



Ruthenium(VI) and osmium(VI) nitrido complexes with halogenated phenoxide and thiophenoxide ligands

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ARTICLE INFO

Article history:

Received 12 May 2009

Received in revised form 27 August 2009

Accepted 11 September 2009

Available online 16 September 2009

Keywords:

Ruthenium

Osmium

Nitrido

Phenoxide

Thiophenoxide

ABSTRACT

Treatment of $[\text{Bu}^n_4\text{N}][\text{Ru}(\text{N})\text{Cl}_4]$ with $\text{Na}(\text{OR})$ afforded $[\text{Bu}^n_4\text{N}][\text{Ru}(\text{N})(\text{OR})_4]$ ($\text{R} = \text{C}_6\text{F}_5$ (**1**), $\text{C}_6\text{F}_4\text{H}$ (**2**), C_6Br_5 (**3**)), whereas that with $[\text{Bu}^n_4\text{N}][\text{Os}(\text{N})\text{Cl}_4]$ gave $[\text{Bu}^n_4\text{N}][\text{Os}(\text{N})(\text{OR})_3\text{Cl}]$ ($\text{R} = \text{C}_6\text{F}_5$ (**4**), $\text{C}_6\text{F}_4\text{H}$ (**5**), C_6Br_5 (**6**)). Treatment of $[\text{Bu}^n_4\text{N}][\text{M}(\text{N})\text{Cl}_4]$ with $\text{Na}(\text{SC}_6\text{F}_4\text{H})$ and $\text{Na}(\text{Sxyl})$ ($\text{xyl} = 2,6\text{-dimethylphenyl}$) afforded $[\text{Bu}^n_4\text{N}][\text{M}(\text{N})(\text{SC}_6\text{F}_4\text{H})_4]$ ($\text{M} = \text{Ru}$ (**7**), Os (**8**)) and $[\text{Bu}^n_4\text{N}][\text{M}(\text{N})(\text{Sxyl})_4]$ ($\text{M} = \text{Ru}$ (**9**), Os (**10**)), respectively. The crystal structures of compounds **1**, **6** and **9** have been determined.

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1. Introduction

Transition-metal nitrido compounds have attracted much attention due to their possible involvements in metal-mediated nitrogen atom transfer reactions and nitrogen fixation [1–4]. There is an increasing interest in nitrido compounds of late transition-metals that are known to exhibit electrophilic behavior [5–18]. In particular, reactions of electrophilic Os(VI) nitrido complexes containing N-donor ligands such as polypyridyl and hydridotris(pyrazolyl)borate with nucleophiles, including amine N-oxides, secondary amines, azide, cyanide, BPh_3 , and thiols have been studied extensively [11–14]. Recently, Lau and coworkers demonstrated that Ru(VI) nitrido compounds with salen ligands are considerably more reactive than the Os(VI) congeners [15]. In donor solvents or in the presence of Lewis bases, $[\text{Ru}(\text{salen})(\text{N})]^+$ complexes undergo facile bimolecular $\text{N} \cdots \text{N}$ coupling to give Ru(III) species and N_2 [16]. In the presence of pyridine, Ru(VI) nitrido complexes reacted with alkenes to give Ru(IV) complexes with deprotonated aziridine ligands [17]. This prompted us to explore the chemistry of Ru(VI) nitrido complexes containing electron-withdrawing halogenated phenoxide and thiophenoxide ligands.

The most common Ru(VI) nitrido complexes are those containing halide, nitrogen, carbon and sulfur donor ligands [19]. Although Ru(VI) nitrido complexes with chelating alkoxide and phenoxide li-

gands are well documented [20–23], to our knowledge, Ru(VI) complexes with simple phenoxide ligands have not been isolated. Our interest in high-valent Ru halogenated phenoxide complexes is also stimulated by a report that Ru(IV) alkylidene pentafluorophenoxide complexes are active catalysts for alkene metathesis [24]. Herein, we describe the synthesis and structures of Ru(VI) and Os(VI) nitrido compounds with halogenated phenoxide and thiophenoxide ligands.

2. Experimental

2.1. General

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300, 282.5 and 121.5 MHz for ^1H , ^{19}F and ^{31}P , respectively. Chemical shifts (δ , ppm) were reported with reference to SiMe_4 (^1H), $\text{CF}_3\text{C}_6\text{H}_5$ (^{19}F) and H_3PO_4 (^{31}P). Infrared spectra (KBr) were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, UK.

The compounds $[\text{Bu}^n_4\text{N}][\text{M}(\text{N})\text{Cl}_4]$ ($\text{M} = \text{Ru}$, Os) were prepared according to literature methods [25,26]. Pentafluorophenol, pentabromophenol, 2,3,5,6-tetrafluorophenol, 2,3,5,6-tetrafluorothiophenol, and 2,6-dimethylthiophenol were purchased from

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Aldrich Ltd. and used as received. Sodium salts of halogenated phenols and thiophenols were prepared by reaction of sodium hydride with halogenated phenols and thiophenols, respectively, in tetrahydrofuran (THF).

2.2. Synthesis of complexes

2.2.1. $[Bu^t_4N][Ru(N)(OR)_4]$ ($R = C_6F_5$ (**1**), C_6F_4H (**2**), C_6Br_5 (**3**))

A mixture of $[Bu^t_4N][Ru(N)Cl_4]$ (100 mg, 0.2 mmol) and Na(OR) (0.8 mmol) in THF (25 mL) was stirred at room temperature overnight. The solvent of filtrate was removed *in vacuo* and the residue was washed with hexane and Et₂O. The solid crude product was recrystallized from THF–Et₂O–hexane to afford crystals or crystalline solid.

Compound 1: Orange-yellow crystals. Yield: 80 mg (37%). ¹H NMR (CDCl₃): δ 3.45 (m, 8H, CH₃CH₂CH₂CH₂), 1.84 (m, 8H, CH₃CH₂CH₂CH₂), 1.46 (m, 8H, CH₃CH₂CH₂CH₂), 1.02 (t, 12H, CH₃CH₂CH₂CH₂). ¹⁹F {¹H} NMR (CDCl₃): δ –157.4, –168.1, –170.2. *Anal. Calc.* for C₄₀H₃₆F₂₀N₂O₄Ru: C, 44.1; H, 3.33; N, 2.57. Found: C, 44.6; H, 3.51; N, 2.71%.

Compound 2: Orange crystalline solid. Yield: 79 mg (39%). ¹H NMR (CDCl₃): δ 6.79 (m, 4H, OC₆F₄H), 3.32 (m, 8H, CH₃CH₂CH₂CH₂), 1.84 (m, 8H, CH₃CH₂CH₂CH₂), 1.44 (m, 8H, CH₃CH₂CH₂CH₂), 0.99 (t, 12H, CH₃CH₂CH₂CH₂). ¹⁹F {¹H} NMR (CDCl₃): δ –145.8, –157.8 ppm. *Anal. Calc.* for C₄₀H₄₀F₁₆N₂O₄Ru: C, 47.2; H, 3.96; N, 2.75. Found: C, 47.0; H, 4.66; N, 2.71%.

Compound 3: Orange-red crystalline solid. Yield: 166 mg (36%). ¹H NMR (CDCl₃): δ 3.60 (m, 8H, CH₃CH₂CH₂CH₂), 1.43 (m, 8H, CH₃CH₂CH₂CH₂), 1.10 (m, 8H, CH₃CH₂CH₂CH₂), 1.05 (t, 12H, CH₃CH₂CH₂CH₂). *Anal. Calc.* for C₄₀H₃₆Br₂₀N₂O₄Ru: C, 20.8; H, 1.57; N, 1.21. Found: C, 20.2; H, 1.90; N, 1.20%.

2.2.2. $[Bu^t_4N][Os(N)(OR)_3Cl]$ ($R = C_6F_5$ (**4**), C_6F_4H (**5**), C_6Br_5 (**6**))

A mixture of $[Bu^t_4N][Os(N)Cl_4]$ (100 mg, 0.17 mmol) and Na(OR) (0.51 mmol) in THF (25 mL) was stirred at room temperature overnight. The solvent of filtrate was removed *in vacuo* and the residue was washed with hexane and Et₂O. The crude product was recrystallized from THF–Et₂O–hexane to afford crystals or crystalline solid.

Compound 4: Yellow solid. Yield: 75 mg (43%). ¹H NMR (CDCl₃): δ 3.15 (m, 8H, CH₃CH₂CH₂CH₂), 1.60 (m, 8H, CH₃CH₂CH₂CH₂), 1.41 (m, 8H, CH₃CH₂CH₂CH₂), 0.99 (t, 12H, CH₃CH₂CH₂CH₂). ¹⁹F {¹H} NMR (CDCl₃): δ –157.8, –158.1, –158.6, –164.6, –167.7, –168.2. *Anal. Calc.* for C₃₄H₃₆ClF₁₅N₂O₃Os: C, 35.60; H, 3.52; N, 2.72. Found: C, 36.20; H, 3.45; N, 2.83%.

Compound 5: Yellow solid. Yield: 75 mg (45%). ¹H NMR (CDCl₃): δ 6.61 (m, 3H, OC₆F₄H), 3.45 (m, 8H, CH₃CH₂CH₂CH₂), 1.88 (m, 8H, CH₃CH₂CH₂CH₂), 2.98 (m, 8H, CH₃CH₂CH₂CH₂), 0.98 (t, 12H, CH₃CH₂CH₂CH₂). ¹⁹F {¹H} NMR (CDCl₃): δ –142.4, –144.4, –156.8, –157.9, 162.9. *Anal. Calc.* for C₃₄H₃₉ClF₁₂N₂O₃Os: C, 41.8; H, 4.02; N, 2.87. Found: C, 41.7; H, 4.10; N, 3.00%.

Compound 6: Red crystals. Yield: 76 mg (23%). ¹H NMR (CDCl₃): δ 3.32 (m, 8H, CH₃CH₂CH₂CH₂), 1.84 (m, 8H, CH₃CH₂CH₂CH₂), 1.44 (m, 8H, CH₃CH₂CH₂CH₂), 0.99 (t, 12H, CH₃CH₂CH₂CH₂). *Anal. Calc.* for C₃₄H₃₆Br₁₅ClN₂O₃Os: C, 21.0; H, 1.87; N, 1.44. Found: C, 21.8; H, 2.00; N, 1.40%.

2.2.3. $[Bu^t_4N][M(N)(SC_6F_4H)_4]$ ($M = Ru$ (**7**), Os (**8**))

A mixture of $[Bu^t_4N][M(N)Cl_4]$ (100 mg; M = Ru (0.2 mmol), Os (0.17 mmol)) and Na(SC₆F₄H) in THF (25 mL) was stirred at room temperature overnight. The solvent of filtrate was removed *in vacuo* and the residue was washed with hexane and Et₂O. The solid crude product was recrystallized from CH₂Cl₂–hexane or THF–Et₂O–hexane to afford crystalline solid.

Compound 7: Orange-yellow solid. Yield: 82 mg (38%). ¹H NMR (CDCl₃): δ 7.24 (m, 4H, SC₆F₄H), 3.67 (m, 8H, CH₃CH₂CH₂CH₂), 1.82

(m, 8H, CH₃CH₂CH₂CH₂), 1.43 (m, 8H, CH₃CH₂CH₂CH₂), 0.98 (t, 12H, CH₃CH₂CH₂CH₂). ¹⁹F {¹H} NMR (CDCl₃): δ –131.3, –142.6. *Anal. Calc.* for C₄₀H₄₀F₁₆N₂S₄Ru: C, 44.4; H, 3.73; N, 2.59. Found: C, 43.0; H, 4.60; N, 2.80%.

Compound 8: Yellow solid. Yield: 70 mg (35%). ¹H NMR (CDCl₃): δ 7.34 (m, 4H, SC₆F₄H), 3.16 (m, 8H, CH₃CH₂CH₂CH₂), 1.85 (m, 8H, CH₃CH₂CH₂CH₂), 1.44 (m, 8H, CH₃CH₂CH₂CH₂), 0.99 (t, 12H, CH₃CH₂CH₂CH₂). ¹⁹F {¹H} NMR (CDCl₃): δ –132.1, –142.6. *Anal. Calc.* for C₄₀H₄₀F₁₆N₂OsS₄?2CH₂Cl₂: C, 37.6; H, 3.31; N, 2.09. Found: C, 37.7; H, 3.21; N, 1.97%.

2.2.4. $[Bu^t_4N][M(N)(Sxyl)_4]$ ($xyl = 2,6$ -dimethylphenyl; $M = Ru$ (**9**), Os (**10**))

A mixture of $[Bu^t_4N][M(N)Cl_4]$ (M = Ru; 100 mg, 0.2 mmol, M = Os; 100 mg, 0.17 mmol) and Na(Sxyl) in THF (25 mL) was stirred at room temperature overnight. The solvent of filtrate was removed *in vacuo* and the residue was washed with hexane and Et₂O. The solid crude product was recrystallized from CH₂Cl₂–hexane or THF–Et₂O–hexane to afford crystals or crystalline solid.

Compound 9: Orange crystals. Yield: 85 mg (47%). ¹H NMR (CDCl₃): δ 6.85 (m, 12H, phenyl), 3.46 (m, 8H, CH₃CH₂CH₂CH₂), 2.71 (s, 24H, Me), 1.85 (m, 8H, CH₃CH₂CH₂CH₂), 1.60 (m, 8H, CH₃CH₂CH₂CH₂), 0.98 (t, 12H, CH₃CH₂CH₂CH₂) ppm. *Anal. Calc.* for C₄₈H₇₂N₂RuS₄?2CH₂Cl₂: C, 59.4; H, 7.52; N, 2.83. Found: C, 59.5; H, 7.70; N, 2.70%.

Compound 10: Yellow solid. Yield: 83 mg (49%). ¹H NMR (CDCl₃): δ 6.83 (m, 12H, phenyl), 3.62 (m, 8H, CH₃CH₂CH₂CH₂), 2.82 (s, 24H, Me), 1.81 (m, 8H, CH₃CH₂CH₂CH₂), 1.43 (m, 8H, CH₃CH₂CH₂CH₂), 0.99 (t, 12H, CH₃CH₂CH₂CH₂). *Anal. Calc.* for C₄₈H₇₂N₂OsS₄?2CH₂Cl₂: C, 54.5; H, 6.90; N, 2.59. Found: C, 54.1; H, 7.02; N, 2.50%.

2.3. X-ray crystallography

Complexes **1**, **6**, and **9**·THF have been characterized by X-ray diffraction studies. Intensity data were collected on a Bruker SMART

Table 1
Crystallographic data and experimental details for $[Bu^t_4N][Ru(N)(OC_6F_5)_4]$ (**1**), $[Bu^t_4N][Os(N)(OC_6Br_5)_3Cl]$ (**6**), and $[Bu^t_4N][Ru(N)(Sxyl)_4]$ ·THF (**9**·THF).

	1	6	9 ·THF
Formula	C ₄₀ H ₃₆ F ₂₀ N ₂ O ₄ Ru	C ₃₃ H ₃₄ Br ₁₅ ClN ₂ O ₃ Os	C ₅₂ H ₈₀ N ₂ ORuS ₄
Formula weight	1089.78	1930.92	978.49
a (Å)	10.0983(7)	16.5100(11)	11.7144(13)
b (Å)	23.3803(17)	18.4444(13)	15.1225(16)
c (Å)	18.5893(14)	19.0686(13)	15.2081(16)
α (°)	90	90	89.812(2)
β (°)	90.9850(10)	111.7590(10)	83.824(2)
γ (°)	90	90	74.508(2)
V (Å ³)	4388.3(6)	5393.0(6)	2580.3(5)
Z	4	4	2
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	P2 ₁ /n	P1̄
D _{calc} (g cm ⁻³)	1.649	2.378	1.259
T (K)	173(2)	173(2)	100(2)
μ (mm ⁻¹)	0.485	13.559	0.503
F(0 0 0)	2184	3552	1044
Number of reflections	13 987	38 629	12 806
Number of independent reflections	3733	11 619	8723
R _{int}	0.0246	0.0426	0.0504
R ₁ , wR ₂ (I > 2σ(I))	0.0356, 0.0876	0.0454, 0.1025	0.0551, 0.0898
R ₁ , wR ₂ (all data)	0.042, 0.090	0.0869, 0.1127	0.1061, 0.1008
Goodness-of-fit (GOF) ^a	1.033	0.951	0.974

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

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