Reactivity of Osmium(VI) Nitrides with the Azide Ion. A New Synthetic Route to Osmium(II) Polypyridyl Complexes

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There is an extensive reactivity chemistry between *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ (**1**) (tpy = 2,2′:6′,2″-terpyridine) and N_3^-. Reaction of **1** with N_3^- in CH_2Cl_2 or acetone occurs by electron transfer to give *trans,trans*-$(tpy)(Cl)_2$-$Os^{II}(N_2)Os^{II}(Cl)_2(tpy)$. In CH_3CN, *trans*-$Os^{II}(tpy)(Cl)_2(N_2)$ forms but undergoes solvolysis to give *trans*-$Os^{II}(tpy)(Cl)_2(CH_3CN)$. **1** reacts with excess N_3^- in CH_3CN to give $Os^{III}(tpy)(Cl)_2(5\text{-}CH_3\text{-tetrazolate})$, which has been characterized by X-ray crystallography. This is the first known Os−tetrazolato complex. **1** reacts with N_3^- in the presence of CS_2 to give *trans*-$[Os^{II}(tpy)(Cl)_2(NS)]^+$, SCN^-, and N_2.

Introduction

In an earlier communication we reported that an extensive chemistry exists between the azide ion (N_3^-) and the Os^{VI} nitrido, *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$, **1a** (tpy = 2,2′:6′,2″-terpyridine).[1] In this manuscript we present a full account of this reactivity which includes formation of terminally bound N_2 Os^{II} and Os^{III} nitriles, Os^{II} thionitrosyls, and Os^{III} tetrazoles, as well as one-electron transfer and coupling to give a μ-N_2 dimer. This adds to the existing chemistry of **1a** which includes *trans* → *cis* isomerization,[2] reversible $4e^-$, $3H^+$ reduction to Os^{II} ammine,[3] oxo transfer from $O=NMe_3$ to give Os^{II} nitrosyl,[4] nucleophilic attack by PR_3 to give Os^{IV} phosphoraniminato,[5] and one-electron reduction of **1a**, followed by N−N coupling to give an $Os^{II}(N_2)Os^{II}$ dimer.[6]

Experimental Section

The following compounds and salts appear in this study: *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](Cl)$ (**1a**); *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (**1b**); *trans*-$[Os^{VI}(tpy)(Cl)_2(^{15}N)](PF_6)$ (**1b***); *cis*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (**1c**); *trans*-$Os^{II}(tpy)(Cl)_2(N_2)$ (**2**); *trans*-$Os^{II}(tpy)(Cl)_2(NCCH_3)$ (**3**); *trans*-Os^{II}-$(tpy)(Cl)_2(NCC_5H_6)$ (**4**); *trans*-$Os^{II}(tpy)(Cl)_2(NCCH_2CH_2CH_3)$ (**5**); *trans*-$Os^{II}(tpy)(Cl)_2(NCCH=CH_2)$ (**6**); *trans,trans*-$(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2$-$(tpy)$ (**7**); *trans*-$[Os^{III}(tpy)(Cl)_2(NCCH_3)](PF_6)$ (**8**); *cis*-$[Os^{III}(tpy)(Cl)_2$-$(NCCH_3)](PF_6)$ (**9**); *cis*-$Os^{III}(tpy)(Cl)_2(N_3)$ (**10**); *trans*-$Os^{II}(tpy)(Cl)_2$-(py) (**11**); *trans*-$Os^{II}(tpy)(Cl)_2(4\text{-}(CH_3)_3C\text{-py})$ (**12**); *trans*-$[Os^{III}(tpy)(Cl)_2$-$(5\text{-}CH_3\text{-tetrazolate})]$ (**13**); *trans*-$[Os^{II}(tpy)(Cl)_2(NS)](SCN)$ (**14**); *trans*-$[Os^{II}(tpy)(Cl)_2(^{15}NS)](SCN)$ (**14***); *cis*-$[Os^{II}(bpy)_2(Cl)(NCCH_3)](PF_6)$ (**15**).

Abbreviations used in the text include the following: tpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine; py = pyridine; PPN = bis-(triphenylphosphoranylidene)ammonium cation; Fc^+ = ferrocenium

cation; S = solvent; tetr = tetrazolate anion; TBAH = tetra-*n*-butylammonium hexafluorophosphate; DMF = dimethylformamide; DMSO = dimethyl sulfoxide.

Materials. Acetonitrile (CaH_2) and dichloromethane (P_2O_5) were dried and distilled under argon and were subsequently deoxygenated by purging with nitrogen prior to use. DMF was distilled from CaH_2 under reduced pressure. DMSO was used as received. Deuterated solvents and isotopically labeled reagents were purchased from Cambridge Isotope Laboratories and used as received. TBAH was recrystallized three times from boiling ethanol and dried under vacuum at 120° for 2 days. All nitriles were obtained from Aldrich and used without further purification. $HBF_4 \cdot Et_2O$ was purchased from Aldrich and stored in a refrigerator.

Physical Measurements and Instrumentation. Electronic absorption spectra were recorded on Beckman 2000, OLIS−modified Cary 14, or Hewlett-Packard 8452A diode array UV−visible spectrophotometers in quartz cuvettes. Electrochemical measurements were carried out in CH_3CN solutions with 0.1 M TBAH as the supporting electrolyte or in aqueous solutions of varying ionic compositions. A platinum bead working electrode was used for measurements in CH_3CN or CH_2-Cl_2, and a Teflon-sheathed glassy carbon working electrode (Bioanalytical Systems, West Lafayette, IN) was used for measurements in aqueous solutions. The surface of the glassy carbon electrode was polished with diamond paste before use. All potentials are referenced to the saturated sodium chloride calomel electrode (SSCE, 0.24 V vs NHE), unless otherwise noted, at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed with the use of a PAR 173 galvanostat/potentiostat. A PAR 179 digital coulometer was used in conjunction with a PAR 173 galvanostat/potentiostat for coulometry experiments. Infrared spectra were recorded as KBr pellets on a Nicolet 20DX FT-IR spectrometer.

Synthesis and Characterization of Compounds and Salts. The salts *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](Cl)$ (**1a**),[2] *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (**1b**),[2] *trans*-$[Os^{VI}(tpy)(Cl)_2(^{15}N)](PF_6)$ (**1b***),[3] *cis*-$[Os^{VI}(tpy)(Cl)_2(N)]$-(PF_6) (**1c**),[2] *trans*-$[Os^{IV}(tpy)(Cl)_2(NPPh_3)](PF_6)$,[5] and *cis*-$[Os^{II}(bpy)_2(Cl)$-$(NCCH_3)](PF_6)$ (**15**)[7] were prepared according to literature procedures.

Bis(triphenylphosphoranylidene)ammonium Azide, $(PPN)N_3$. This reagent was prepared by mixing equimolar amounts of $(PPN)Cl$ and NaN_3 in EtOH. Stirring for 5 h, filtration (to remove NaCl), evaporation of the solvent, and recrystallization from CH_3CN/Et_2O afforded a white powder in nearly quantitative yield. Infrared (cm^{-1}, KBr disks): ν-(N_3) 2013, $\nu(P=N)$ 1114.

Reaction of *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (1b) with $(PPN)N_3$. An amount of *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (**1b**, 50 mg, 75 μmol) was

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(5) (a) Demadis, K. D.; Bakir, M.; Klesczewski, B. G.; Williams, D. S.; White, P. S.; Meyer, T. J. *Inorg. Chim. Acta* **1998**, *270*, 511. (b) Bakir, M.; White, P. S.; Dovletoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2835.
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dissolved in 20 mL of CH_3CN, and $(PPN)N_3$ (45 mg, 75 μmol) was added to it immediately as a solid in small portions. Some effervescence was noted, the solution became very dark in color, and a black powder started precipitating. After being stirred for 30 min, the solution was filtered and the black powder was isolated. It is a mixture of *trans*-Os^{II}(tpy)(Cl)$_2$(N$_2$) (**2**, minor product) and *trans*-Os^{II}(tpy)(Cl)$_2$-(NCCH$_3$) (**3**, major product). Pure **3** can be obtained by recrystallization from a 5:1:10 mixture of DMF/CH$_3$CN/Et$_2$O. Yield: quantitative. Anal. Calcd for OsCl$_2$N$_4$C$_{17}$H$_{14}$·DMF (MW 608.5): C, 39.44; H, 3.45; N, 11.50. Found: C, 39.06; H, 3.69; N, 11.22.

Following the same method as above for **3** and with the appropriate nitrile as solvent gave a variety of Os^{II} nitriles.

***trans*-Os^{II}(tpy)(Cl)$_2$(NCC$_6$H$_5$) (4).** Yield: 58%. Anal. Calcd for OsCl$_2$N$_4$C$_{22}$H$_{16}$ (MW 597.5): C, 44.22; H, 3.02; N, 10.57. Found: C, 43.53; H, 3.69; N, 9.73.

***trans*-Os^{II}(tpy)(Cl)$_2$(NCCH$_2$CH$_2$CH$_3$) (5).** Yield: 49%. Anal. Calcd for OsCl$_2$N$_4$C$_{19}$H$_{18}$ (MW 563.5): C, 40.46; H, 3.19; N, 9.94. Found: C, 40.31; H, 3.40; N, 9.86.

***trans*-Os^{II}(tpy)(Cl)$_2$(NCCH=CH$_2$) (6).** Yield: 90%. Anal. Calcd for OsCl$_2$N$_4$C$_{18}$H$_{14}$ (MW 547.5): C, 39.45; H, 2.56; N, 10.23. Found: C, 39.53; H, 2.90; N, 10.97.

***trans,trans*-(tpy)(Cl)$_2$Os^{II}(N$_2$)Os^{II}(Cl)$_2$(tpy) (7).** An amount of *trans*-[Os^{VI}(tpy)(Cl)$_2$(N)](PF$_6$) (**1b**, 50 mg, 75 μmol) was dissolved in 20 mL of CH$_2$Cl$_2$, and (PPN)N$_3$ (45 mg, 75 μmol) was added to it as a solid very slowly in small portions. The solution became very dark blue in color, and a black powder started precipitating. After being stirred for 30 min, the solution was filtered and a black powder was isolated. It was washed with small amounts of CH$_3$CN, CH$_2$Cl$_2$, and 3 × 30 mL portions of anhydrous Et$_2$O and finally air-dried. Yield: 87%. The resulting material can be purified by recrystallization from DMF/Et$_2$O. Anal. Calcd for Os$_2$Cl$_4$N$_8$C$_{30}$H$_{22}$·2DMF (MW 1162.9): C, 37.15: H, 3.10; N, 12.04. Found: C, 37.24; H, 3.04; N, 13.90. Infrared (cm^{-1}, KBr disks): ν(N≡N) 2035 (vw); ν(^{15}N≡^{15}N) 1972 (vw); ν(tpy) 1448 (vs), 1435 (vs), 1383 (vs). **7** can be also prepared in excellent yields by reacting **1b** with Et$_3$N or Et$_4$SH in CH$_3$CN.

***trans*-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](PF$_6$) (8). Method A.** To an amount of *trans*-[Os^{VI}(tpy)(Cl)$_2$(N)](PF$_6$) (100 mg, 94 μmol) was added 1 equiv of Fc(PF$_6$) (31 mg, 94 μmol). Then, (PPN)N$_3$ (55 mg, 94 μmol) was added to the mixture in small portions. The color changed to brown-yellow. Precipitation with ether and recrystallization from CH$_3$CN/Et$_2$O afforded a brown-black microcrystalline material. Yield: 82%. Anal. Calcd for OsCl$_2$BF$_4$N$_4$C$_{17}$H$_{14}$ (MW 680.3): C, 29.99; H, 2.06; N, 8.23. Found: C, 29.91; H, 1.83; N, 8.31.

Method B. An amount of *trans*-[Os^{IV}(tpy)(Cl)$_2$(NPPh$_3$)](PF$_6$) (100 mg, 94 μmol) was dissolved in CH$_3$CN (40 mL), and a few drops of HBF$_4$×Et$_2$O were added under vigorous stirring. The color changed from deep brown to brown-yellow, and the reaction mixture was stirred for 1 h. Filtration and addition of Et$_2$O (100 mL) caused a brown powder to precipitate. Final recrystallization from CH$_3$CN/Et$_2$O gave an analytically pure material. The properties of this salt, formulated as *trans*-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](BF$_4$), match those of the material from method A.

***cis*-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](BF$_4$) (9).** This salt was prepared by following method A for *trans*-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](PF$_6$) (**8**) and starting with *cis*-[Os^{VI}(tpy)(Cl)$_2$(N)](PF$_6$) (**1c**) and Fc(BF$_4$). Anal. Calcd for OsCl$_2$BF$_4$N$_4$C$_{17}$H$_{14}$ (MW 622.2): C, 32.79; H, 2.25; N, 9.00. Found: C, 32.76; H, 2.52; N, 9.30. The cis configuration was confirmed by X-ray crystallography (see below).

***cis*-Os^{III}(tpy)(Cl)$_2$(N$_3$) (10).** *trans*-[Os^{VI}(tpy)(Cl)$_2$(N)](Cl) (**1a**, 200 mg, 0.37 mmol) was dissolved in H$_2$O (20 mL). After being stirred for 30 min the solution turned from pink to tan, indicating the formation of *cis*-[Os^{VI}(tpy)(Cl)$_2$(N)](Cl) (**1c**). At this point, NaN$_3$ (48 mg, 0.72 mmol) was added to it as a solid. Vigorous evolution of a gas was observed, and the solution became dark in color, while a black powder began to precipitate. After being stirred for 2 h the mixture was filtered and a black microcrystalline solid was isolated. This was washed several times with H$_2$O and Et$_2$O and air-dried. Yield: 154 mg (78%). Anal. Calcd for OsCl$_2$N$_6$C$_{15}$H$_{11}$ (MW 536.4): C, 33.56; H, 2.05; N, 15.66. Found: C, 33.00; H, 2.24; N, 15.23. Infrared (cm^{-1}, KBr disks): ν(N$_3$) 2041.

***cis*-Os^{III}(tpy)(Cl)$_2$(^{15}N$_3$) (10*)** was prepared by the same method by using N$_3$$^-$ labeled at the α-nitrogen. Infrared (cm^{-1}, KBr disks): ν(^{15}N$_3$) 2033.

Following the same method as above for **3** and by using the appropriate pyridine as solvent, the following Os^{II} pyridine complexes were synthesized.

***trans*-Os^{II}(tpy)(Cl)$_2$(py) (11).** Yield: 65%. Anal. Calcd for OsCl$_2$N$_4$C$_{20}$H$_{15}$ (MW 573.1): C, 41.88; H, 2.62; N, 9.77. Found: C, 41.21; H, 2.78; N, 9.62.

***trans*-Os^{II}(tpy)(Cl)$_2$(^{t}Bu-py) (12).** Yield: 70%. Anal. Calcd for OsCl$_2$N$_4$C$_{24}$H$_{24}$ (MW 629.6): C, 45.74; H, 3.81; N, 8.89. Found: C, 45.17; H, 4.29; N, 9.49.

***trans*-Os^{III}(tpy)(Cl)$_2$(5-CH$_3$-tetrazolate) (13). Method A.** *trans*-[Os^{VI}(tpy)(Cl)$_2$(N)] (PF$_6$) (**1b**, 23 mg, 35.2 μmol) was dissolved in 10 mL of CH$_3$CN and (PPN)N$_3$ (0.04 g, 71 μmol) rapidly added. The solution was stirred for 3 h and filtered. Addition of 50 mL Et$_2$O to the filtrate caused the precipitation of a brown powder. This was recrystallized from CH$_3$CN/DMF/Et$_2$O mixtures to give black crystals. Yield: 16 mg (70%). Anal. Calcd for OsCl$_2$N$_7$C$_{17}$H$_{14}$·DMF (MW 650.5): C, 36.89; H, 3.23; N, 17.22. Found: C, 36.29; H, 3.32; N, 16.69.

Method B. *trans*-Os^{II}(tpy)(Cl)$_2$(NCCH$_3$), **3**, was allowed to react with (PPN)N$_3$ in a 1:1 ratio in CH$_3$CN. After the solution was stirred for 3 h, Et$_2$O was added to precipitate **3** as a brown solid in quantitative yield. This compound exhibits spectroscopic characteristics identical to the one obtained by method A.

trans*-[Os^{II}(tpy)(Cl)$_2$(NS)](SCN) (14).** A quantity of *trans*-[Os^{VI}-(tpy)(Cl)$_2$(N)](PF$_6$) (**1b**, 30 mg, 46 μmol) was dissolved in 5 mL of acetone. To this solution was added 20 mL of CS$_2$. A solution of (PPN)N$_3$ (27 mg, 46 mmol) in 20 mL of acetone was added to the above mixture dropwise while stirring, which caused the color of the solution to turn dark brown. The reaction mixture was stirred at room temperature for 2 h. During that time a brown solid formed. This solid was filtered off, washed with acetone and Et$_2$O, and recrystallized from DMF/Et$_2$O to afford golden-brown crystals. Yield: 27 mg (82%). Anal. Calcd for OsCl$_2$S$_2$N$_5$C$_{16}$H$_{11}$ (MW 598.94): C, 32.06, H, 1.85, N; 11.69. Found: C, 31.63, H, 2.07, N, 11.46. Infrared (cm^{-1}, KBr disks): ν(^{14}N≡S) 1295 (vs); ν(tpy) 1476 (vs), 1450 (vs), 1384 (vs); ν(SCN) 2047 (vs). The salt *trans*-[Os^{II}(tpy)(Cl)$_2$(^{15}NS)](SCN) (**14) was prepared by the same method starting with *trans*-[Os^{VI}(tpy)(Cl)$_2$-(^{15}N)](PF$_6$) (**1b***). Infrared (cm^{-1}, KBr disks): ν(^{15}N≡S) 1265 (vs).

Reaction of *cis*-Os^{III}(tpy)(Cl)$_2$(N$_3$) (10) with Ce^{IV}. An amount of **10** (20 mg, 37 μmol) was suspended in H$_2$O (20 mL). To that suspension, Ce(NH$_4$)$_2$(NO$_3$)$_6$ (41 mg, 75 μmol) was added. While the mixture was stirred vigorously, intense bubbling was noted and the color of the solution became tan. Stirring was continued until effervescence ceased (1 h). The resulting solution had a UV−vis spectrum identical with that of *cis*-[Os^{VI}(tpy)(Cl)$_2$(N)]$^+$ (**1c**).[2] Quantitation based on ϵ = 250 M^{-1} cm^{-1} for the absorption band at 470 nm showed that conversion of **10** to **1c** was quantitative.
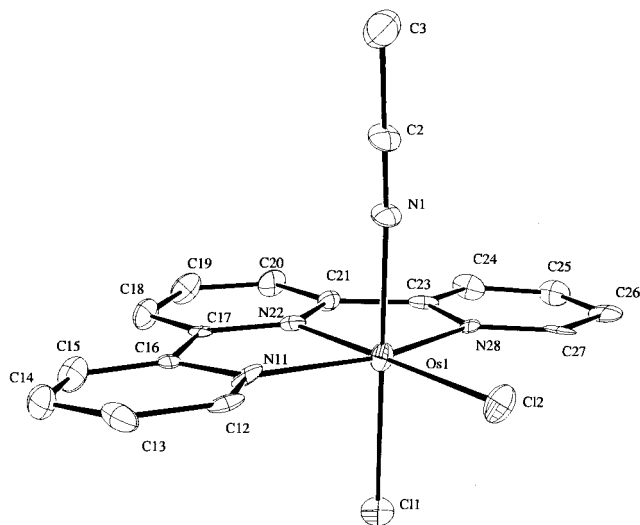
X-ray Structural Determinations. Data Collection, Solution, and Refinement of the Structures. Single crystals of **13** and **14** were obtained by slow diffusion of Et$_2$O into DMF solutions of the salts. Single crystals of **9** and **15** were obtained by slow diffusion of Et$_2$O into CH$_3$CN solutions of the salts. Crystal data, intensity collection information, and structure refinement parameters for the structures are provided in Table 1. The structures were solved by either Patterson or direct methods. The remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Empirical absorption corrections were applied for all structures with DIFABS or SADABS. The ORTEP plotting program was used to computer generate the structures shown in Figures 1−3.[8] An ORTEP diagram for **13** has been published.[1] Hydrogen atoms were included in calculated positions with thermal parameters derived from the atom to which they were bonded. All computations were performed by using the NRCVAX suite of

(8) Johnson, C. K. *ORTEP: A Fortran thermal ellipsoid plot program*; Technical Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 1. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for *cis*-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](PF$_6$) (**9**), *trans*-[Os^{III}(tpy)(Cl)$_2$(5-CH$_3$-tetrazolate) (**13**), *trans*-[Os^{II}(tpy)(Cl)$_2$(NS)](SCN) (**14**), and *cis*-[Os^{II}(bpy)$_2$(Cl)(NCCH$_3$)](PF$_6$) (**15**)

compd	**9**	**13**	**14**	**15**
formula	OsCl$_2$C$_{17}$H$_{14}$BF$_4$N$_4$	OsCl$_2$C$_{17}$H$_{15}$N$_7$·DMF	OsCl$_2$C$_{16}$H$_{11}$S$_2$N$_5$	OsClC$_{22}$H$_{19}$OPF$_6$N$_5$·Et$_2$O
MW	622.23	604.47	598.52	798.16
a (Å)	8.518(2)	22.321(5)	24.785(4)	10.6156(5)
b (Å)	12.234(2)	13.146(2)	11.766(3)	11.4668(5)
c (Å)	18.783(6)	14.549(5)	13.090(3)	12.7977(6)
α (deg)	90	90	90	70.957(1)
β (deg)	92.88(2)	105.37(2)	104.07(2)	85.743(2)
γ (deg)	90	90	90	82.762(2)
V (Å^3)	1954.8(8)	4116(2)	3703(1)	1459.9(1)
Z	4	8	8	2
cryst system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$
cryst size (mm)	0.4 × 0.2 × 0.1	0.15 × 0.20 × 0.45	0.08 × 0.10 × 0.50	0.20 × 0.25 × 0.10
d_{calcd} (g/cm^3)	2.114	1.951	2.147	1.816
diffractometer	Rigaku	Rigaku	Rigaku	Siemens SMART diffr
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)	Mo Kα ($\lambda = 0.710\ 73$ Å)	Mo Kα ($\lambda = 0.710\ 73$ Å)	Mo Kα ($\lambda = 0.710\ 73$ Å)
collcn temp (°C)	−100	−100	−100	−100
abs coeff μ, cm^{-1}	6.84	6.47	7.41	4.58
$F(000)$	1178.47	2304.59	2270.41	779.30
$2\theta_{max}$ (deg)	46	50	50	60
tot. reflcns	4034	6586	3246	20 666
unique reflcns	2712	3625	3246	8220
refined reflcns	1999	2860	2275	7927
merging R value	0.048	0.038	0.035	0.025
no. of params	262	266	235	370
R (%)^a	5.3	3.0	3.6	2.3
R_w (%)^b	6.3	3.7	3.7	3.0
goodness of fit^c	2.00	1.21	1.27	2.01
deepest hole (e/Å^3)	−2.750	−1.050	−0.920	−1.950
highest peak (e/Å^3)	3.580	1.260	1.160	1.610

^{a} $R = \sum(|F_o - F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum(w|F_o - F_c|)^2/\sum w(F_o)^2]^{1/2}$. ^{c} GoF $= [\sum w(F_o - F_c)^2/(\text{no. of reflections} - \text{no. of parameters})]^{1/2}$.

Figure 1. ORTEP diagram (30% probability ellipsoids) for the *cis*-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)]$^+$ cation in **9**.

Figure 2. ORTEP diagram (30% probability ellipsoids) for the *cis*-[Os^{II}(bpy)$_2$(Cl)(NCCH$_3$)]$^+$ cation in **15**.

programs.[9] Atomic scattering factors were taken from a standard source[10] and corrected for anomalous dispersion.

The crystal of **13** contains one molecule of dimethylformamide per asymmetric unit, which exhibited some disorder. This disorder was modeled successfully. The crystal of **15** contains one molecule of diethyl ether per asymmetric unit. The final positional parameters, along with their standard deviations as estimates from the inverse matrix, and tables of hydrogen atom parameters and anisotropic thermal parameters are available as Supporting Information. Bond lengths and angles of the compounds are given in Tables 2−5.
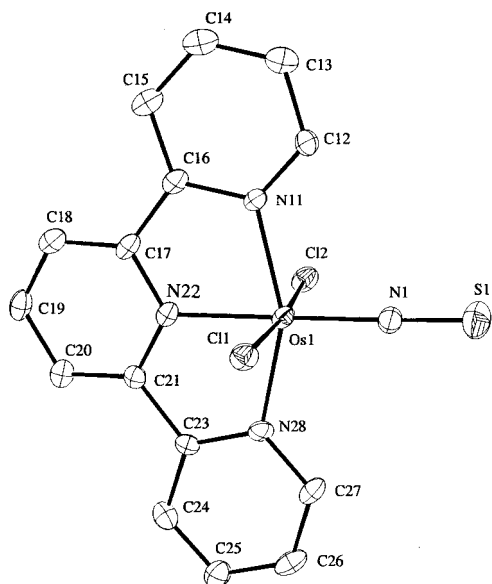
Results

Synthetic Studies. Addition of stoichiometric amounts of N$_3^-$ to magenta *trans*-[Os^{VI}(tpy)(Cl)$_2$(N)]$^+$ in CH$_3$CN causes an immediate reaction that yields a mixture of products. The minor product is **2**, and the major product is **3**. They form roughly in a 1:3 ratio. Both compounds precipitate from CH$_3$-CN and are isolated as black powders. **2** was detected by infrared spectroscopy from its characteristic ν(N≡N) stretch at 2090 cm^{-1} in KBr. Allowing **1b*** to react with N$_3^-$ in CH$_3$CN

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(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmigham, U.K., 1974; Vol. IV.

Figure 3. ORTEP diagram (30% probability ellipsoids) for the cation *trans*-[Os^{II}(tpy)(Cl)$_2$(NS)]$^+$ in **14**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for *cis*-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](PF$_6$) (**9**)

Bonds			
Os(1)−Cl(1)	2.346(4)	Os(1)−N(22)	1.995(12)
Os(1)−Cl(2)	2.354(4)	Os(1)−N(28)	2.063(12)
Os(1)−N(1)	2.039(13)	N(1)−C(2)	1.102(21)
Os(1)−N(11)	2.072(12)	C(2)−C(3)	1.46(3)

Angles			
Cl(1)−Os(1)−Cl(2)	91.84(15)	Cl(2)−Os(1)−N(28)	100.8(3)
Cl(1)−Os(1)−N(1)	179.8(4)	N(1)−Os(1)−N(11)	87.8(5)
Cl(1)−Os(1)−N(11)	92.3(4)	N(1)−Os(1)−N(22)	92.6(5)
Cl(1)−Os(1)−N(22)	87.6(4)	N(1)−Os(1)−N(28)	92.7(5)
Cl(1)−Os(1)−N(28)	87.3(3)	N(11)−Os(1)−N(22)	79.3(5)
Cl(2)−Os(1)−N(1)	87.9(4)	N(11)−Os(1)−N(28)	158.7(5)
Cl(2)−Os(1)−N(11)	100.4(4)	N(22)−Os(1)−N(28)	79.4(5)
Cl(2)−Os(1)−N(22)	179.4(4)	Os(1)−N(1)−C(2)	174.9(13)
		N(1)−C(2)−C(3)	178.8(17)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for *trans*-[Os^{III}(tpy)(Cl)$_2$(5-CH$_3$-tetrazolate) (**13**)

Bonds			
Os(1)−Cl(1)	2.3453(18)	N(19)−N(20)	1.321(9)
Os(1)−Cl(2)	2.3425(18)	C(22)−N(23)	1.328(9)
Os(1)−N(1)	2.087(5)	N(19)−N(23)	1.328(8)
Os(1)−N(12)	1.990(5)	N(20)−N(21)	1.345(9)
Os(1)−N(18)	2.085(6)	N(21)−C(22)	1.323(11)
Os(1)−N(19)	2.093(5)	C(22)−C(24)	1.484(11)

Angles			
Cl(1)−Os(1)−Cl(2)	178.86(6)	N(12)−Os(1)−N(18)	79.1(2)
Cl(1)−Os(1)−N(1)	89.30(14)	N(18)−Os(1)−N(19)	101.1(2)
Cl(1)−Os(1)−N(12)	92.47(15)	N(20)−N(21)−C(22)	105.9(6)
Cl(1)−Os(1)−N(18)	89.67(16)	N(19)−N(20)−N(21)	107.1(6)
Cl(1)−Os(1)−N(19)	90.55(16)	N(20)−N(19)−N(23)	110.9(5)
Cl(2)−Os(1)−N(12)	88.59(15)	N(20)−N(19)−N(23)	110.9(5)
Cl(2)−Os(1)−N(1)	90.46(14)	N(21)−C(22)−N(23)	111.6(6)
Cl(2)−Os(1)−N(18)	90.96(16)	N(21)−C(22)−C(24)	124.3(7)
Cl(2)−Os(1)−N(19)	88.40(16)	N(23)−C(22)−C(24)	124.1(7)
N(1)−Os(1)−N(12)	79.5(2)	N(19)−N(23)−C(22)	104.4(6)
N(1)−Os(1)−N(18)	158.5(2)	N(12)−Os(1)−N(19)	177.0(2)
N(1)−Os(1)−N(19)	100.5(2)		

afforded a mixture of **3** and *trans*-Os^{II}(tpy)(Cl)$_2$(^{15}N≡N) (**2***) for which ν(^{15}N≡N) = 2062 cm^{-1} in KBr. The shift is consistent with the increase in reduced mass. Portions of the infrared spectra which illustrate the isotopic shift for mixtures of **2** and **3** and **2*** and **3** are provided in the Supporting
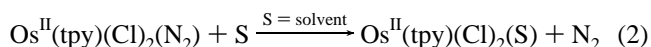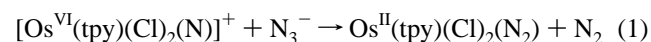
Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for *trans*-[Os^{II}(tpy)(Cl)$_2$(NS)](SCN) (**14**)

Bonds			
Os(1)−Cl(1)	2.3663(22)	Os(1)−N(22)	2.032(7)
Os(1)−Cl(2)	2.3600(22)	Os(1)−N(28)	2.084(7)
Os(1)−N(1)	1.834(7)	S(1)−N(1)	1.459(8)
Os(1)−N(11)	2.079(7)		

Angles			
Cl(1)−Os(1)−Cl(2)	174.17(8)	Cl(2)−Os(1)−N(28)	91.04(21)
Cl(1)−Os(1)−N(1)	92.40(25)	N(1)−Os(1)−N(11)	101.2(3)
Cl(1)−Os(1)−N(11)	89.85(20)	N(1)−Os(1)−N(22)	179.7(3)
Cl(1)−Os(1)−N(22)	87.67(20)	N(1)−Os(1)−N(28)	102.9(3)
Cl(1)−Os(1)−N(28)	89.11(21)	N(11)−Os(1)−N(22)	78.6(3)
Cl(2)−Os(1)−N(1)	93.24(25)	N(11)−Os(1)−N(28)	155.9(3)
Cl(2)−Os(1)−N(11)	87.63(20)	N(22)−Os(1)−N(28)	77.4(3)
Cl(2)−Os(1)−N(22)	86.68(21)	Os(1)−N(1)−S(1)	178.5(5)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for *cis*-[Os^{II}(bpy)$_2$(Cl)(CH$_3$CN)](PF$_6$) (**15**)

Bonds			
Os(1)−Cl(1)	2.4199(6)	Os(1)−N(31)	2.0440(21)
Os(1)−N(1)	2.0187(22)	Os(1)−N(41)	2.0477(21)
Os(1)−N(11)	2.0755(21)	N(1)−C(2)	1.143(3)
Os(1)−N(21)	2.0365(21)	C(2)−C(3)	1.455(4)

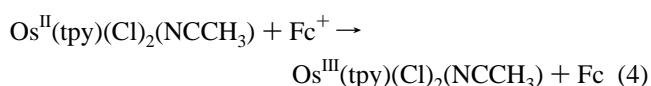| Angles			
Cl(1)−Os(1)−N(1)	90.24(6)	N(11)−Os(1)−N(31)	176.63(8)
Cl(1)−Os(1)−N(11)	96.02(6)	N(11)−Os(1)−N(41)	99.85(8)
Cl(1)−Os(1)−N(21)	173.66(6)	N(21)−Os(1)−N(31)	98.65(8)
Cl(1)−Os(1)−N(31)	86.96(6)	N(21)−Os(1)−N(41)	89.47(8)
Cl(1)−Os(1)−N(41)	88.74(6)	N(31)−Os(1)−N(41)	78.59(8)
N(1)−Os(1)−N(11)	85.62(8)	Os(1)−N(1)−C(2)	178.74(22)
N(1)−Os(1)−N(21)	92.10(8)	N(1)−C(2)−C(3)	177.7(3)
N(1)−Os(1)−N(31)	95.98(8)	Os(1)−N(11)−C(12)	125.66(18)
N(1)−Os(1)−N(41)	174.52(8)	Os(1)−N(11)−C(16)	115.86(17)
N(11)−Os(1)−N(21)	78.30(8)	C(12)−N(11)−C(16)	118.12(22)

Information. An attempt to separate neutral **2** and **3** by selective crystallization from DMF/CH$_3$CN mixtures resulted in loss of N$_2$ from **2** and isolation of pure **3** in quantitative yields. On the basis of these observations, it appears that the initial reaction with N$_3^-$ forms the N$_2$ complex, followed by solvolysis,

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + N_3^- \rightarrow Os^{II}(tpy)(Cl)_2(N_2) + N_2 \quad (1)$$

$$Os^{II}(tpy)(Cl)_2(N_2) + S \xrightarrow{\text{S = solvent}} Os^{II}(tpy)(Cl)_2(S) + N_2 \quad (2)$$

The general scope of the reaction between **1b** and N$_3^-$ was investigated by using a variety of nitriles as solvents. This led to the synthesis and isolation of compounds **4**−**6**. If pyridine or substituted pyridines are used as solvents the final products are Os^{II} pyridine complexes (compounds **11** and **12**).
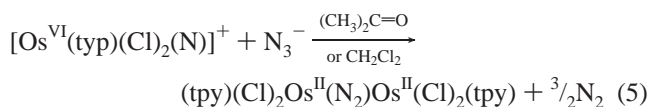
$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + N_3^- + S \xrightarrow{\text{S = RCN, py}}$$
$$Os^{II}(tpy)(Cl)_2(S) + 2N_2 \quad (3)$$

3 can be oxidized to **8** with Fc$^+$ salts in CH$_3$CN.

$$Os^{II}(tpy)(Cl)_2(NCCH_3) + Fc^+ \rightarrow$$
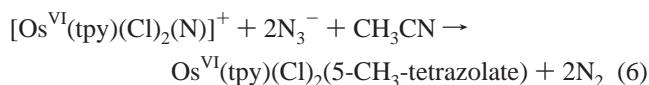$$Os^{III}(tpy)(Cl)_2(NCCH_3) + Fc \quad (4)$$

Trans → *cis* isomerization of the starting nitrido occurs in coordinating solvents such as H$_2$O, MeOH, and CH$_3$CN,[2] which provides access to the corresponding *cis*-nitrile complexes as well. Isomerization of **1b** prior to reaction with N$_3^-$ can be prevented in CH$_3$CN by rapid addition of N$_3^-$ once **1b** is dissolved.
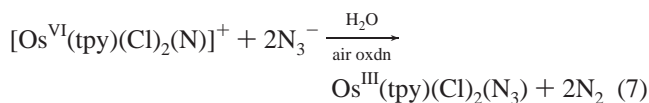
The reaction between **1b** and N_3^- is highly solvent dependent. In nonpolar solvents such as acetone or CH_2Cl_2 electron transfer occurs from N_3^- to Os^{VI} to give blue *trans,trans*-(tpy)(Cl)$_2$Os^{II}-(N$_2$)Os^{II}(Cl)$_2$(tpy) (**7**) as the product in high yield.

$$[Os^{VI}(typ)(Cl)_2(N)]^+ + N_3^- \xrightarrow[\text{or } CH_2Cl_2]{(CH_3)_2C=O}$$
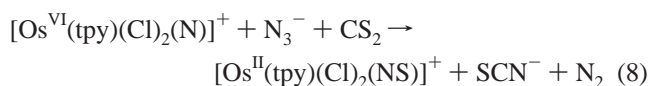$$(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy) + {}^3/_2N_2 \quad (5)$$

In CH_3CN the reaction of **1b** with N_3^- in excess takes a different course. Initial N_3^- attack on **1b** and solvolysis gives *trans*-Os^{II}(tpy)(Cl)$_2$(NCCH$_3$) (**3**). Once formed, it undergoes a second reaction with N_3^- by a [3 + 2] cycloaddition to the bound CH_3CN followed by air oxidation to give *trans*-Os^{III}(tpy)-(Cl)$_2$(5-CH$_3$-tetrazolate) (**13**). The N^2-bound isomer shown in **13** is favored on steric grounds. It forms by linkage isomerization of the initially formed N^1-bound isomer. It was shown independently that a reaction occurs between Os^{II}(tpy)(Cl)$_2$-(NCCH$_3$) and N_3^- in the presence of air to give the same product.
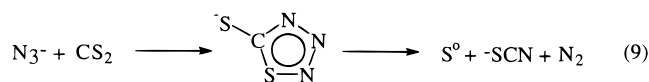
$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + 2N_3^- + CH_3CN \rightarrow$$
$$Os^{VI}(tpy)(Cl)_2(5\text{-}CH_3\text{-tetrazolate}) + 2N_2 \quad (6)$$

In H_2O with 2 equiv of N_3^-, the azido complex *cis*-Os^{III}-(tpy)(Cl)$_2$(N$_3$) (**10**) forms. Its formation can be rationalized by initial *trans → cis* isomerization of *trans*-[Os^{VI}(tpy)(Cl)$_2$(N)]$^+$, followed by attack of N_3^- on nitrido **1c** to give Os^{II}–N$_2$. Substitution of coordinated N_2 by N_3^- and final air oxidation would result in **10**.

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + 2N_3^- \xrightarrow[\text{air oxdn}]{H_2O}$$
$$Os^{III}(tpy)(Cl)_2(N_3) + 2N_2 \quad (7)$$

Reaction between **1** and N_3^- in the presence of CS_2 in acetone gives the thionitrosyl *trans*-[Os^{II}(tpy)(Cl)$_2$(NS)](SCN) (**14**).

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + N_3^- + CS_2 \rightarrow$$
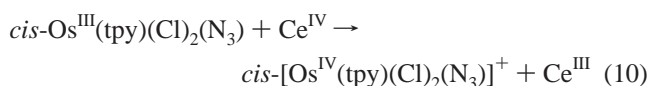$$[Os^{II}(tpy)(Cl)_2(NS)]^+ + SCN^- + N_2 \quad (8)$$

In acetone, **1b** is unreactive with CS_2 or S_8 separately. Reaction between N_3^- and CS_2 is known to occur to give the 5-thio-1,2,3,4-thiatriazolato ring anion,
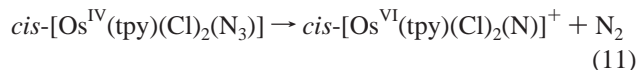
$$N_3^- + CS_2 \longrightarrow \text{[ring structure]} \longrightarrow S^\circ + {}^-SCN + N_2 \quad (9)$$

It decomposes to give SCN^-, N_2, and S^0.[11] In the presence of **1b**, nucleophilic attack on $Os^{VI}\equiv N$ by the thiolato portion of the ring takes place with sulfur atom transfer. This is accompanied by reduction of Os^{VI} to Os^{II} and formation of thionitrosyl **14**.

Finally, reaction between **10** and Ce^{IV} proceeds via initial one-electron transfer,

$$cis\text{-}Os^{III}(tpy)(Cl)_2(N_3) + Ce^{IV} \rightarrow$$
$$cis\text{-}[Os^{IV}(tpy)(Cl)_2(N_3)]^+ + Ce^{III} \quad (10)$$

followed by elimination of N_2 and formation of *cis*-[Os^{VI}(tpy)-(Cl)$_2$(N)]$^+$,

$$cis\text{-}[Os^{IV}(tpy)(Cl)_2(N_3)] \rightarrow cis\text{-}[Os^{VI}(tpy)(Cl)_2(N)]^+ + N_2$$
$$(11)$$

Structural Studies. *cis*-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](PF$_6$) (**9**) and *cis*-[Os^{II}(bpy)$_2$(Cl)(NCCH$_3$)](PF$_6$) (**15**). ORTEP diagrams of the cations of these salts are shown in Figure 1 (**9**) and Figure 2 (**15**). Having the crystal structures of **9** and **15** provides an Os^{II}–Cl and Os^{III}–Cl bond lengths comparison. Os–Cl bond lengths in Os^{III} (**9**, 2.346(4) and 2.354(4) Å) are shorter than in Os^{II} (**15**, 2.4199(6) Å). From literature structures Os^{III}–Cl bond lengths fall in the range 2.34–2.36 Å[12] and Os^{II}–Cl bond lengths fall in the range 2.43–2.45 Å.[13]

In **9** the Os–N$_{22}$ (tpy, central) bond length is 1.995(12) Å, and the Os–N$_{11}$ and Os–N$_{28}$ (tpy, peripheral) lengths are 2.072-(12) and 2.063(12) Å, respectively. The shortening of the "central" M–N(tpy) bond is a characteristic structural feature of metal–terpyridine complexes in the absence of trans influence ligands.[14] It is dictated by the geometrical constraints of tpy as a ligand and its inability to span the 180° required for a planar terdentate ligand. In **9**, $\angle N_{28}$–Os–N$_{11}$ is 158.7°.

Bond lengths within the Os–N≡CCH$_3$ unit are normal with Os–N$_1$ 2.039(13) Å typical for metal nitriles,[15] N$_1$–C$_2$ 1.102-(21) Å consistent with a N≡C triple bond, and C$_2$–C$_3$ 1.46(3) Å consistent with a C–C single bond.

In **15** the Os–N(bpy) bond distances range from 2.0365(21) to 2.0755(21) Å and are similar to Os–N(bpy) bond distances in [Os^{II}(bpy)$_3$](PF$_6$)$_2$ (2.056(8) Å). The bond lengths within the Os–N≡CCH$_3$ unit are similar to those of **9** with Os–N$_1$ 2.0187(22) Å shorter that Os–N$_1$ in **9** due to Os^{II} → NCCH$_3$ π-back-bonding, N$_1$–C$_2$ 1.143(3) Å consistent with a N≡C triple bond, and C$_2$–C$_3$ 1.455(4) Å, consistent with a C–C single bond.

***trans*-[Os^{III}(tpy)(Cl)$_2$(5-CH$_3$-tetrazolate) (13).** The crystal structure of **13** (for an ORTEP diagram, see ref 1) reveals that the *trans* geometry of the starting nitrido is retained. The 5-CH$_3$-tetrazolato ring is coplanar with tpy. N–N and C–N bond lengths within the tetrazolato ring range from 1.321(9) to 1.345(9) Å consistent with extensive π-electronic delocalization.[16] The Os–Cl bond lengths are 2.3453(18) and 2.3425-

(11) (a) Lieber, E.; Pillai, C. N.; Ramachandran, J.; Hites, R. D. *J. Org. Chem.* **1957**, *22*, 1750. (b) Lieber, E.; Oftedahl, E.; Rao, C. N. R. *J. Org. Chem.* **1963**, *28*, 194. (c) Browne, A. W.; Hoel, A. B.; Smith, G. B. L.; Swezey, F. H. *J. Am. Chem. Soc.* **1923**, *45*, 2541. (d) *Carbon Disulphide in Organic Chemistry*; Dunn, A. D., Rudorf, W.-D., Eds.; Ellis Horwood Ltd.: New York, 1989.

(12) Os^{III}–Cl bond lengths: (a) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1078. (b) Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1979**, 30. (c) Champness, N. R.; Levason, W.; Mould, R. A. S.; Pletcher, D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2777. (d) Champness, N. R.; Levason, W.; Pletcher, D.; Spicer, M. D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2201.

(13) Os^{II}–Cl bond lengths: (a) Chakravarty, A. R.; Cotton, F. A.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *84*, 179. (b) Cotton, F. A.; Diebold, M. P.; Matusz, M. *Polyhedron* **1987**, *6*, 1131. (c) Robinson, P. D.; Ali, I. A.; Hinckley, C. C. *Acta Crystallogr.* **1991**, *C47*, 651. (d) Levason, W.; Champness, N. R.; Webster, M. *Acta Crystallogr.* **1993**, *C49*, 1884.

(14) (a) Beck, J.; Schweda, E.; Strähle, J. *Z. Naturforsch.* **1985**, *B40*, 1073. (b) Bardwell, D. A.; Cargill Thompson, M. W.; McCleverty, J. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1996**, 873. (c) Constable, E. C.; Edwards, A. J.; Haire, G. R.; Hannon, M. J.; Raithby, P. R. *Polyhedron* **1998**, *17*, 243. (d) Kožíšek, J.; Jaromír, M.; Baloghová; Valigura, D. *Acta Crystallogr.* **1997**, *C53*, 1813. (e) Constable, E. C. *Metals and Ligand Reactivity*; VCH Publishers: New York, 1996, and references therein.

(15) (a) Storhoff, B. N. *Coord. Chem. Rev.* **1977**, *23*, 1. (b) Hodges, L. M.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 371.

(16) (a) Moore, D. S.; Robinson, S. D. *Adv. Inorg. Chem.* **1988**, *32*, 171. (b) Butler, R. N. In *Tetrazoles*; Katritzky, A. R., Rees, C. W., Eds.; Comprehensive Heterocyclic Chemistry 5; Pergamon Press: Oxford, U.K., 1984; p 791. (c) Koldobskii, G. I.; Ostrovskii, V. A. *Russ. Chem. Rev.* **1994**, *63*, 797.

(18) Å, consistent with Os^{III}.[12] Shortening of the central Os−N(tpy) bond length to 1.990(5) Å is apparent, compared with the peripheral Os−N(tpy) bond lengths of 2.087(5) and 2.085-(5) Å. The Os−N(tetr) bond length, 2.093(5) Å, is similar to other metal tetrazolate complexes.[17] To our knowledge, this is the first Os−tetrazolato complex which has been isolated and structurally characterized.

***trans*-[Os^{II}(tpy)(Cl)₂(NS)](SCN) (14).** The crystal structure of **14** (Figure 3) shows that the Cl⁻ ligands are in the *trans* configuration, a feature retained from **1**. Os−Cl bond distances are 2.366(2) and 2.360(2) Å. The Os−N(S) and the N−S bond distances are 1.834(7) and 1.459(8) Å. The N−S bond length in the NS⁺ ion is 1.495 Å.[18] The ∠Os−N−S is almost linear, at 178.5(5)° consistent with thionitrosyl coordinated as "NS⁺" rather than "NS⁻". In structurally characterized $Os^{II}(PPh_3)_2$-(Cl)₃(NS), Os−N(S) and the N−S bond distances are 1.779(9) and 1.503(10) Å, respectively, and ∠Os−N−S is 180.0(1)°.[19] For comparison, in *trans*-[Os^{II}(tpy)(Cl)₂(NO)](BF₄) the Os−N(O) and N−O bond distances are 1.704(14) and 1.188(19) Å and ∠Os−N−O is 176.6(10)°.[4] Os−N(thionitrosyl) bond lengths in the literature fall in the range of 1.73−1.84 Å,[19] consistent with sp hybridization if the NS ligand is treated as a 3e⁻ donor. This predicts multiple bond character in the M−N bond in agreement with the short M−N bond distances and the linearity of the thionitrosyl.

Spectroscopic and Electrochemical Studies. The results of UV−vis and electrochemical studies are compiled in Table 6. The UV−vis spectra of the Os^{II} complexes are dominated by intense $Os^{II} \rightarrow$ tpy or $Os^{II} \rightarrow$ bpy MLCT bands in the visible region and intense $\pi \rightarrow \pi^*$(tpy) or $\pi \rightarrow \pi^*$(bpy) bands in the UV region.[6,7]

For the Os^{II} and Os^{III} nitrile complexes $\nu(C\equiv N)$ appears in the infrared at 2190−2260 cm⁻¹ of medium-to-strong intensity, consistent with Os−N end-on binding.[20] $\nu(N\equiv N)$ for **2** appears at 2090 cm⁻¹, shifted by 28 cm⁻¹ to 2062 cm⁻¹ in **2*** (calculated 33 cm⁻¹). Several other N₂ complexes exhibit intense $\nu(N\equiv N)$ bands in this region.[21] For comparison, in $Os^{II}(tpm)(Cl)_2(N_2)$ $\nu(N\equiv N)$ appears at 2068 cm⁻¹ in KBr ($\nu(^{15}N\equiv^{14}N)$ at 2032 cm⁻¹).[1] In μ-N₂-bridged **7** a very weak $\nu(N\equiv N)$ stretch appears at 2035 cm⁻¹ in KBr ($\nu(^{15}N\equiv^{15}N)$ appears at 1972 cm⁻¹).

For **10** a very intense $\nu(N_3)$ vibration appears at 2041 cm⁻¹,

typical for metal azido complexes.[22] **14** exhibits an intense band at 1295 cm⁻¹ assignable to $\nu(N\equiv S)$ ($\nu(^{15}N\equiv S)$ 1265 cm⁻¹). Several Os thionitrosyl complexes have been characterized by infrared spectroscopy, and these results have been reviewed elsewhere.[23] The usual range for $\nu(N\equiv S)$ is 1150−1400 cm⁻¹. In the infrared spectrum of **13**, bands at 1094 and 1295 cm⁻¹ appear that can be assigned to tetrazolate ring modes as proposed previously.[24] Additional ring modes are expected but are apparently obscured by tpy bands.

In the electrochemical studies (Table 6), the Os^{II} and Os^{III} nitrile complexes exhibit waves corresponding to Os^{III}/Os^{II} and Os^{IV}/Os^{III} couples. More specifically, for **3** a reversible Os^{III}/Os^{II} couple appears at $E_{1/2}$ = +0.15 V and a reversible Os^{IV}/Os^{III} couple at $E_{1/2}$ = +1.46 V, in CH₂Cl₂, vs SSCE in 0.1 M TBAH. Similar results were obtained for Os^{II} nitriles **4−6**. For **8**, a reversible Os^{III}/Os^{II} couple appears at $E_{1/2}$ = +0.04 V and a reversible Os^{IV}/Os^{III} couple at $E_{1/2}$ = +1.37 V, in CH₃CN, vs SSCE in 0.1 M TBAH. For **15** there are reversible Os^{III}/Os^{II} and Os^{IV}/Os^{III} couples at $E_{1/2}$ = +0.41 V and $E_{1/2}$ = +1.87 V, respectively, in CH₃CN, vs SSCE in 0.1 M TBAH.[7] Ligand-based (bpy) reductions appear at −1.45 and −1.72 V.

In cyclic voltammograms of **10**, a reversible Os^{III}/Os^{II} wave appears at $E_{1/2}$ = +0.06 V and chemically irreversible Os^{IV}/Os^{III} couple at $E_{p,a}$ = +0.85 V in CH₃CN. After minutes, waves corresponding to the Os^{III}/Os^{II} and Os^{IV}/Os^{III} couples of **3** appear. Apparently, in this solvent $N_3^- \rightarrow Os^{III}$ intramolecular electron transfer takes place to give **3** and N₂. The Os^{II} pyridine complexes exhibit $E_{1/2}$ values for Os^{III}/Os^{II} and Os^{IV}/Os^{III} couples at +0.12 and +1.49 V, for **11**, and +0.08 and +1.46 V, for **12**, respectively. In cyclic voltammograms of **7** in DMF, reversible $Os^{III}-Os^{II}/Os^{II}-Os^{II}$ and $Os^{III}-Os^{III}/Os^{III}-Os^{II}$ couples appear at +0.21 and +0.77 V vs SSCE ($\Delta E_{1/2}$ = 560 mV). The propereties of the mixed-valence form have been described and are discussed elsewhere.[6]

$E_{1/2}$ values for the $Os^{III/II}$ and $Os^{IV/III}$ couples of **13** are −0.26 and +1.01 V, respectively, in 0.1 M TBAH, vs SSCE, in DMSO. In cyclic voltammograms of **14** in CH₃CN, a reversible ligand-based reduction wave is observed at −0.30 V vs SSCE in 0.1 M TBAH. Similar ligand-based reductions have been observed in $Os^{II}-NO$ complexes.[25] No oxidation waves are observed for **14** to the solvent limit.

Discussion

In this manuscript we document the extraordinarily rich reactivity chemistry that exists between **1** and N_3^-. It is summarized in Figure 4. In all cases, the basic chemistry is the same, attack of a redox nucleophile on a coordinated ligand, in competition with electron transfer.

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Table 6. UV–Vis, Electrochemical (0.1 M TBAH vs SSCE), and Infrared Data for Compounds **3**–**15**

complex or salt	λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$)	solvent for cyclic voltammetry	$E_{1/2}(Os^{IV/III})$, V	$E_{1/2}(Os^{III/II})$, V	other waves	IR bands, cm^{-1} (in KBr)
trans-Os^{II}(tpy)(Cl)$_2$(NCCH$_3$) (**3**)	in DMF: 736 (2900), 662 (4100), 580 (6550), 482 (8300), 418 (7300), 372 (9200), 328 (28 100), 284 (23 100), 274 (22 200)	CH$_2$Cl$_2$	+1.46	+0.15		2250, ν(C≡N)
trans-Os^{II}(tpy)(Cl)$_2$(NCC$_5$H$_6$) (**4**)	in DMF: 728 (1920), 648 (3850), 578 (5850), 474 (7090), 418 (6760), 368 (9940), 326 (22 930), 282 (21 370), 272 (22 440)	CH$_2$Cl$_2$	+1.54	+0.20		2204, ν(C≡N)
trans-Os^{II}(tpy)(Cl)$_2$-(NCCH$_2$CH$_2$CH$_3$) (**5**)	in DMF: 736 (3090), 658 (4270), 576 (6760), 480 (8410), 420 (7700), 364 (9580), 326 (31 660), 284 (25 000), 272 (24 470)	CH$_2$Cl$_2$	+1.51	+0.18		2242, 2227, ν(C≡N)
trans-Os^{II}(tpy)(Cl)$_2$(NCCH=CH$_2$) (**6**)	in DMF: 722 (1740), 648 (2610), 554 (4720), 480 (5050), 406 (4970), 368 (6360), 330 (23 560), 284 (16 440), 272 (15 510)	CH$_2$Cl$_2$	+1.54	+0.30	+0.87^a	2190, ν(C≡N); 1606, ν(C=C)
trans,trans-(tpy)(Cl)$_2$Os^{II}-(N$_2$)Os^{II}(Cl)$_2$(tpy) (**7**)	in DMF: 885 (9100), 660 (14 500), 592 (16 000), 444 (10 800), 394 (13 000), 364 (16 400), 332 (46 600), 272 (48 800)	DMF			+0.21,^{b} +0.77^c	2035, ν(N≡N)
trans-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](PF$_6$) (**8**)	in CH$_3$CN: 616 (400), 540 (1200), 516 (1700), 488 (2500), 456 (3200), 438 (3100), 396 (2400), 354 (sh, 7900), 318 (24 000), 276 (19 400), 230 (36 300)	CH$_3$CN	+1.37	+0.04		2256, 2213, ν(C≡N)
cis-[Os^{III}(tpy)(Cl)$_2$(NCCH$_3$)](PF$_6$) (**9**)	in CH$_3$CN: 604 (390), 500 (1440), 440 (3500), 374 (2950), 326 (16 290), 306 (18 800), 282 (18 720), 274 (12 990), 226 (26 300)	CH$_3$CN	+1.38	+0.03		2326, 2283, (C≡N)
cis-Os^{III}(tpy)(Cl)$_2$(N$_3$) (**10**)	in H$_2$O: 660 (2750), 470 (4320), 402 (3940), 332 (10 549), 310 (14 200), 272 (14 440), 224 (18 690)	CH$_3$CN	+0.85	+0.06		2041, ν(N$_3$)
trans-Os^{II}(tpy)(Cl)$_2$(py) (**11**)	in DMF: 754 (990), 680 (1330), 592 (2420), 496 (2760), 418 (3240), 380 (4160), 328 (8000), 275 (9000), 272 (9100)	CH$_2$Cl$_2$	+1.49	+0.12		
trans-Os^{II}(tpy)(Cl)$_2$(4-(CH$_3$)$_3$C-py) (**12**)	in DMF: 752 (800), 678 (1390), 592 (2140), 500 (2110), 420 (2510), 380 (3290), 330 (7910), 276 (8900), 270 (8980)	CH$_2$Cl$_2$	+1.46	+0.08		
trans-[Os^{III}(tpy)(Cl)$_2$(5-CH$_3$-tetr) (**13**)	in DMSO: 570 (1350), 526 (1400), 472 (1900), 406 (1800), 324 (10 300), 278 (9500)	CH$_3$CN	+1.01	−0.26		1094, 1295, ν(CH$_3$-tetr)
trans-[Os^{II}(tpy)(Cl)$_2$(NS)](SCN) (**14**)	in CH$_3$CN: 742 (110), 522 (340), 430 (600), 362 (3800), 278 (10 900), 240 (16 300), 208 (12 800)	CH$_3$CN			−0.30^d	1295, ν(NS); 2047, ν(SCN)
cis-[Os^{II}(bpy)$_2$(Cl)(NCCH$_3$)](PF$_6$) (**15**)	in CH$_3$CN: 690 (2800), 650 (sh), 495 (8700), 411 (8200), 375 (sh), 350 (8300), 293 (54 000), 255 (sh), 243 (sh), 236 (24 000)	CH$_3$CN	+1.87	+0.21		2255, ν(C≡N)

^{a} The origin of this wave is uncertain. It could be due to oxidation of bound NCCH=CH$_2$. ^{b} Os^{III}−Os^{II}/Os^{II}−Os^{II} couple. ^{c} Os^{III}−Os^{III}/Os^{III}−Os^{II} couple. ^{d} Thionitrosyl-based couple.
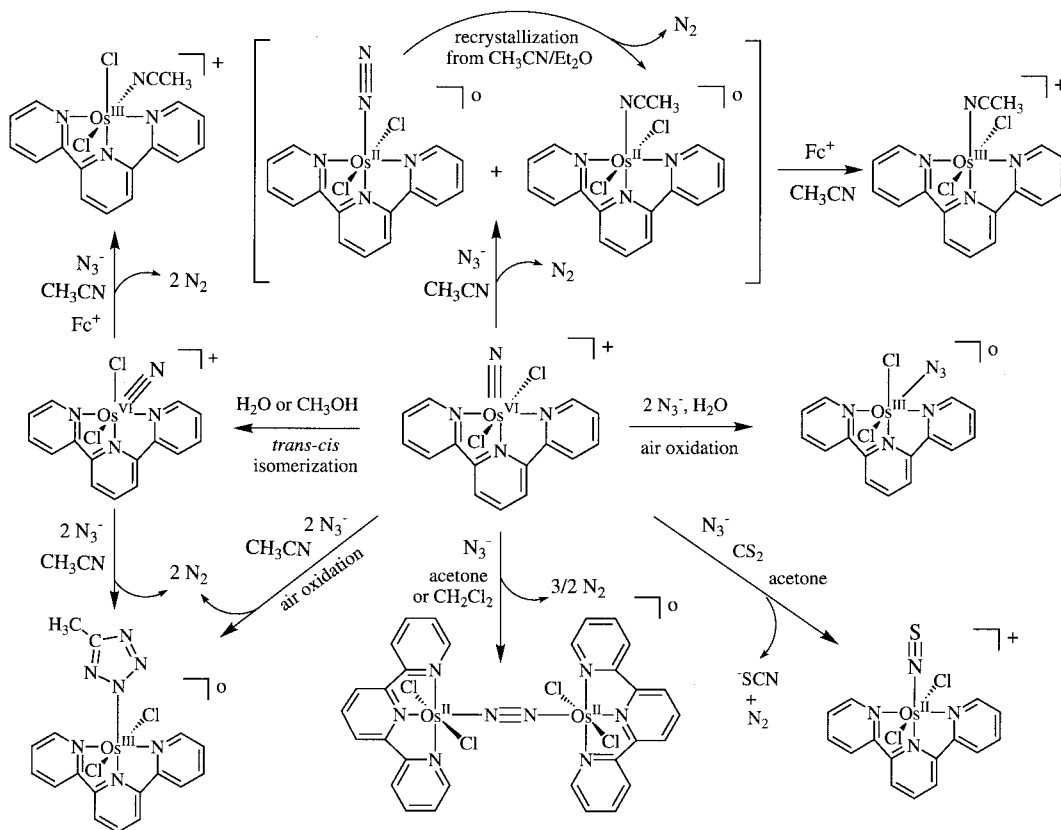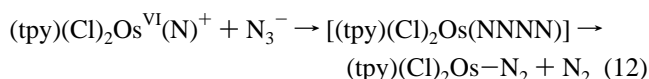
Figure 4. Reactivity between *trans*-[Os^{VI}(tpy)(Cl)$_2$(N)]$^+$ (**1**) and N$_3^-$.
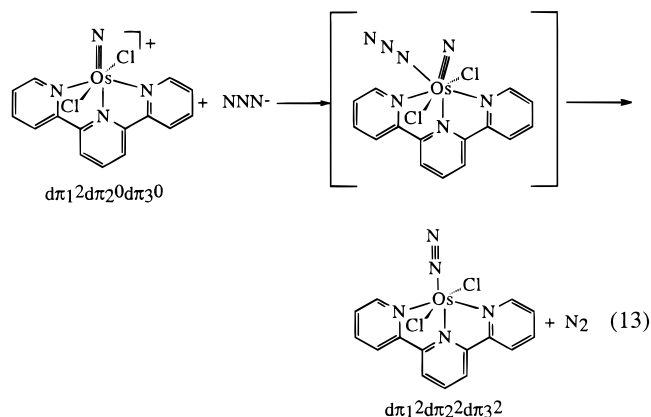
The fact that reaction between **1** and N$_3^-$ occurs by attack of N$_3^-$ on the nitrido ligand with retention of the nitrido N is shown by the result of the ^{15}N-labeling experiment and the appearance of Os(tpy)(Cl)$_2$(^{15}N^{14}N). Although we have no spectroscopic evidence for its formation, this reaction presumably occurs via an Os–N$_4$ intermediate which decomposes to give bound and free N$_2$,
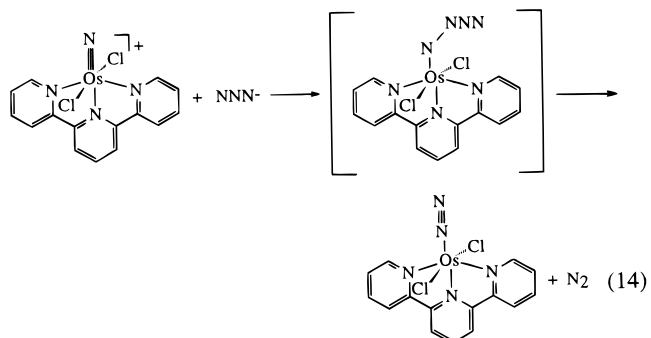
$$(tpy)(Cl)_2Os^{VI}(N)^+ + N_3^- \rightarrow [(tpy)(Cl)_2Os(NNNN)] \rightarrow$$
$$(tpy)(Cl)_2Os-N_2 + N_2 \quad (12)$$

In a formal sense this reaction involves the transfer of N$^-$ from N$_3^-$ to the nitrido atom with multiple intramolecular electron transfer to give Os^{II}–N$_2$. Dehnicke *et al.* have isolated and structurally characterized a W dimer in which there is an N$_4$ bridging ligand.[26] Except for the ^{15}N-labeling experiment, we have no detailed mechanistic information about how this reaction proceeds. However, there are two reasonable possibilities. Both are speculative since there is no evidence for an intermediate.

1 is a d^2 Os^{VI} complex with electronic configuration dπ_1^2dπ_2^0dπ_3^0. If the z axis is defined to lie along the Os–N bond, dπ_2 and dπ_3 are largely d$_{xz}$, d$_{yz}$, with considerable Os–N antibonding character because of extensive mixing with the filled 2p$_x$, 2p$_y$ orbitals of the nitrido ligand. With dπ_2, dπ_3 empty, the lowest available levels for electron pair attack on the nitrido are at the metal with, possibly, coordination sphere expansion, followed by intracoordination sphere N–N coupling. Alternatively, the initial electronic interaction could be envisioned as

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occurring between the σ_N-based lone pair on the nitrido and

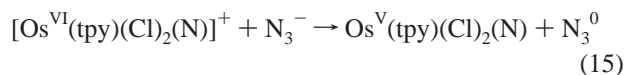the lowest antibonding level on N$_3^-$ without coordination sphere expansion,

This would be followed by intramolecular electronic redistribution and N–N bond cleavage.

The reaction between **1** and N_3^- is solvent dependent. In acetone or CH_2Cl_2 the product is the μ-N_2 complex *trans,trans*-(tpy)(Cl)$_2$Os^{II}(N$_2$)Os^{II}(Cl)$_2$(tpy) (**7**). It presumably forms by initial electron transfer to give Os^V,

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + N_3^- \rightarrow Os^V(tpy)(Cl)_2(N) + N_3^0 \tag{15}$$

followed by N—N coupling,

$$Os^V(tpy)(Cl)_2(N) \rightarrow {}^1/_2(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy) \tag{16}$$

$$N_3^0 \rightarrow {}^3/_2N_2 \tag{17}$$

The solvent effect in this case may simply reflect the solvent dependences of the potentials for the N_3^-/N_3^0 and $[Os^{VI}(tpy)(Cl)_2(N)]^{+/0}$ couples. The ions are favored in polar solvents which decreases the driving force for electron transfer. It has been reported that $E^{o'}(N_3^-/N_3^0) = 0.73$ V in CH_3CN vs SSCE in 0.1 M TBAH at a Pt electrode.[27] In polar solvents, the driving force and rate constant for electron transfer are decreased allowing the electron pair interactions in eq 13 or 14 to compete.

Once formed in CH_3CN, the N_2 complex is labile toward loss of N_2 and solvolysis on a time scale of minutes. This is somewhat surprising since the coordination environment is relatively electron rich. The potential for the *trans*-[Os(tpy)-(Cl)$_2$(NH$_3$)]$^{+/0}$ couple is -0.10 V vs SSCE in CH_3CN. By contrast, we have found recently that the N_2 complex Os^{II}(tpm)-(Cl)$_2$(N$_2$) (tpm = tris(1-pyrazolyl)methane) formed by reaction between N_3^- and the corresponding nitrido is stable under the same conditions.[1]

The reaction between **1** and 2-fold excess N_3^- in H_2O can be rationalized as occurring, in the initial stages, as in CH_3CN but preceded by *trans* → *cis* isomerization, which is rapid. Presumably, attack of N_3^- on the nitrido nitrogen of the cis isomer is followed by solvation to give Os^{II}—H_2O. Anation of the aqua complex by the second N_3^- would give Os^{II}—N_3 and subsequent air oxidation of Os^{II} to Os^{III} final product.
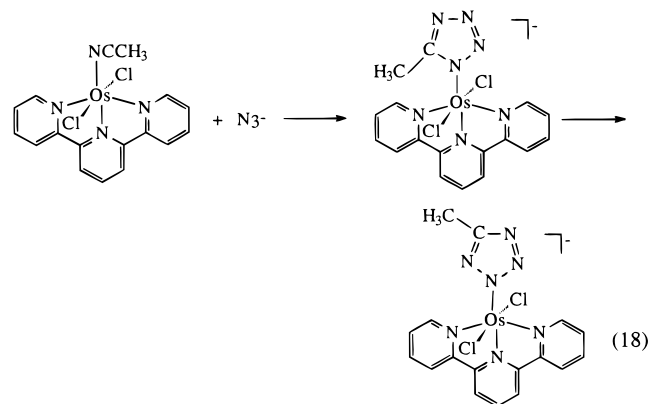
Ware and Taube studied the same reaction and reported *trans*-[Os^{III}(tpy)(Cl)$_2$(H$_2$O)]$^+$ as the product in 10% yields.[28] However, these authors note that when the reaction mixture was passed through a Sephadex SP cation exchange column, a considerable amount of colored material remained on the column, presumably **10**.

The conversion of **10** to **1** by Ce^{IV} oxidation, eqs 10 and 11, proceeds cleanly with evolution of N_2 (as evidenced by the rigorous effervesence). This is a known reaction for other metal azides to give metal nitrides which occur with elimination of N_2.[29] It involves a net intramolecular two-electron transfer from

Os^{IV} to azide, to give Os^{VI}, stabilized by Os—N multiple bonding, and N_2. It returns the complex to the original nitride form.

The lability of N_2 in Os^{II}—N_2 makes it a synthetically useful intermediate. We exploited this aspect of the chemistry in the preparation of the series of nitriles, **3**−**6** and the series of pyridines, **11** and **12**, by using the entering group as solvent. Although somewhat restricted in scope, this represents a synthetically useful, high-yield route to a series of polypyridyl complexes of Os^{II} which are otherwise difficult to prepare.

The formation of the tetrazolate complex is also a stepwise reaction, first involving Os—N_2 formation, eq 1, followed by solvolysis, eq 2, to give the CH_3CN complex **3**. The bound CH_3CN is activated toward attack by N_3^-. Attack of N_3^- most likely takes place at Os^{II}—NCCH$_3$, because **3** is air stable. Metal−tetrazolates form by cycloaddition either by reaction of N_3^- with metal nitriles[30] or by reaction of nitriles with metal azides.[31] Linkage isomerization of the resulting metal−tetrazolate is common and gives the least sterically hindered structure.[32] Based on mechanistic studies on related reactions, the pathway for formation of **13** can be described as initial cycloaddition to give the N^1-bound isomer, followed by isomerization to the more stable N^2-bound isomer.

$$\tag{18}$$

The final product is the Os^{III} complex formed by air oxidation.

Formation of the Os^{II} thionitrosyl also involves attack of a redox nucleophile on the nitrido, in this case by initial cyclic adduct formation between CS_2 and N_3^- to give 5-thio-1,2,3,4-thiatriazolato anion, eq 9. This adduct is known to be unstable and explosive.[11] The only evidence we have for its formation is the literature precedence, the absence of reaction between **1** and CS_2 in acetone, and the fact that the reaction between N_3^- and **1** in acetone gives the μ-N_2 dimer *trans,trans*-(tpy)(Cl)$_2$-Os^{II}(N$_2$)Os^{II}(Cl)$_2$(tpy) (**7**). Once the adduct forms, it apparently attacks the electrophilic nitrido in **1**. The N atom of the nitrido group is retained in the thionitrosyl as shown by the ^{15}N-labeling experiment (see Experimental Section). Initial attack on the nitrido is followed by internal electronic redistribution and net electron transfer,

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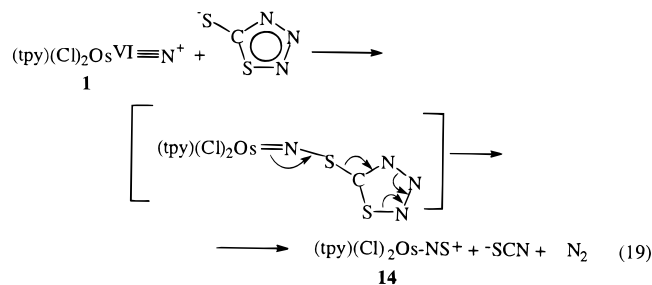(28) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4605.
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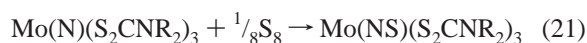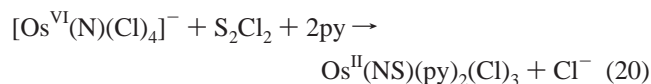(31) (a) Kreutzer, P.; Weis, C.; Boheme, H.; Kemmerich, T.; Beck, W.; Spencer, C.; Mason, R. *Z. Naturforsch.* **1972**, *B27*, 745. (b) Beck, W.; Fehlhammer, W. P.; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 169. (c) Paul, P.; Nag, K. *Inorg. Chem.* **1987**, *26*, 2969.
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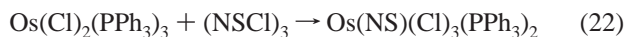
$$(tpy)(Cl)_2Os^{VI}\equiv N^+ + \text{(heterocycle)} \longrightarrow$$

$$\left[(tpy)(Cl)_2Os=N\text{(structure)} \right] \longrightarrow$$

$$\longrightarrow (tpy)(Cl)_2Os\text{-}NS^+ + {}^-SCN + N_2 \quad (19)$$

$$\mathbf{14}$$

The SCN$^-$ formed acts as the counterion for **14** and was identified by IR and X-ray crystallography.

This is the first example of preparation of metal thionitrosyls with the sulfur atom coming from CS$_2$. Common methods available for the preparation of metal thionitrosyls include (a) reaction between metal nitridos and sulfur transfer reagents,[33]

$$[Os^{VI}(N)(Cl)_4]^- + S_2Cl_2 + 2py \rightarrow$$
$$Os^{II}(NS)(py)_2(Cl)_3 + Cl^- \quad (20)$$

$$Mo(N)(S_2CNR_2)_3 + {}^1/_8 S_8 \rightarrow Mo(NS)(S_2CNR_2)_3 \quad (21)$$

(b) transfer of NS from NS precursors,[19,34]

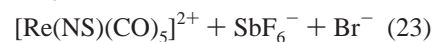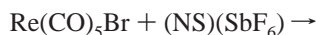$$Os(Cl)_2(PPh_3)_3 + (NSCl)_3 \rightarrow Os(NS)(Cl)_3(PPh_3)_2 \quad (22)$$
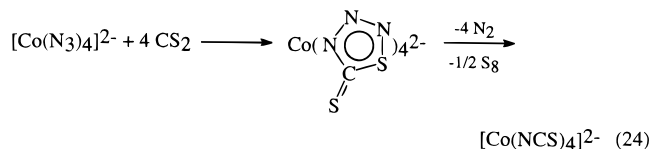
and (c), transfer of NS$^+$,[35]

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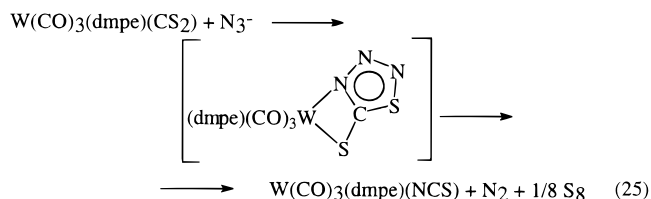
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$$Re(CO)_5Br + (NS)(SbF_6) \rightarrow$$
$$[Re(NS)(CO)_5]^{2+} + SbF_6^- + Br^- \quad (23)$$

There is also a coordination chemistry of CS$_2$N$_3^-$. Metal−azido complexes are known to undergo reaction with CS$_2$ to give isothiocyanates (*N*-bound), S$_8$, and N$_2$, e.g.,[36]

$$[Co(N_3)_4]^{2-} + 4 CS_2 \longrightarrow Co(\text{structure})_4^{2-} \xrightarrow[-1/2\,S_8]{-4\,N_2}$$

$$[Co(NCS)_4]^{2-} \quad (24)$$

There is a complementary chemistry based on reaction between metal−CS$_2$ complexes and N$_3^-$, also to give metal isothiocyanates (*N*-bound).[37]

$$W(CO)_3(dmpe)(CS_2) + N_3^- \longrightarrow$$

$$\left[(dmpe)(CO)_3W\text{(structure)} \right] \longrightarrow$$

$$\longrightarrow W(CO)_3(dmpe)(NCS) + N_2 + 1/8\,S_8 \quad (25)$$

Supporting Information Available: Portions of infrared spectra with isotopic shifts for **2**, **3**, **2***, and **3***, text providing additional details of the crystallographic analyses of compounds **9** and **13**−**15**, a fully labeled ORTEP diagram, and tables of atomic coordinates and *B* values, isotropic thermal parameters, and bond distances and angles (29 pages). Ordering information is given on any current masthead page.

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