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Notes

N- versus S-Metalation of Nitridobis(3,4-toluenedithiolato)osmium(VI)

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Introduction

Nitridometal complexes have attracted attention because these complexes are believed to be involved in biological nitrogen fixation process[1,2] and have been employed as reagents for nitrogen atom transfer.[3] One important reaction for nitridometal complexes is electrophilic attack on the nitride ligand resulting in the formation of nitrogen bridges between the metal ion with a metal or nonmetal ion. Of particular interest is the electropilic attack on nitridometal complexes with thiolate ligands, which contain two potential nucleophilic sites. Shapley and co-workers reported that alkylation of [*n*-Bu_4N][$OsN(CH_2SiMe_3)_2(SCH_2CH_2S)$] occurs at the more basic sulfur site.[4] More recently, Sellmann and co-workers reported that the position of alkylation for [*n*-Bu_4N][$OsN(C_6H_4S_2)_2$] is dependent on the entering electrophiles. While methyl triflate alkylates the sulfur atom of the benzendithiolate ligand, trityl cation preferentially attacks on the less hindered nitride ligand.[5] It would be of interest to see if this kind of N- versus S-selectivity for nitridoosmium thiolates will also hold for other types of electrophiles such as organometallic fragments. Recently we found that cationic organometallic fragments including $[Au(PPh_3)]^+$ and $[Ir(CO)(PPh_3)_2]^+$ react with $[OsO_3N]^-$ to give nitrido-bridged bimetallic complexes.[6] As our continuous effort to explore the reactivity of nitridometal complexes, we herein describe the reaction of nitridobis(3,4-toluenedithiolato)osmium(VI) with organometallic electrophiles and the isolation of the corresponding bimetallic complexes.

Experimental Section

Solvents were purified and distilled prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^1H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Mass spectra were obtained on a Finnigan TSQ-7000 spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 273A potentiostat. The working and reference electrodes are glassy carbon and Ag/$AgNO_3$ (0.1 M in acetonitrile), respectively. Potentials were reported with reference to $Cp_2Fe^{+/0}$. Elemental analyses were performed by Medac Ltd, Surrey, U.K.

Materials. H_2L (L = 3,4-toluenedithiol) was purchased from Strem Ltd. and used as received. [Bu_4N][$OsNCl_4$],[7] $Au(PPh_3)Cl$,[8] and *trans*-$Ir(CO)Cl(PPh_3)_2$[9] were prepared according to the literature methods.

Preparations. [*n*-Bu_4N][$OsNL_2$] (1). This was prepared by a modification of the literature method. To a solution of [*n*-Bu_4N]-[$OsNCl_4$] (0.07 g, 0.12 mmol) in MeOH (20 mL) was added H_2L (0.05 g, 0.32 mL) and Et_3N (0.05 mL). The solution was stirred at room temperature in air for 1 h, during which a yellow solid precipitated. The solid was collected and washed with ether and the filtrate evaporated to dryness and recrystallization from CH_2Cl_2/Et_2O to give a yellow solid. Recrystallization from CH_2Cl_2/Et_2O afforded yellow crystals (yield 80%). ^1H NMR ($CDCl_3$): δ 0.79 (s, 12 H, CH_3 of *n*-Bu), 2.27 (m, 16H, CH_2 of *n*-Bu), 2.27 (s, 6H, CH_3 of L), 2.60 (t, 8H, NCH_2), 6.64−7.45 (m, 6 H, phenyl protons). $^{31}P\{^1H\}$ ($CDCl_3$): δ 36.22. IR (cm^{-1}): 1112 $\nu(Os{\equiv}N)$. MS(CI), *m/z*: 514 (M − *n*-Bu_4N)$^+$. Anal. Calcd for $OsC_{30}H_{48}N_2S_4$: C, 47.7; H, 6.4; N, 3.7. Found: C, 47.4; H, 6.3; N, 3.6.

$OsNL[SC_7H_6S(AuPPh_3)]$ (2). To a solution of **1** (0.1 g, 0.13 mmol) in CH_2Cl_2 (10 mL) was added 1 equiv of $Au(PPh_3)(OTf)$, which was prepared from $Au(PPh_3)Cl$ (0.066 g, 0.13 mmol) and AgOTf (0.034 g, 0.13 mmol) in THF (10 mL), and the mixture was stirred overnight and filtered. Evaporation of the filtrate to dryness and recrystallization from CH_2Cl_2/hexane afforded orange crystals (yield 25%). ^1H NMR ($CDCl_3$): δ 2.35 (s, 6H, CH_3), 6.81−7.61 (m, 21 H, phenyl protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.23 (s). IR (cm^{-1}): 1102 $\nu(Os{\equiv}N)$. MS(CI), *m/z*: 1256 (M)$^+$. Anal. Calcd for $OsC_{30}H_{48}N_2S_4$: C, 39.6; H, 2.8; N, 1.4. Found: C, 39.6; H, 3.0; N, 1.4.

$L_2OsNIr(CO)(PPh_3)_2$ (3). To a solution of **1** (0.08 g, 0.1 mmol) in CH_2Cl_2 (10 mL) was added 1 equiv of $Ir(CO)(PPh_3)_2(OTf)$, prepared from *trans*-$Ir(CO)Cl(PPh_3)_2$ (0.03 g, 0.1 mmol) with AgOTf (0.03 g, 0.1 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room-temperature overnight, during which the color changed from yellow to green, and filtered. Evaporation of the solvent and recrystallization from CH_2Cl_2/hexane afforded green crystals (yield 75%). ^1H NMR ($CDCl_3$): δ 2.21 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 6.64−7.45 (m, 36H, phenyl protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.82 (s). IR (cm^{-1}): 1984 $\nu(C{\equiv}O)$, 1100 $\nu(Os{\equiv}N)$. Anal. Calcd for $OsC_{30}H_{48}N_2S_4$: C, 47.7; H, 6.4; N, 3.7. Found: C, 47.4; H, 6.3; N, 3.6.

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(1) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955.

(2) (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. (b) Che, C. M.; Lam, H.-W.; Tong, W.-F.; Lai, T. F.; Lau, T. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1883. (c) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4605. (d) Coia, G. M.; White, P. S.; Meyer, T. J.; Wink, D. A.; Keefer, L. K.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 3649. (e) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861. (f) Ishitani, O.; White, P.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2167.

(3) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Groves, J. T.; Takahashi, T. Butler, W. *Inorg. Chem.* **1983**, *22*, 884. (c) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517. (d) Evans, D A.; Faul, M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742 and references therein. (e) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364 and references therein.

(4) Zhang, N.; Wilson, S. R. Shapley, P. A. *Organometallics* **1988**, *7*, 1126.

(5) Sellmann, D.; Wemple, M. W.; Donaubauer, W.; Heinemann, F. W. *Inorg. Chem.* **1997**, *36*, 1397.

(6) (a) Leung, W.-H.; Chim, J. L. C.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.***1996**, 3153. (b) Leung, W.-T.; Chim, J. L. C.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1997**, 3277.

(7) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315.

(8) Braunstein, P. B.; Lehner, H.; Matt, D.; Burgess, K.; Ohlmeyer, M. J. *Inorg. Synth.* **1990**, *27*, 218.

(9) Collman, J. P.; Kubota, M. *Inorg. Synth.* **1990**, *28*, 92.

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Table 1. Crystal Data and Experimental Details for $OsN(L)[SC_7H_6S(AuPPh_3)]$ (**2**) and $L_2OsNIr(CO)(PPh_3)_2$ (**3**)

	2	**3**
formula	$AuOsC_{32}H_{27}NPS_4$	$IrOsC_{51}H_{42}NOPS_4$
fw	971.95	1257.51
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	15.128(4)	16.811(1)
b, Å	11.961(5)	13.911(1)
c, Å	11.196(4)	21.341(1)
β, deg	90.40(3)	108.850(2)
V, Å^3	3211(1)	4723.1(4)
Z	4	4
ρ_{calcd} (g cm^{-3})	2.010	1.768
color, habit	brown, prism	yellow, rod
λ, Å	0.710 73	0.710 73
T, °C	25	25
μ, cm^{-1}	88.63	57.92
total no. of reflcns	4551	8434
no. of obsd reflcns ($I > 3.00\sigma(I)$)	2197	4638
weighting scheme	$1/[\sigma^2(F) + 0.002F^2/4]$	$1/[\sigma^2(F) + 0.025F^2/4]$
R^a	0.040	0.027
$R_w{}^b$	0.034	0.027
goodness of fit^c	1.82	1.11

^{a} $R = \sum|F_o| - |F_c|/|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$. ^{c} $[\sum w(|F_c| - |F_o|)^2/(N_{obs} - N_{param})]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $OsN(L)[SC_7H_7S(AuPPh_3)]$

Au(1)−S(2)	2.379(5)	Au(1)−P(1)	2.266(5)
Os(1)−S(1)	2.324(6)	Os(1)−S(2)	2.366(5)
Os(1)−S(3)	2.297(6)	Os(1)−S(4)	2.315(5)
Os(1)−N(1)	1.65(2)		
S(2)−Au(1)−P(1)	171.8(2)	S(1)−Os(1)−S(2)	86.0(2)
S(1)−Os(1)−S(3)	83.8(2)	S(1)−Os(1)−S(4)	147.6(2)
S(1)−Os(1)−N(1)	106.5(6)	S(2)−Os(1)−S(3)	145.8(2)
S(2)−Os(1)−S(4)	84.6(2)	S(2)−Os(1)−N(1)	108.4(6)
S(3)−Os(1)−S(4)	86.7(2)	S(3)−Os(1)−N(1)	108.4(6)
S(4)−Os(1)−N(1)	105.9(6)		

X-ray Crystallography. A summary of crystal and data processing parameters for **2** and **3** is given in Table 1. Single crystals of **2** and **3** were grown from CH_2Cl_2/hexane at room temperature. Data for **2** and **3** were collected on a Rigaku AFC7R and an MAR-Research Image Plate diffractometer, respectively. Intensity data were corrected for Lorentz and polarization effects. The space groups of all crystals were determined from a Laue symmetry check and their systematic absences were confirmed by successful refinement of the structures. For **2**, although the β angle is close to 90°, the Laue symmetry is $2/m$ instead of *mmm*. Therefore a monoclinic system is used. There were some positional disorder problems associated with the 3,4-toluenedithiolate (L) ligands in **2** and **3**. In **2**, the L exhibits a 2-fold disorder and was modeled by two sites each with occupancy factors 0.6 and 0.4 while a similar problem in **3** was modeled by two sites with occupancy factors 0.7 and 0.3. Both structures were solved by Direct methods (SHELXS 86[10] and SIR 88[11] for **2** and **3**, respectively) and refined by a full-matrix least-squares analysis. Some non-hydrogen atoms were refined anistropically, while the rest were refined isotropically. Hydrogen atoms were included and fixed in their idealized positions (C−H = 0.95 Å). Selected bond lengths and angles for **2** and **3** are given in Tables 2 and 3, respectively.

Results and Discussion

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $L_2OsNIr(CO)(PPh_3)_2$

Ir(1)−P(1)	2.318(2)	Ir(1)−P(2)	2.322(2)
Ir(1)−N(1)	2.002(5)	Ir(1)−C(1)	1.814(9)
Os(1)−S(1)	2.310(2)	Os(1)−S(2)	2.300(2)
Os(1)−S(3)	2.294(2)	Os(1)−S(4)	2.301(2)
Os(1)−N(1)	1.676(5)		
P(1)−Ir(1)−P(2)	177.05(6)	P(1)−Ir(1)−N(1)	887.9(2)
P(1)−Ir(1)−C(1)	91.5(2)	P(2)−Ir(1)−N(1)	89.3(2)
P(2)−Ir(1)−C(1)	91.3(2)	N(1)−Ir(1)−C(1)	179.2(2)
S(1)−Os(1)−S(2)	85.61(7)	S(1)−Os(1)−S(3)	84.42(7)
S(1)−Os(1)−S(4)	147.43(8)	S(1)−Os(1)−N(1)	106.5(2)
S(2)−Os(1)−S(3)	142.75(7)	S(2)−Os(1)−S(4)	83.59(7)
S(2)−O(1)−N(1)	109.5(2)	S(3)−Os(1)−S(4)	85.84(8)
S(3)−Os(1)−N(1)	107.8(2)	S(4)−Os(1)−N(1)	106.1(2)
Ir(1)−N(1)−Os(1)	176.1(3)	Ir(1)−C(1)−O(1)	179.2(7)

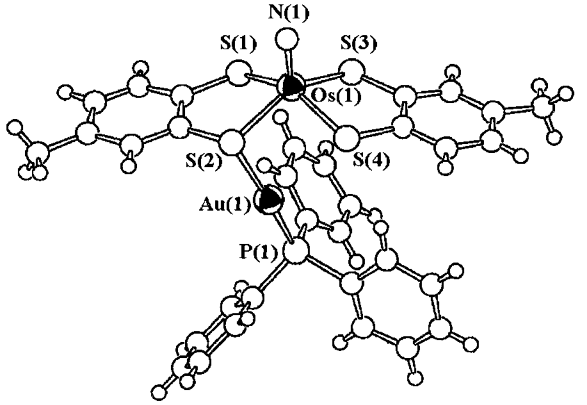

Figure 1. Perspective view of $OsN(L)[SC_7H_6S(Au(PPh_3)]$, **2**.

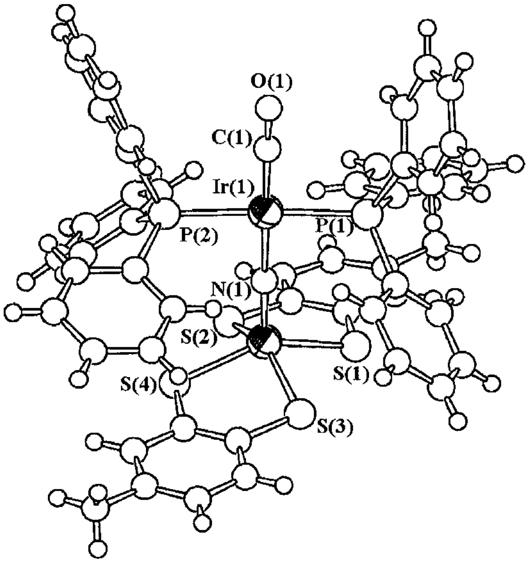

Figure 2. Perspective view of $L_2OsNIr(CO)(PPh_3)_2$, **3**.

The nitridoosmium(VI) complex $[n\text{-}Bu_4N][OsNL_2]$ **1** was prepared from $[n\text{-}Bu_4N][OsNCl_4]$ and H_2L (3,4-toluenedithiol) according to Sellmann's method, isolated as an air-stable yellow solid. Treatment of **1** with $Au(PPh_3)(OTf)$ afforded the Au^I−Os^{VI} complex $OsN(L)[SC_7H_6S(AuPPh_3)]$, **2**, which has been characterized by X-ray crystallography. Figure 1 shows a diagram of the molecule; selected bond lengths and angles are given in Table 2. As would be anticipated, the $Au(PPh_3)$ fragment binds to one sulfur atom of L with the S−Au−P angle of 171.8(2)°. Unexpectedly, only one signal for the methyl protons of L was observed in the ^1H NMR spectrum possibly because the two methyl signals are very close and accidentally coincide with each other. Although there is no significant difference in Os−N bond length between **2** (1.65(2) Å) and

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[10] SHELX86: Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: 1985; p 175.

[11] SIR88: Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, D.; Polidori, G.; Spagna, R.; Viterbo, D. *J. App. Crystallogr.* **1989**, *22*, 389.

[*n*-Bu_4N][$OsN(C_6H_4S_2)_2$] (1.64(1) Å),[5] the ν(Os≡N) decreases slightly to 1112 cm^{-1} (cf. 1102 cm^{-1} for **1**) on binding to $AuPPh_3$. The formation of Au−S(2) bond also results in lengthening of the Os−S(2) (2.366(5) Å) and shortening of the Os−S(3) (2.297(6) Å).

On the other hand, treatment of **1** with $Ir(CO)(PPh_3)_2(OTf)$ afforded the nitrido-bridged bimetallic complex $L_2OsNIr(CO)(PPh_3)_2$, **3**. Figure 2 shows the molecular structure of **3**; selected bond lengths and angles are given in Table 3. Apparently the bulky $Ir(CO)(PPh_3)_2$ fragment binds to nitride instead of the more basic sulfur site in **1** in order to minimize the nonbonding repulsion between the PPh_3 and L. Because of the steric congestion around **3**, the Os-to-basal plane distance for **3** (ca. 0.69 Å) is longer than that for $[Os(N)(C_6H_4S_2)_2]^-$ (0.63 Å).[5] The Ir−N distance of 2.002(5) Å is similar to that in *trans*-$Ir(CO)(PPh_3)_2(NOsO_3)$ (1.998(7) Å).[6b] The long Ir−N bond and short Os−N bond and linear Os−N−Ir linkage for **3** is indicative of the asymmetric bridging mode of the nitride, i.e., Ir−N≡Os. The Os−N distance in **3** (1.676(5) Å) is longer than that for $[Os(N)(C_6H_4S_2)_2]^-$ (1.64(1) Å)[5] and the ν(Os≡N) (1100 cm^{-1}) for **3** is lower than that for **1** (1112 cm^{-1}), suggesting that the Os−N triple bond is weakened upon coordination to $Ir(CO)(PPh_3)_2$. The cyclic voltammogram of **3** in CH_2Cl_2 shows an irreversible oxidation wave at ca. 0.36 V and an irreversible reduction at −1.72 V vs ferrocene-ferrocenium. The oxidation wave is assigned to the osmium-centered oxidation while the reduction wave is attributed to the Ir(I/0) reduction. For comparison, under the same conditions, **1** exhibits a reversible Os(VII/VI) couple at 0.39 V. The Ir(I/0) potential reduction as well as ν(C≡O) (1984 cm^{-1}) for **3** are similar to those for $Ir(CO)(PPh_3)_2(NOsO_3)$ (−1.67 V and 1986 cm^{-1}, respectively),[6b] suggesting that the donor strength of $[Os^{VI}NL_2]^-$ is comparable to that for $[Os^{VIII}O_3N]^-$.

In summary, we have demonstrated that $[OsNL_2]^-$ reacts with organometallic electrophiles to give heterobimetallic complexes in a way similar to its alkylation reactions. Small electrophiles such as $[Au(PPh_3)]^+$ and methyl attack the more basic sulfur while bulky electrophiles such as $[Ir(CO)(PPh_3)_2]^+$ and trityl add to the less-hindered nitride ligand of $[OsNL_2]^-$.

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Supporting Information Available: Listings of crystal data, complete bond lengths and angles, and atomic coordinates with isotropic parameters (6 pages). Ordering information is given on any current masthead page.

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