling when **10** is electrochemically reduced to Os(V). Reduction of **10** places an electron in a 2e orbital that is the LUMO in this system. These orbitals are π^* levels and are antibonding with respect to the metal–nitride bond. Population of this antibonding orbital weakens the metal–nitride bond and provides a strong driving force for coupling. Coupling leaves the electron in a t_{2g} orbital, which can back-bond with the dinitrogen ligand.

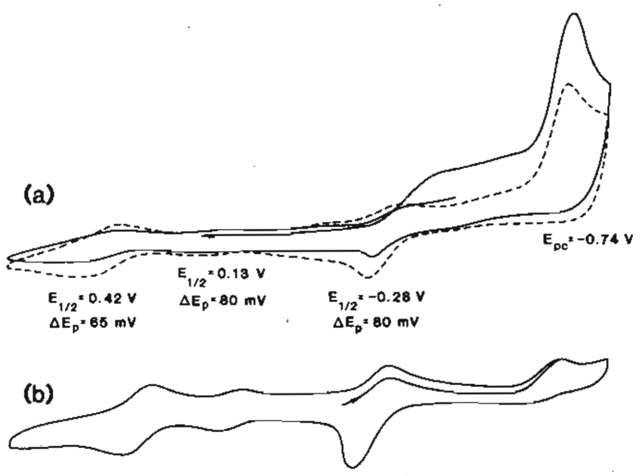


Figure 5. Cyclovoltammetric properties of $[OsNCl_2(terpy)]PF_6$ (5×10^{-3} M) in 0.1 M TBAB/CH_3CN (room temperature; sweep rate 100 mV s^{-1}; Pt working electrode; reference electrode Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN): (a) Full line, trace for first cycle; broken line, trace for fifth continuous cycle; (b) trace after electrochemical reduction at controlled potential (-1.0 V vs $Ag/AgNO_3$) (Pt gauze working electrode; 0.80 equiv passed).

It should be noted that N–N coupling in the oxidation state VI to produce a μ-N_2 species leaves the osmium atoms in the oxidation state III. When, as in this case, the metals bear π acids as auxiliary ligands, such species are rather unstable with respect to nitrogen loss, and it is therefore remarkable that a μ-N_2 complex survives. To withstand the separation procedure, at least one osmium atom in each binuclear complex must be reduced to the 2+ state. The stoichiometry of this reduction is not known, but it is reasonable to suppose that it takes place at the expense of oxidizing some osmium to a state above 3+, with concomitant loss of N_2. In any case, it is not surprising that the yield of μ-N_2 species is far from quantitative. The coupling to a binuclear species brought about by reduction of **10** at a cathode in solution is quite efficient. When even one of the participants in the coupling to form a μ-N_2 species is reduced to the 5+ state, coupling is favored compared to Os(VI) reacting with Os(VI), because now one of the metal atoms in the final product is in the 2+ state and can take advantage of stabilization by back-bonding. Coupling of this kind has literature precedent: irradiation of a solution of $[Os^{VI}N(NH_3)_4](CF_3SO_3)_3$ in CH_3CN containing also an electron donor leads to the formation of $\{[Os(NH_3)_4(CH_3CN)]_2(\mu\text{-}N_2)\}^{5+}$ in good yield.[18] It should be noted that the electrochemical results we report differ from those described for the same cation in CH_3CN but with 3 M HCl also present.[19] As is to be expected, protonation of an Os(V) species would tend to favor reduction to mononuclear ammine species.[1,19]

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Registry No. **1**, 136599-31-0; **2**, 61558-07-4; **3**, 136538-71-1; **4**, 136538-72-2; **6**, 136538-69-7; **7**, 136538-65-3; **8**, 136538-66-4; **9**, 136538-67-5; **10**, 127571-48-6; **11**, 136569-04-5; **12**, 136538-74-4; $\mathbf{12}^{2+}$, 136538-75-5; **12**·Cl, 136538-68-6; $[OsNCl_3(\eta^2\text{-terpy})]$, 136538-70-0; N^{3-}, 18851-77-9; N_2, 7727-37-9; $[n\text{-}Bu_4N][OsNCl_4]$, 42531-46-4; *fac-mer*-$[(pic)_3Cl_2OsN{\equiv}NOsCl_2(pic)_3]$ (isomer 1), 136656-37-6; *fac-mer*-$[(pic)_3Cl_2OsN{\equiv}NOsCl_2(pic)_3]$ (isomer 2), 136538-73-3.

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(17) Dubois, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1977**, *1*, 479.

(18) Che, C.-M.; Lam, H.-W.; Tong, W.-F.; Lau, T.-F.; Lau, T.-C. *J. Chem. Soc., Chem. Commun.* **1989**, 1883.

(19) Pipes, D. W.; Bakir, M.; Vitols, S. E.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5507.