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Synthesis, Structure, and Reactivity of Ruthenium and Osmium Nitrido Complexes with 1,2-Benzenedithiolate Ligands: N- versus S-Alkylation

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The reactivity of the nitrido complexes $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**) and $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**) ($C_6H_4(SH)_2$ = 1,2-benzenedithiol) toward electrophiles, R^+ (R = Me, Et, Ph_3C), is described. While **1** yielded intractable mixtures of products, **2** could be cleanly alkylated. The synthesis of **1** has been reported previously (*Z. Naturforsch.* **1987**, *42B*, 341); complex **2** can be synthesized by treating $(N^nBu_4)[Os(N)Cl_4]$ with deprotonated 1,2-benzenedithiol in acetone/MeOH at 0 °C. Complexes **1** and **2** are isostructural and crystallize in the orthorhombic space group $Pna2_1$, $Z = 8$, with $a = 36.881(6)$ Å, $b = 9.402(2)$ Å, and $c = 17.652(2)$ Å for **1** and $a = 37.042(4)$ Å, $b = 9.375(2)$ Å, and $c = 17.671(2)$ Å for **2**. The anions of both compounds consist of a five-coordinate mononuclear center with a distorted square-pyramidal geometry; a terminal nitrido ligand occupies the apical position and two chelating $(S_2C_6H_4)^{2-}$ ligands form the basal plane. Treatment of **2** with R_3OBF_4 in CH_2Cl_2 yields $[Os(N)(S_2C_6H_4)(SC_6H_4SR)]$ (R = Me, **3**; R = Et, **4**) where one thiolate donor is alkylated. Alkylation of the sulfur of the 1,2-benzenedithiolate ligand was confirmed by NMR spectroscopy and X-ray crystallography (for **3**). Complex $\mathbf{3}\cdot CH_2Cl_2$ crystallizes in the orthorhombic space group $P2_12_12_1$, $Z = 4$, with $a = 8.551(1)$ Å, $b = 10.772(2)$ Å, and $c = 19.716(3)$ Å. In contrast, treatment of **2** with Ph_3CPF_6 in CH_2Cl_2 yields $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**5**), whose ^1H and ^{13}C NMR spectra indicate that the terminal nitride is the site of electrophilic attack. X-ray crystallography further confirms the alkylation at the nitrogen atom; complex **5** crystallizes in the triclinic space group $P\bar{1}$, $Z = 2$, with $a = 9.338(8)$ Å, $b = 10.001(3)$ Å, $c = 16.280(6)$ Å, $\alpha = 75.88(3)°$, $\beta = 74.29(6)°$, and $\gamma = 69.55(5)°$.

Introduction

Transition metal complexes with terminal nitrido ligands[1] are of interest as intermediates in nitrogen fixation[2] and for their involvement in nitrogen atom transfer reactions to both inorganic[3] and organic[4] substrates. Nitrido complexes have also been used as precursors for the formation of unusual metal−nitrogen bridges such as Re−N−Ga and Os−N−Ag[5] and for the formation of nitrogen bridges between metal ions and nonmetallic atoms.[1,6] Our interest in nitrido complexes derives from our investigation of the reactivity of small molecules bound to metal complexes with sulfur-rich coordination.[7] This work had previously led to the discovery of several N−O bond cleavage reactions. For example, treatment of $[Mo(NO)_2(‘S_4’)]$ ($‘S_4’^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethanate(2−)) with phosphines led to the formation of phosphoraniminato complexes with the general formula $[Mo(NPR_3)(NO)(‘S_4’)]$;[8] these complexes formally contain a nitride bridge between the molybdenum and the phosphorus atoms. Treatment of $(N^nBu_4)[Ru(NO)(S_2C_6H_4)_2]$ with $NaBH_4$ in MeOH yielded the nitrido complex, $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**; $C_6H_4(SH)_2$ = 1,2-benzenedithiol) (eq 1).[9] This reaction is remarkable because the reduction of the nitrosyl ligand to a nitride is accompanied by an oxidation of the metal center despite the presence of a strong reducing agent ($NaBH_4$). More recent examples of the cleavage of the nitrosyl N−O bond by the addition of a reducing agent yielded nitride-bridged dinuclear complexes.[10]

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(1) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988. (b) Dehnicke, K.; Strähle, J. *Angew. Chem.* **1992**, *104*, 978−1000; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955. (c) Dehnicke, K.; Strähle, J. *Angew. Chem.* **1981**, *93*, 451−464; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413.

(2) (a) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861−863. (b) Leigh, G. H. *Science* **1995**, *268*, 827−828. (c) Ishitani, O.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2167−2168. (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*, 3649−3650. (e) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4605−4610. (f) Pipes, D. W.; Bakir, M.; Vitols, S. E.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5507−5514. (g) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589−625. (h) Kondo, M.; Oku, H.; Ueyama, N.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 117−123.

(3) (a) Tong, C.; Bottomley, L. A. *Inorg. Chem.* **1996**, *35*, 5108−5109. (b) Laplaza, C. E.; Johnson, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **1996**, *118*, 709−710. (c) Bottomley, L. A.; Neely, F. L. *Inorg. Chim. Acta* **1992**, *192*, 147−149. (d) Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478−8484. (e) Bakir, M.; White, P. S.; Dovletoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2836−2838. (f) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989**, *111*, 5955−5957. (g) Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125−1136.

(4) (a) Bois, J. D.; Hong, J.; Carreira, E. M.; Day, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 915−916. (b) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073−2074.

(5) (a) Ritter, S.; Hübener, R.; Abram, U. *J. Chem. Soc., Chem. Commun.* **1995**, 2047−2048. (b) Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1991**, *10*, 1671−1676.

(6) For recent examples see: (a) Shapley, P. A.; Shusta, J. M.; Hunt, J. L. *Organometallics* **1996**, *15*, 1622−1629. (b) Williams, D. S.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 823−824. (c) Kim, J. C.; Rees, W. S., Jr.; Goedken, V. L. *Inorg. Chem.* **1995**, *34*, 2483−2486. (d) Ritter, S.; Abram, U. *Inorg. Chim. Acta* **1995**, *231*, 245−248. (e) Yoshida, T.; Adachi, T.; Yabunouchi, N.; Ueda, T.; Okamoto, S. *J. Chem. Soc., Chem. Commun.* **1994**, 151−152. (f) Ritter, S.; Abram, U. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1786−1792.

(7) Sellmann, D. In *Molybdenum Enzymes, Cofactors and Model Systems*; Stiefel, E. I., Coucouvanis, D., Newton, W. E., Eds.; ACS Symposium Series 535; American Chemical Society: Washington, DC, 1993; pp 332−345.

(8) (a) Sellmann, D.; Keller, J.; Moll, M.; Beck, H. P.; Milius, W. Z. *Z. Naturforsch.***1986**, *41B*, 1551−1560. (b) Sellmann, D.; Keller, J.; Moll, M.; Campana, C. F.; Haase, M. *Inorg. Chim. Acta* **1988**, *141*, 243−252.

(9) Sellmann, D.; Binker, G. *Z. Naturforsch.* **1987**, *42B*, 341−347.

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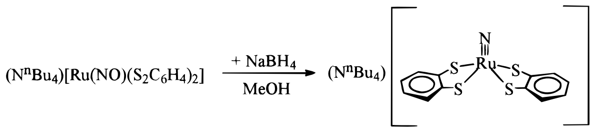

(1)

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The aim of the work presented here was to explore the reactivity of the nitrido complex, **1**, in order to determine the preferred site of electrophilic attack. The most likely sites of **1** to be attacked by an electrophile are the thiolate donors. In fact, Shapley *et al.* have shown that alkylation of either $(N^nBu_4)[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]$[11] or $(N^nBu_4)[Os(N)(CH_2SiMe_3)_2(WS_4)]$[12] occurs at a sulfur atom and not at the nitride ligand. Nevertheless, *four* thiolate donors could be sufficiently π-donating to weaken the M≡N bond and make the nitrogen atom more prone to react with an electrophile. All experiments designed to determine the most nucleophilic site of **1** yielded only intractable solids.[13] For this reason, we prepared the analogous $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**) to take advantage of the greater kinetic stability of osmium complexes. Complex **2** proved to have two nucleophilic sites and can be alkylated either at one of the thiolate donors (with Me^+ or Et^+) or at the nitride (with Ph_3C^+) depending on the attacking electrophile.

Experimental Section

General Procedures. All manipulations were performed under anaerobic conditions using standard Schlenk techniques; solvents were dried before use. 1,2-Benzenedithiol,[14] $(N^nBu_4)[Os(N)Cl_4]$,[15] and $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$[9] (**1**) were prepared by literature methods. $(N^nBu_4)OH$ (1 *M* in MeOH) and Ph_3CPF_6 were purchased from Aldrich; Me_3OBF_4 and Et_3OBF_4 were purchased from Fluka. Elemental analyses were performed with a Carlo Erba EA 1106 or 1108 analyzer. Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL JNM GX-270 spectrometer with the protiosolvent signal used as a reference; chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane. Mass spectra were recorded on a JEOL MSTATION 700 mass spectrometer.

$(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (2). $(N^nBu_4)OH$ (21 mL of a 1 *M* solution, 21 mmol) was added dropwise to a solution of 1,2-benzeneditiol (1.17 mL, 10.2 mmol) in acetone (20 mL) that had been previously cooled to 0 °C in an ice bath. The final mixture was slowly added to a red solution of $(N^nBu_4)[Os(N)Cl_4]$ (3.00 g, 5.10 mmol) in acetone (50 mL) at 0 °C. The color of the solution changed to yellow over the course of the addition, and toward the end of the addition, a yellow precipitate could be observed. When addition was complete, the volume of the mixture was reduced to about 20 mL under vacuum. A yellow precipitate was isolated by filtration and washed with cold MeOH (2 × 5 mL) and Et_2O. The solid was dried under vacuum; yield 75% (2.78 g). Anal. Calcd (found) for $C_{28}H_{44}N_2OsS_4$ (fw = 727.11): C, 46.25 (46.33); H, 6.10 (6.33); N, 3.85 (3.67). IR (KBr, cm^{-1}): 1063 (vs, $\nu_{Os\equiv N}$). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 7.61, 6.89 (AA′ and BB′ parts of an AA′BB′ spin system, 8 H, C_6H_4), 2.84 ("t", 8 H, NCH_2), 1.19−1.42 (m, 16 H, CH_2), 0.90 (t, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm, 67.7 MHz): δ 148.6, 128.3, 124.1 (C_6H_4), 58.6 (t), 24.0, 19.9, 13.7 (C_4H_9).

$[Os(N)(S_2C_6H_4)(SC_6H_4SMe)]$ (3). Solid Me_3OBF_4 (0.075 g, 0.51 mmol) was added to a stirred yellow solution of complex **2** (0.36 g, 0.50 mmol) in CH_2Cl_2 (30 mL); the color of the solution changed to red-brown. After 30 min, the solvent was removed under vacuum and the residue was redissolved in toluene (40 mL). An oily yellow-green material was removed by filtration, and the filtrate was stored at −30 °C overnight to give an additional precipitate. This precipitate was removed by filtration, hexane (50 mL) was added to the filtrate, and the mixture was again stored at −30 °C overnight. During this time, an orange solid precipitated which was collected by filtration, washed with hexane (3 × 5 mL), and dried under vacuum; yield 62% (0.16 g). The analysis sample was recrystallized from a CH_2Cl_2 solution at −30 °C and dried overnight under vacuum. Anal. Calcd (found) for $C_{13.3}H_{11.7}NCl_{0.7}OsS_4$ ($\mathbf{3}\cdot{}^1/_3CH_2Cl_2$; fw = 527.99): C, 30.33 (30.13); H, 2.23 (2.15); N, 2.65 (2.67); S, 24.29 (24.12). IR (KBr, cm^{-1}): 1058 (vs, $\nu_{Os\equiv N}$). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 7.89 ("dd"), 7.83−7.76 (m), 7.39 ("td"), 7.21 ("td"), 7.14−7.04 (m) (from two ABCD spin systems, 8 H, C_6H_4), 3.05 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm, 67.7 MHz): δ 152.1, 145.9, 145.7, 133.4, 132.1, 131.2, 130.7, 129.0, 128.5, 126.9, 126.2, 125.4 (C_6H_4), 33.4 (CH_3). MS (FD^+): *m/z* 501 (M^+); the correct isotope pattern was observed.

$[Os(N)(S_2C_6H_4)(SC_6H_4SEt)]$ (4). The procedure employed for **3** was repeated using solid Et_3OBF_4 (0.095 g, 0.50 mmol); yield 74% (0.19 g). Anal. Calcd (found) for $C_{14}H_{13}NOsS_4$ (fw = 513.70): C, 32.73 (33.04); H, 2.55 (2.66); N, 2.73 (2.69); S, 24.96 (25.05). IR (KBr, cm^{-1}): 1056 (vs, $\nu_{Os\equiv N}$). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 7.89 ("dd"), 7.84−7.73 (m), 7.40 ("td"), 7.20 ("td"), 7.13−7.04 (m) (from two ABCD spin systems, 8 H, C_6H_4), 3.70, 3.29 (dq, ^3J = 7.3, ^2J = 14.3, 2 H, CH_2), 0.98 (t, ^3J = 7.3, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm, 67.7 MHz): δ 153.4, 146.1, 145.8, 132.1, 131.4, 131.0, 130.4, 128.9, 128.5, 126.5, 126.0, 125.4 (C_6H_4), 43.5 (CH_2), 11.9 (CH_3). MS (FD^+): *m/z* 515 (M^+); the correct isotope pattern was observed.

$[Os(NCPh_3)(S_2C_6H_4)_2]$ (5). Solid Ph_3CPF_6 (0.19 g, 0.49 mmol) was added to a stirred yellow solution of complex **2** (0.36 g, 0.50 mmol) in CH_2Cl_2 (30 mL); the color of the solution changed to black within a few minutes. After 1 h, the solvent was removed under vacuum and the residue was redissolved in toluene (20 mL). An undissolved black material was removed by filtration and washed with toluene (2 × 5 mL). The toluene washes were combined with the filtrate, and the solvent was removed under vacuum to give a black powder. This powder was washed with MeOH (30 mL) and petroleum ether and was dried under vacuum; yield 55% (0.20 g). Anal. Calcd (found) for $C_{31}H_{23}NOsS_4$ (fw = 727.97): C, 51.15 (50.90); H, 3.18 (3.27); N, 1.92 (1.95); S, 17.62 (17.36). IR (KBr, cm^{-1}): 1178 (vs; *vide infra*). ^1H NMR (CD_2Cl_2, ppm, 270 MHz): δ 7.82 (AA′ of an AA′BB′ spin system, 4 H, $S_2C_6H_2$), 7.21 (m, 3 H, p-C_6H of CPh_3), 7.16−7.08 (m, 10 H, $S_2C_6H_2$, m-C_6H_2 of CPh_3), 6.77 (m, 6 H, o-C_6H_2 of CPh_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm, 67.7 MHz): δ 151.1, 137.9, 128.9, 128.8, 128.7, 128.4, 126.2 ($S_2C_6H_4$, C_6H_5), 95.9 (CPh_3). MS (FD^+): *m/z* 729 (M^+), 486 ($M^+ - CPh_3$); the correct isotope pattern was observed in each case.

X-ray Crystallography and Structure Solution. Brown single crystals (columns) of $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**) were obtained by slowly cooling a hot saturated THF solution of **1**. Yellow single crystals (columns) of $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**) formed when a concentrated THF solution of **2** was slowly evaporated. Orange single crystals (prisms) of $[Os(N)(S_2C_6H_4)(SC_6H_4SMe)]\cdot CH_2Cl_2$ ($\mathbf{3}\cdot CH_2Cl_2$) were grown from a CH_2Cl_2 solution at −30 °C. Black single crystals (plates) of $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**5**) formed when a solution of **5** in a CH_2Cl_2/hexane mixture was slowly evaporated. Crystals of **1** ,**2**, $\mathbf{3}\bullet CH_2Cl_2$, and **5** were sealed in glass capillaries. Data were collected on a Siemens P4 diffractometer at 200(2) K; data collection parameters ($4.5 \le 2\theta \le 54.1$ for **1** and **2**; $4.1 \le 2\theta \le 50$ for $\mathbf{3}\cdot CH_2Cl_2$; $4.4 \le 2\theta \le 44.1$ for **5**) are summarized in Table 1. For all complexes, crystal systems were determined photographically and space groups were assigned by systematic absences; further refinement confirmed the space group assignments. For complex **1**, no correction was made for absorption; for complexes **2**, $\mathbf{3}\cdot CH_2Cl_2$, and **5**, data were corrected for

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(10) (a) Debad, J. D.; Legzdins, P.; Reina, R.; Young, M. A.; Batchelor, R. J.; Einstein, W. B. *Organometallics* **1994**, *13*, 4315−4321. Nitrosyl N−O bond cleavage has also been achieved via other routes: (b) Odom, A. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 6613−6614. (c) Brouwer, E. B.; Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1994**, *13*, 2088−2091. (d) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41−48. (e) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; pp 279−280. (f) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988; p 71. (g) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41−85.

(11) Zhang, N.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1988**, *7*, 1126−1131.

(12) Shapley, P. A.; Zhang, N. *J. Am. Chem. Soc.* **1993**, *115*, 7866−7867.

(13) Binker, G. Dissertation, Universität Erlangen-Nürnberg, Jan 1987.

(14) Degani, J.; Fochi, R. *Synthesis*, **1976**, *7*, 471−472.

(15) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315−1320. See also: Willilams, D. S.; Coia, G. M.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 586−592.

Table 1. Crystallographic Data for $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**), $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**), $[Os(N)(S_2C_6H_4)(SC_6H_4SMe)]\cdot CH_2Cl_2$ (**3**$\cdot CH_2Cl_2$), and $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**5**)

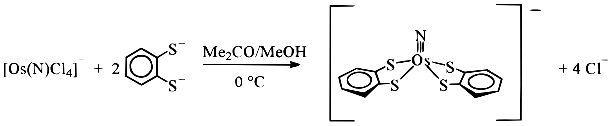
	1	**2**	**3**$\cdot CH_2Cl_2$	**5**
formula	$C_{28}H_{44}N_2RuS_4$	$C_{28}H_{44}N_2OsS_4$	$C_{14}H_{13}Cl_2NOsS_4$[a]	$C_{31}H_{23}NOsS_4$
fw	637.96	727.09	584.59[a]	727.94
space group	$Pna2_1$ (No. 33)	$Pna2_1$ (No. 33)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a, Å	36.881(6)	37.042(4)	8.552(1)	9.338(8)
b, Å	9.402(2)	9.375(2)	10.772(2)	10.001(3)
c, Å	17.652(2)	17.761(2)	19.716(3)	16.280(6)
α, deg				75.88(3)
β, deg				74.20(6)
γ, deg				69.55(5)
V, Å^3	6121(2)	6137(2)	1816.3(5)	1352(1)
Z	8	8	4	2
T, K	200(2)	200(2)	200(2)	200(2)
λ, Å[b]	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calc}, g/cm^3	1.385	1.574	2.138	1.788
μ, mm^{-1}	0.805	4.448	7.768	5.047
T_{max}, T_{min}		0.357, 0.097	0.145, 0.084	0.145, 0.072
R1 (wR2),[c,d] %	2.52 (4.20)	3.86 (8.03)	3.62 (8.48)	3.44 (8.97)

[a] Including solvent molecule. [b] Mo K_α; graphite monochromator. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F > 4\sigma(F)$. [d] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0009P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$.

absorption using an empirical method (XABS2).[16] Structures were solved by direct methods (SHELXS-86);[17] refinement on F^2 was carried out by full-matrix least-squares cycles (SHELXL-93).[18] All non-hydrogen atoms were refined anisotropically. For complexes **1** and **3**$\cdot CH_2Cl_2$, hydrogen atom positions were determined from the difference Fourier maps and were refined isotropically. For complexes **2** and **5**, hydrogen atoms were refined with a fixed isotropic thermal parameter calculated by multiplying the equivalent isotropic thermal parameter, U_{eq}, of the corresponding carbon atom by a factor of 1.5. Final values of R1 ($F > 4\sigma(F)$) and wR2 (all unique data) are listed in Table 1. Final difference Fourier map for **1** was essentially featureless, the largest peak being 0.317 and the deepest hole being −0.446 e/Å^3. For complexes **2**, **3**$\cdot CH_2Cl_2$, and **5**, all remaining residual electron density was located in the area of the strongly absorbing Os atom.

Results and Discussion

Treatment of $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**) with various electrophiles (such as Me^+, Et^+, and H^+) resulted, in all cases, in the formation of black materials. These products were insoluble in all common solvents; therefore, further characterization was not possible. For example, treatment of complex **1** with Me_3OBF_4 in CH_2Cl_2 gave an insoluble black precipitate that analyzed for the methyl derivative, $[\{Ru(N)(S_2C_6H_4)_2\}CH_3]_x$.[13] This product did not show a $\nu_{Ru\equiv N}$, but due to the insolubility of the material, the site of methylation could not be ascertained. Because of these difficulties, the analogous complex $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**) was prepared in order to exploit the greater kinetic stability of osmium complexes. Complex **2** could be prepared by simply treating the readily available $(N^nBu_4)[Os(N)Cl_4]$ with deprotonated 1,2-benzenedithiol (eq 2). Complex **2** was isolated as a yellow powder



(2)

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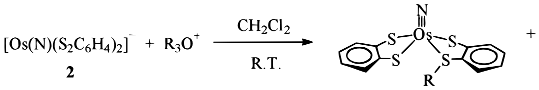
and identified by common spectroscopic methods. The NMR spectra of **2** are consistent with the square-pyramidal geometry of the anion shown in eq 2. The diagnostic $\nu_{Os\equiv N}$ of **2** is at 1063 cm^{-1}; this value is higher than the $\nu_{Ru\equiv N}$ of **1** (1024 cm^{-1}) but significantly lower than the $\nu_{Os\equiv N}$ of the starting material, $(N^nBu_4)[Os(N)Cl_4]$ (1126 cm^{-1}). This shift indicates that substitution of the chloro ligands with thiolato ligands weakens the Os≡N bond, suggesting that the four thiolate donors are significantly electron donating. π-Donation of the thiolate sulfur atoms to the osmium center could make the nitride more electron-rich and the sulfur atoms more electron-poor.[11] It should be noted that the $\nu_{Os\equiv N}$ for **2** is even lower than that reported for both $(N^nBu_4)[Os(N)(CH_2SiMe_3)_2(WS_4)]$ (1105 cm^{-1})[12] and $(N^nBu_4)[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]$ (1091 cm^{-1}).[11]

In contrast to our expectations, treatment of **2** with Me_3OBF_4 or Et_3OBF_4 in CH_2Cl_2 led to S-alkylation and gave the orange products $[Os(N)(S_2C_6H_4)(SC_6H_4SR)]$ (**3**, R = Me^+; **4**, R = Et^+) (eq 3). The alkylation of a thiolate donor was confirmed by



(3)

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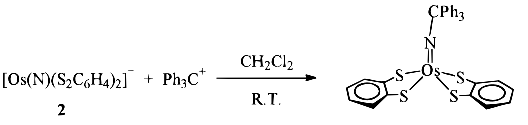
3, R = Me$^+$

4, R = Et$^+$

IR and NMR spectroscopy as well as by X-ray crystallography (for **3**). The $\nu_{Os\equiv N}$ values for **3** and **4** (1058 and 1056 cm^{-1}, respectively) are only slightly lower than that for **2**, and the NMR spectra of **3** and **4** indicate C_1 symmetry for both complexes. For example, the ^{13}C NMR spectrum of the starting complex, **2**, displays only three signals assignable to the aromatic C atoms of the $[Os(N)(S_2C_6H_4)_2]^-$ anion, but 12 signals for the aromatic ^{13}C atoms can be identified in the ^{13}C NMR spectra of **3** and **4**. As was the case with complex **1**, treatment of complex **2** with 1 equiv of HBF_4 (or $CF_3SO_3SiMe_3$) led to the formation of a black insoluble precipitate that could not be characterized fully.

In one case, alkylation at the nitrogen was observed and the product could be characterized. Treatment of **2** with Ph_3CPF_6 in CH_2Cl_2 resulted in the formation of a black product, $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**4**) (eq 4). The formation of the imido



(4)

2

5

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(16) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53−56.

(17) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *A46*, 467−473.

(18) Sheldrick, G. M. SHELXL-93. Universität Göttingen, Germany, 1993.

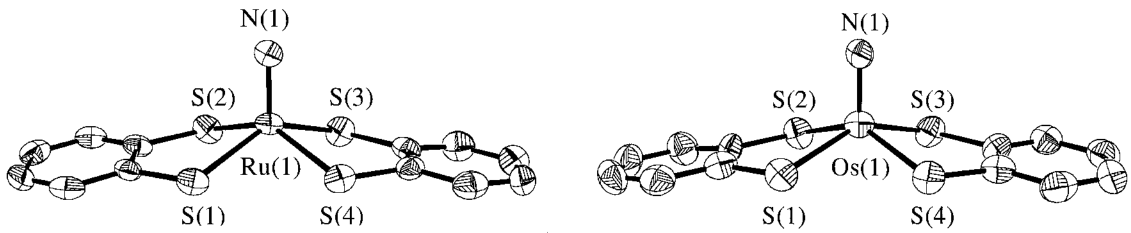

Figure 1. ORTEP diagrams of the anions of $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**) (left) and $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**) (right) at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Distances (Å) and Angles (deg) for $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**) and $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**)

	complex (M)			complex (M)	
	1 (Ru)	**2** (Os)		**1** (Ru)	**2** (Os)
			Distances		
M(1)−N(1)	1.613(5)	1.64(1)	M(2)−N(2)	1.621(5)	1.66(1)
M(1)−S(1)	2.328(1)	2.337(4)	M(2)−S(5)	2.325(1)	2.319(4)
M(1)−S(2)	2.319(1)	2.326(4)	M(2)−S(6)	2.325(2)	2.336(4)
M(1)−S(3)	2.330(2)	2.311(4)	M(2)−S(7)	2.319(2)	2.316(4)
M(1)−S(4)	2.325(1)	2.325(4)	M(2)−S(8)	2.317(2)	2.315(4)
			Angles		
N(1)−M(1)−S(1)	108.5(2)	107.7(3)	N(2)−M(2)−S(5)	106.0(2)	107.4(5)
N(1)−M(1)−S(2)	107.6(2)	107.9(4)	N(2)−M(2)−S(6)	108.3(2)	107.8(3)
N(1)−M(1)−S(3)	108.5(2)	105.2(3)	N(2)−M(2)−S(7)	107.3(2)	108.8(4)
N(1)−M(1)−S(4)	106.0(2)	107.7(4)	N(2)−M(2)−S(8)	108.5(2)	105.3(3)
S(1)−M(1)−S(2)	85.76(5)	85.8(1)	S(5)−M(2)−S(6)	85.64(5)	85.2(1)
S(1)−M(1)−S(4)	83.07(5)	83.7(1)	S(5)−M(2)−S(8)	83.18(5)	85.2(1)
S(2)−M(1)−S(3)	84.36(5)	84.8(1)	S(6)−M(2)−S(7)	84.60(5)	83.6(1)
S(3)−M(1)−S(4)	85.70(5)	85.8(1)	S(7)−M(2)−S(8)	85.78(5)	85.7(1)

ligand, $NCPh_3^-$, in complex **4** was confirmed by both IR and NMR spectroscopy and by X-ray crystallography. The strong $\nu_{Os\equiv N}$ present in the IR spectrum of complex **2** is absent in **4**. Furthermore, **4** exhibits a new band at 1178 cm^{-1}; imido complexes commonly possess a band in this region.[19] The number of aromatic ^{13}C signals observed in the ^{13}C spectrum of **4** is consistent with a higher symmetry for **4** as compared to **3** and further supports the formation of the $NCPh_3^-$ ligand. The resonance of the quaternary carbon of the trityl group was located at 95.9 ppm in the ^{13}C NMR spectrum. This value is significantly upfield from the position of the central carbon atom in the free Ph_3C^+ cation (214 ppm in CF_3CO_2D).[20] The ^{13}C chemical shifts for the α-carbon atoms of *tert*-butylimido complexes are reported to be between 64 to 84 ppm,[21] and the shift of the quaternary carbon atom of the trityl group of $Ph_3C-N{=}C{=}NSiMe_3$ is reported at 73 ppm.[22] Complex **4** is soluble in organic solvents like toluene and ether and is insoluble in solvents like methanol. Other examples of the formation of an imido complex from the reaction of the Ph_3C^+ cation with a nitrido complex have been reported in the literature.[23] The reason that Ph_3CPF_6 alkylates the N atom of **2** but R_3OBF_4 alkylates a S atom of **2** may be found in the electronic differences between the Ph_3C^+ and the Me^+ or Et^+ cations. More important, however, are probably steric factors; the planar and more bulky trityl cation preferentially attacks the more exposed nitrogen atom.

Description of Structure. Compounds **1** and **2** both crystallize in the orthorhombic space group $Pna2_1$. ORTEP representations of the anions of **1** and **2** are shown in Figure 1. Selected distances and angles are listed in Table 2. Both compounds contain two independent molecules in the asymmetric unit; in each case, the two molecules are statistically identical and only one molecule has been arbitrarily chosen for display. The $(N^nBu_4)^+$ cations in both structures will not be discussed. The anions of **1** and **2** are mononuclear with square-pyramidal geometry; the terminal nitrido ligand occupies the apical position, and two chelating $(S_2C_6H_4)^{2-}$ ligands form the basal plane. The metal atoms are 0.69 Å (for **1**) and 0.68 Å (for **2**) above the plane of the basal ligands. The anions possess no crystallographically imposed symmetry but can be considered to possess idealized C_{2v} symmetry with the C_2 axis lying along the M≡N bond, a fact supported in solution by the ^{13}C NMR spectra of **1**[9] and **2**. Complexes **1** and **2** are isostructural and are statistically identical. The only noticeable difference between the two structures is that the M≡N bond lengths for the two independent molecules of **2**, 1.64(1) and 1.66(1) Å, are slightly longer than those for **1**, 1.613(5) and 1.621(5) Å; this difference, however, is small and cannot be considered significant within the 3σ criterion. The average N−M−S angles are 107.6 and 107.2° for **1** and **2**, respectively; the N−Ru−S angles for **1** are similar to the N−Ru−S angles reported for $(N^nBu_4)[Ru(N)(NHCOCH_2CH_2S)_2]$ (107.1 and 109.7°), and likewise, the N−Os−S angles for **2** are in the range of the N−Os−S angles reported for $(N^nBu_4)[Os(N)\{O_2CCH(NHCOCH_3)CH_2S\}_2]$ and $(N^nBu_4)[Os(N)(O_2CCH_2CH_2S)_2]$ (107.1°−111.9°).[24] N−M−Cl angles are reported to be 104.58° for $(AsPh_4)[Ru(N)Cl_4)]$[25] and 104.29° for $(AsPh_4)[Os(N)Cl_4)]$,[26] and the bend of the basal ligands away from the plane of the metal has been attributed to the repulsion between the π-electrons of the metal−nitrogen triple bond and the metal−Cl bonding electrons.[26] The greater

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(19) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988; pp 123−125.

(20) Hellwinkel, D.; Fritsch, H. *Chem. Ber.* **1989**, *122*, 2351−2360.

(21) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988; p 133.

(22) Ruppert, I. *Tetrahedron Lett.* **1977**, 1987−1990.

(23) (a) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Neaves, B. D.; Dahlstrom, P.; Hyde, J.; Zubieta, J. *J. Organomet. Chem.* **1981**, *213*, 109−124. (b) Fenske, D.; Kujanek, R.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1983**, *507*, 51−58.

(24) Schwab, J. J.; Wilkinson, E. C.; Wilson, S. R.; Shapley, P. A. *J. Am. Chem. Soc.* **1991**, *113*, 6124−6129.

(25) Phillips, F. L.; Skapski, A. C. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2667−2670.

(26) Phillips, F. L.; Skapski, A. C. *J. Cryst. Mol. Struct.* **1975**, *5*, 83−92.

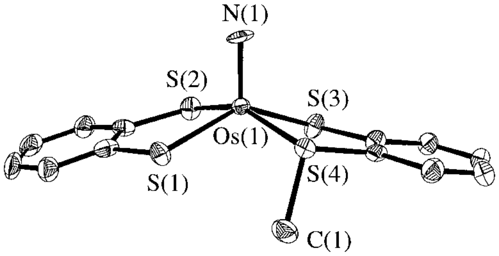

Figure 2. ORTEP diagram of $[Os(N)(S_2C_6H_4)(SC_6H_4SMe)]$ (**3**) at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Distances (Å) and Angles (deg) for $[Os(N)(S_2C_6H_4)(SC_6H_4SMe)]\cdot CH_2Cl_2$ ($\mathbf{3}\cdot CH_2Cl_2$)

Distances			
Os(1)−N(1)	1.639(9)	Os(1)−S(3)	2.318(3)
Os(1)−S(1)	2.298(3)	Os(1)−S(4)	2.403(3)
Os(1)−S(2)	2.312(3)	S(4)−C(1)	1.83(1)
Angles			
N(1)−Os(1)−S(1)	107.6(4)	S(1)−Os(1)−S(2)	86.9(1)
N(1)−Os(1)−S(2)	105.1(4)	S(1)−Os(1)−S(4)	87.5(1)
N(1)−Os(1)−S(3)	112.2(4)	S(2)−Os(1)−S(3)	83.8(1)
N(1)−Os(1)−S(4)	98.6(4)	S(3)−Os(1)−S(4)	85.7(1)

bend observed for thiolate-ligated nitrido complexes when compared to the choride-ligated complexes reflects the greater donor ability of the sulfur atom. The $M\equiv N$ and M−S bond lengths for **1** and **2** are consistent with others reported in the literature.[11,24,27]

Methylation of **2** yielded $[Os(N)(S_2C_6H_4)(SC_6H_4SMe)]$ (**3**) (eq 3), and the alkylation of the sulfur atom of a 1,2-benzenedithiolate ligand was confirmed by X-ray crystallography. Complex $\mathbf{3}\cdot CH_2Cl_2$ crystallizes in the orthorhombic space group $P2_12_12_1$. An ORTEP representation of **3** is shown in Figure 2. Selected distances and angles are listed in Table 3. Complex **3** is mononuclear with distorted square-pyramidal geometry; the terminal nitrido ligand occupies the apical position, and chelating $(S_2C_6H_4)^{2-}$ and $(SC_6H_4SMe)^-$ ligands form the basal plane. The metal atom is 0.63 Å above the plane of the basal ligands. The distortion seen here is due to the smaller N(1)−Os(1)−S(4) angle at the thioether sulfur atom, 98.6(4)°, and the larger N(1)−Os(1)−S(3) angle for the thiolate sulfur atom, 112.2(4)°, of the $(SC_6H_4SMe)^-$ ligand as compared to the average N−Os−S angle for **2** (107.2°). Also, the Os−S bond length of the S(4) (thioether) atom, 2.403(3) Å, is longer than the other Os−S (thiolate) bond lengths, 2.298(3)−2.318(3) Å, as expected. The S(4)−C(1) distance of 1.83(1) Å is consistent with literature values reported for other complexes with a chelating $(SC_6H_4SMe)^-$ ligand.[28]

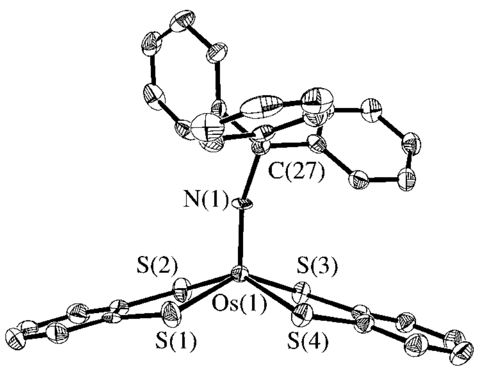

Figure 3. ORTEP diagram of $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**5**) at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Distances (Å) and Angles (deg) for $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**5**)

Distances			
Os(1)−N(1)	1.710(6)	Os(1)−S(3)	2.279(2)
Os(1)−S(1)	2.302(2)	Os(1)−S(4)	2.280(3)
Os(1)−S(2)	2.304(2)	N(1)−C(27)	1.47(1)
Angles			
N(1)−Os(1)−S(1)	109.6(2)	S(1)−Os(1)−S(4)	83.08(9)
N(1)−Os(1)−S(2)	108.2(2)	S(2)−Os(1)−S(3)	83.29(8)
N(1)−Os(1)−S(3)	107.0(2)	S(3)−Os(1)−S(4)	86.28(9)
N(1)−Os(1)−S(4)	106.9(2)	Os(1)−N(1)−C(27)	163.3(5)
S(1)−Os(1)−S(2)	85.63(8)		

The alkylation at the nitrogen atom of **2** with the trityl cation to form $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**5**) (eq 4) was also confirmed by X-ray crystallography. Complex **5** crystallizes in the triclinic space group $P\bar{1}$. An ORTEP representation of **5** is shown in Figure 3. Selected distances and angles are listed in Table 4. Complex **5** possesses no crystallographically imposed symmetry, but can be considered to posses idealized C_{2v} symmetry with the C_2 axis lying along the Os=N bond, a fact supported in solution by the ^{13}C NMR spectrum. Complex **5** is also mononuclear with square-pyramidal geometry; the terminal $NCPh_3^-$ ligand occupies the apical position, and the two chelating $(S_2C_6H_4)^{2-}$ ligands form the basal plane. The metal atom is 0.70 Å above the plane of the basal ligands. Alkylation at the nitrogen results in the lengthening of the Os−N bond from 1.65 Å (an average of the two independent molecules of **2**) to 1.710(6) Å (**5**). The Os(1)−N(1)−C(27) angle, 163.3(5)°, is slightly smaller than the M−N−C angles in $[Mo(NCPh_3)(S_2CNMe_2)_3]^+$ (175.1°)[23a] and $[(Ph_3CN)WCl_4(\mu\text{-}F)WNCl_2(\mu\text{-}F)Cl_4W(NCPh_3)]^+$ (179°)[23b] but identical to the Os−N−C angle found in $[Os(NMe)(CH_2SiMe_3)_4]$ (163.6°).[29] The C(27)−N(1) bond length of 1.47(1) Å is identical with those of other $NCPh_3^-$ ligands reported in the literature.[23] The average Os−S bond length for **5** (2.29 Å) is shorter than that for **2** (2.32 Å), indicating a stronger Os−S bond in **5** which may be due to the lower Os−N bond order in **5**; however, the average N−Os−S angle does not change (107.9° for **5** and 107.2° for **2**).

Concluding Remarks. The synthesis and structure of three new osmium complexes, $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**), $[Os(N)(S_2C_6H_4)(SC_6H_4SMe)]$ (**3**), and $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**5**), have been presented here. The structure of $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**) was also determined, and **1** was found to be isostructural with **2**. Complex **2** was treated with various electrophiles (Me^+, Et^+, and Ph_3C^+) in order to determine the most nucleophilic site of **2**. It turned out that **2** could be alkylated either at a sulfur atom of a 1,2-benzenedithiolate ligand (with Me^+ and Et^+) or at the nitrogen atom (with Ph_3C^+). It may be concluded, however, that the sulfur atoms of **2** are more nucleophilic than the nitride ligand and that the trityl cation attacks the nitrogen of **2** for steric reasons.

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(27) (a) Liang, H.-C.; Shapley, P. A. *Organometallics* **1996**, *15*, 1331−1333. (b) Shapley, P. A.; Liang, H.-C.; Shusta, J. M.; Schwab, J. J.; Zhang, N.; Wilson, S. R. *Organometallics* **1994**, *13*, 3351−3359. (c) Shapley, P. A.; Gebeyehu, Z.; Zhang, N.; Wilson, S. R. *Inorg. Chem.* **1993**, *32*, 5646−5651.

(28) (a) Sellmann, D.; Lanzrath, G.; Huttner, G.; Zsolnai, L.; Krüger, C.; Claus, K. H. *Z. Naturforsch.* **1983**, *38B*, 961−981. (b) Sellmann, D.; Binker, G.; Schwarz, J.; Knoch, F.; Böse, R.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1987**, *323*, 323−338. (c) Sellmann, D.; Fetz, A.; Moll, M.; Knoch, F. *J. Organomet. Chem.* **1988**, *355*, 495−511. (d) Sellmann, D.; Fetz, A.; Moll, M.; Knoch, F. *Polyhedron* **1989**, *8*, 613−625. (e) Sellmann, D.; Schillinger, H.; Knoch, F.; Moll, M. *Inorg. Chim. Acta* **1992**, *198*, 351−357. (f) Sellmann, D.; Schillinger, H.; Knoch, F. *Z. Naturforsch.* **1992**, *47B*, 748−753.

(29) Shapley, P. A.; Own, Z.-Y.; Huffman, J. C. *Organometallics* **1986**, *5*, 1269−1271.

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Supporting Information Available: X-ray crystallographic data, in CIF format, for compounds **1**, **2**, **3**·CH_2Cl_2, and **5** are available on the Internet. Access information is given on any current masthead page. Details of the X-ray crystallography have also been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen mbH, D-76344 Eggenstein-Leopoldshafen, Germany, and can be obtained by citing the depository numbers CSD 406342 for $(N^nBu_4)[Ru(N)(S_2C_6H_4)_2]$ (**1**), CSD 406343 for $(N^nBu_4)[Os(N)(S_2C_6H_4)_2]$ (**2**), CSD 406344 for $[Os(N)(S_2C_6H_4)(SC_6H_4SMe)]$·$CH_2Cl_2$ (**3**·CH_2Cl_2), and CSD 406345 for $[Os(NCPh_3)(S_2C_6H_4)_2]$ (**5**), the authors, and the reference.

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