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Chalcogen Atom Transfer to a Metal Nitrido. The First Transition Metal Selenonitrosyl Complex

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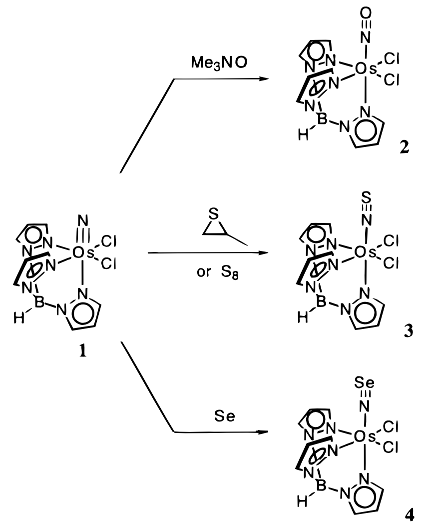
NO is a common and important ligand in transition metal chemistry, from biological systems to organometallic compounds to industrial catalysts.[1] Complexes of the analogous sulfur-containing ligand, thionitrosyl, are less common and were not known until 1974.[2] Despite synthetic efforts, related complexes containing the heavier chalcogens, selenium and tellurium, have not yet been reported in the literature.[3] This contrasts with chalcocarbonyl ligands, for which the first complete series was described in 1980.[4] In this report, we detail the synthesis and properties of a homologous series of chalconitrosyls, TpOs(NE)Cl$_2$ (E = O (**2**), S (**3**), Se (**4**); Tp = hydrotris(1-pyrazolyl)borate), including the first example of a transition metal selenonitrosyl complex. Compounds **2**−**4** were synthesized by atom transfer to the terminal nitrido complex TpOs(N)Cl$_2$ (**1**).

The syntheses of compounds **2**−**4** are outlined in Scheme 1.[5] The light purple nitrosyl complex, TpOs(NO)Cl$_2$ (**2**), is formed in 20% yield by treatment of **1** with excess trimethylamine-*N*-oxide in methylene chloride at 80 °C for 2 days. The only other example of an oxygen atom transfer to a nitrido complex to give a nitrosyl is the formation of [Os(tpy)(NO)Cl$_2$][BF$_4$] from Me$_3$NO and [Os(tpy)(N)Cl$_2$][BF$_4$] (tpy = 2,2′:6′,2″-terpyridine).[6] In both cases the nitrido seems to be acting as an electrophile as no reaction is observed with use of the less nucleophilic pyridine-*N*-oxide. The forest green thionitrosyl complex, TpOs(NS)Cl$_2$ (**3**), is prepared in 77% yield by sulfur atom transfer from propylene sulfide at ambient temperatures. S$_8$ can also serve as the sulfur atom source, but reaction with **1** requires heating and proceeds only in moderate yield. Such sulfur atom transfer to metal nitrido complexes is a common route to thionitrosyl complexes.[7]

Scheme 1



The selenonitrosyl complex, TpOs(NSe)Cl$_2$ (**4**), is slowly formed by heating **1** in the presence of excess selenium metal (gray) in methylene chloride. After 5 days at 80 °C, a 28% yield of forest green **4** is isolated after chromatography on silica gel, in addition to ∼50% unreacted **1**. Attempts to extend this methodology to tellurium have been unsuccessful, as no reaction is observed on extended heating of **1** in the presence of finely divided tellurium metal. This synthetic approach is limited by the small number of selenium-atom and tellurium-atom donor reagents. The common use of phosphine selenides and phosphine tellurides is not practical in this system as **1** reacts very rapidly with phosphines.[8] Compounds **2**−**4** are all stable to air and water and have been characterized by ^{1}H NMR, ^{15}N NMR, EI/MS, IR, and elemental analysis. ^{15}N labeled samples of **2**−**4** have been synthesized from **1**-*^{15}N*. Compounds **2** and **4** have also been characterized by X-ray crystallography.

The structure of the selenonitrosyl complex **4** contains isolated molecules of close to octahedral geometry, with all three trans angles greater than 170° (Figure 1).[9] The selenonitrosyl ligand is slightly bent (164.7(6)°) and has a trans influence a little larger than chloride (Os−N(1), 2.101(7) Å; Os−N(3), 2.066(8) Å; Os−N(5), 2.069(7) Å). The N−Se bond length of 1.629(10) Å is one of the two shortest N−Se bonds of the over one hundred that have been crystallographically characterized,[10] and is slightly shorter than that in gas-phase NSe (Table 1). The nitrosyl complex **2** crystallizes in space group $P\bar{3}$, with the B−Os vector coincident with the crystallographic 3-fold axis.[11] The resulting disorder of the NO and Cl ligands, a common occurrence in nitrosyl chemistry,[1] was successfully modeled as a composite N−[Cl]−O ligand with occupancies of $^2/_3$ for Cl and $^1/_3$ for nitrosyl.[11] While the disorder limits the accuracy of the metrical data, the nitrosyl ligand is also bent (Os−N−O = 171(3)°). A more complicated NS/Cl disorder has thus far prevented full solution of the structure of **3**, but preliminary refinement confirms

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(9) Crystal data for **4**, C$_9$H$_{10}$BCl$_2$N$_7$SeOs: mol wt 567.11, monoclinic, $P2_1$, $a = 7.7710(2)$ Å, $b = 12.9160(4)$ Å, $c = 8.4680(2)$ Å, $\alpha = 90°$, $\beta = 113.212(2)°$, $\gamma = 90°$, $V = 781.13(4)$ Å^3, $Z = 2$, $T = 296(2)$ K, μ(Mo Kα) = 108.35 cm^{-1}, $D_{\mathrm{calc}} = 2.411$ g/cm^3, $R(F) = 3.27\%$ for 3044 observed independent reflections ($5° \le 2\theta \le 55°$), GOF = 1.070.

(10) From the Cambridge Structure Database (January, 1998): Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31−37. The other short N−Se bond is in a disordered structure: Chivers, T.; Doxsee, D. D.; Hilts, R. W.; Parvez, M. *Can. J. Chem.* **1993**, *71*, 1821−7.

(11) Crystal data for **2·$^1/_2$C$_6$H$_6$**, C$_{12}$H$_{13}$BCl$_2$N$_7$OOs: mol wt 543.20, trigonal, $P\bar{3}$, $a = 11.3735(2)$ Å, $c = 7.7134(2)$ Å, $V = 864.10(2)$ Å^3, $Z = 2$, $T = 213(2)$ K, μ(Mo Kα) = 77.0 cm^{-1}, $D_{\mathrm{calc}} = 2.088$ g/cm^3, $R(F) = 4.20\%$ for 1275 observed independent reflections ($4° \le 2\theta \le 56°$), GOF = 1.164. All non-hydrogen atoms except for the NO ligand were refined anisotropically. An ORTEP diagram and full structural details are provided in the Supporting Information.

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Table 1. Infrared,[a] ^{15}N NMR,[b] and Crystallographic Data for TpOs(NE)Cl$_2$ Compounds (**2**−**4**)

compound	$\nu_{^{14}N\equiv E}$	$\nu_{^{15}N\equiv E}$ (calc[c])	$^{14}N\equiv E$ (g)[d] $\nu_{^{14}N\equiv E}$	r_e	δ^{15}N	d(Os−N)	d(N−E)	∠Os−N−O
TpOs(NO)Cl$_2$ (**2**)	1832	1792 (1799)	1875	1.151 Å	−34.4	1.65 (3) Å	1.19 (4) Å	171 (3)°
TpOs(NS)Cl$_2$ (**3**)	1284	1248 (1254)	1205	1.494 Å	26.0			
TpOs(NSe)Cl$_2$ (**4**)	1156	∼1115[e](1125)	945[f]	1.652 Å[f]	65.6[g]	1.800 (10) Å	1.629 (10) Å	164.7 (6)°

[a] IR spectra on thin film samples on NaCl plates, reported in cm^{-1}. [b] Recorded at 50.66 MHz in d_6-DMSO, referenced to 90:10 nitromethane/d_6-DMSO. [c] Calculated assuming a diatomic harmonic oscillator model. [d] Reference 12. [e] Overlapping with a band from the Tp ligand. [f] ^{14}N≡^{80}Se. [g] $^1J_{^{15}N^{77}Se}$ = 140 ± 6 Hz.

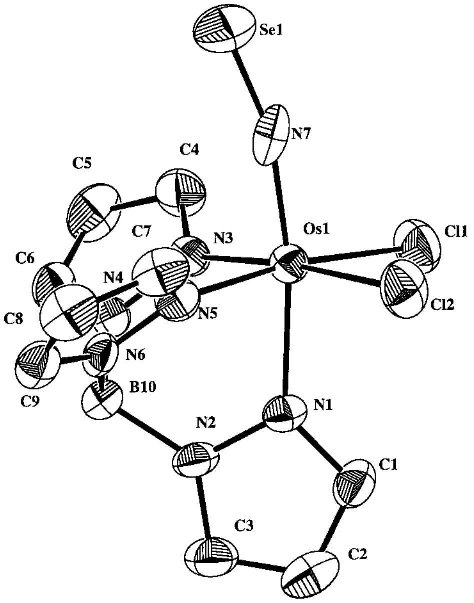

Figure 1. ORTEP drawing of TpOs(NSe)Cl$_2$ (**4**), with hydrogen atoms omitted for clarity.

the connectivity. The slightly elongated N7 thermal ellipsoid in the selenonitrosyl complex **4** may be indicative of a small amount of similar disorder, so the stated error may be an underestimate. The Os−N distance in **4** of 1.800(10) Å appears to be longer than the 1.65(3) Å bond length in the nitrosyl **2**. This contrasts with the pattern seen in chalcocarbonyl complexes, where the M−C distances typically shorten as the chalcogen gets heavier.[4] While both distances are indicative of multiple bonding, the Os−N(O) value is typical of an osmium−nitrido bond length (1.525−1.703 Å, average 1.629 Å).[10]

Infrared spectra of the ^{14}N and ^{15}N derivatives allow assignment of the chalconitrosyl stretching frequencies (Table 1). The ratio of NO to NS stretching frequencies in **2** and **3** is 1.426, a typical value for related NO and NS compounds,[1,7] but much larger than predicted by the difference in reduced mass (1.142 assuming diatomic harmonic oscillators). The N−O force constant is much higher than that for N−S, as expected because bonds get weaker on descending the periodic table. Such a decrease is observed for the gas-phase NE diatomics (Table 1[12]). Surprisingly, the ν_{NS}/ν_{NSe} ratio in **3** and **4** (1.111) is within experimental error of the ratio predicted solely from the change in reduced mass, 1.105. This is most likely due to the 1156 cm^{-1} band not being a simple NSe stretch, but rather having some of the character of an Os−N−Se asymmetric stretch. Vibrational analysis of selenocarbonyl compounds has shown substantial mixing of M−C and C−Se modes.[13] The NSe stretch in **1** is at much higher frequency than the gas-phase ν_{NSe}, by 211 cm^{-1} (22%; Table 1). This is likely due both to the mode mixing and to the bound ligand having NSe$^+$ character. The ^{15}N chemical shifts of the enriched complexes (Table 1) are in the normal range for nitrosyl and thionitrosyl complexes.[1,14]

Chalcogen abstraction from both **3** and **4** can be accomplished with PPh$_3$. Complex **3** is desulfurized in a few hours at 60 °C, while **4** is deselenized almost instantly at room temperature. The expected terminal nitrido product **1** is not observed because it rapidly reacts with PPh$_3$ to form the phosphiniminato complex, TpOs(NPPh$_3$)Cl$_2$.[8] Abstraction of sulfur atoms from thionitrosyl complexes by phosphines is well precedented.[7] Oxygen atom abstraction was not observed from complex **2** even after extended heating in the presence of excess PPh$_3$.[15] This trend in ease of chalcogen removal is mirrored in the fragmentation patterns seen in electron-impact mass spectra, that loss of S and Se from **3** and **4** are major fragmentation modes while no scission of the NO bond is seen for **2**. Weaker abstraction agents, such as AsPh$_3$, do not react with **3** or **4** even after heating at 75 °C for several days. Reaction of **3** with 1 equiv of PhMgBr led to desulfurization and isolation of **1** in good yield after chromatography. We have found no precedent for reactivity of this kind for thionitrosyl ligands and plan further study of this interesting transformation.

In sum, atom transfer to the terminal nitrido ligand in TpOs(N)Cl$_2$ has been used to prepare a homologous series of chalconitrosyl complexes **2**−**4**, including the first example of a selenonitrosyl complex. The NS and NSe complexes appear to have similar bonding and reactivity.

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Supporting Information Available: Full experimental and characterizational data for compounds **1**−**4**, and procedures, drawings, and tables for the X-ray structures of **2** and **4** (19 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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