(Nitrido)ruthenium(VI) and -osmium(VI) Complexes with Catecholate Auxiliaries: Synthesis, Structure, and Conversion into a (Phosphoraniminato)osmium(V) Complex

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Treatment of $[NnBu_4][M^{VI}NCl_4]$ (where M = Ru, Os) with catechol (H_2Cat) and 3,5-di-*tert*-butylcatechol (H_2DBCat) in the presence of 2,6-dimethylpyridine (2,6-Me_2Py) gave $[NnBu_4][M^{VI}N(Cat)_2]$ (where M = Ru **1a**, Os **1b**) and [2,6-Me_2PyH][$M^{VI}N(DBCat)_2$] (where M = Ru **2a**, Os **2b**), respectively, in 75–90 % yields. Reaction of **2b** with triphenylphosphane afforded the (phosphoraniminato)osmium(V) complex $[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$ (**3**) in 90 % yield. X-ray crystal structure determinations on **1a**, **1b** and **3** reveal M≡N distances of 1.603(4) and 1.641(8) Å (for **1a** and **1b**, respectively) and an Os–N($NPPh_3$) distance of 2.077(3) Å (for **3**). The C–O distances in the three complexes range from 1.341(4) to 1.374(7) Å, indicating that the coordinated catecholate ligands adopt the catecholate(2–) state, rather than the semiquinonate(1–) or quinone states.

Introduction

(Nitrido)ruthenium and -osmium complexes are among the most extensively studied high-valent ruthenium and osmium compounds.[1] Stable mononuclear species with Ru≡N or Os≡N bonds have become accessible through many types of auxiliary ligands, including halides,[2] phosphanes/arsanes/stibanes[3−5] silyloxy,[6] alkyl,[6−8] thiocyanate,[7] thiolate or dithiolene,[7,9−11] ammine,[12,13] cyanide,[14] pyridine or polypyridine,[4,15−18] ureato,[19] cysteine(2−),[20] alkoxide,[21] diamine,[22] *N*-pyridinecarbonyl and/or *N*-hydroxybenzoyl diamide,[23] hydrotris(pyrazolyl)-borate,[24−27] trispyrazolylmethane,[28,29] imidodiphosphanylchalcogenido,[30,31] Schiff bases,[32] *meso*-octamethylporphrinogen,[33] porphyrin,[34,35] and aryl/alkyl acetylide.[36] The ruthenium and osmium ions in these nitrido complexes have exclusively a high oxidation state of +6 and therefore demonstrate the remarkable ability of the nitrido group to stabilize ruthenium(VI) and osmium(VI) species.

We have recently been interested in exploring the chemistry of (nitrido)ruthenium and -osmium complexes bearing catecholate ligands (the oxygen analogues of dithiolenes such as 1,2-benzenedithiolates), which is an important type of non-innocent ligands known to have three oxidation states, namely, catecholate(2−), semiquinonate(1−), and quinone, in complexes with metal ions.[37,38] We envisage that this new class of (nitrido)ruthenium and -osmium complexes may exhibit rich redox chemistry. The different oxidation states of the coordinated catecholate ligands, if achievable, would significantly regulate the reactivity of the Ru≡N and Os≡N functional groups. On the other hand, given the remarkable ability of the nitrido group to stabilize ruthenium(VI) and osmium(VI) species and the ambiguity in charge distribution in ruthenium and osmium catecholate complexes such as $[Os(Cat)_3]$ (H_2Cat = catechol), $[Ru(DBCat)_3]$ (H_2DBCat = 3,5-di-*tert*-butylcatechol), and $[Os(DBCat)_3]$,[39,40] a ruthenium(VI)/osmium(VI) catecholate complex with clear charge distribution might be obtained by introducing a nitrido group in the complex. The structure determination of the (nitrido)metal catecholates may provide a unique opportunity to examine the structural features of genuine Ru^{VI}- or Os^{VI}-catecholate(2−) bonds.

In the present work, we report on the synthesis of (nitrido)ruthenium(VI) and -osmium(VI) complexes $[M^{VI}N(L)_2]^-$ (where L = Cat, M = Ru **1a**, Os **1b**; L = DBCat, M = Ru **2a**, Os **2b**) and the crystal structures of $[NnBu_4][Ru^{VI}N(Cat)_2]$ (**1a**) and $[NnBu_4][Os^{VI}N(Cat)_2]$ (**1b**). These, to the best of our knowledge, are the first examples of isolated mononuclear (nitrido)metal complexes containing catecholate auxiliaries. Prior to this work, only dinuclear (μ-nitrido)metal complexes, such as the Fe(μ-N)Fe complexes prepared by Wieghardt and co-workers,[41,42] were known to contain catecholate ligands. Interestingly, the (nitrido)osmium complex $[Os^{VI}N(DBCat)_2]^-$ reacted with tri-

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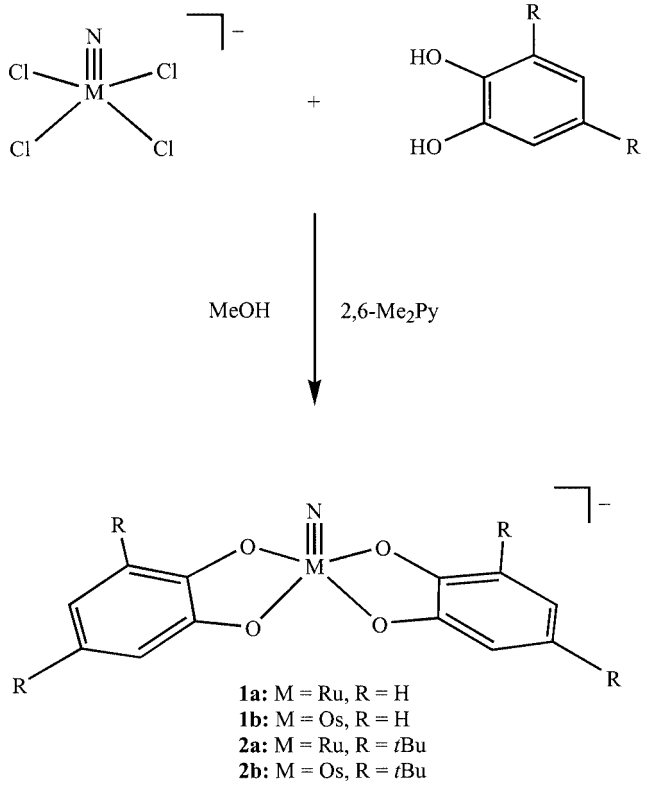
phenylphosphane to afford an unprecedented (phosphoraniminato)osmium(v) complex, $[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$ (**3**). This unusual reaction, along with the crystal structure of **3**, is also described here.

Results and Discussion

Synthesis and Characterization of $[M^{VI}N(Cat)_2]^-$ and $[M^{VI}N(DBCat)_2]^-$ (M = Ru, Os)

Treatment of $[NnBu_4][M^{VI}NCl_4]$ (M = Ru/Os) with two equivalents of catechol in methanol in the presence of 2,6-dimethylpyridine readily gave a solution containing mainly the (nitrido)ruthenium/osmium catecholate complex **1a/1b** (see Scheme 1), which was isolated in approximately 80 % yield upon workup. By employing 3,5-di-*tert*-butylcatechol instead of catechol, the same reactions afforded **2a/2b** as a precipitate (Scheme 1, note that **2a/2b** could have two geometrical isomers but only one of them is shown), which can be readily separated from the reaction mixtures by filtration. An NMR-pure product of **2a/b** was obtained in up to 90 % yield after washing with diethyl ether and drying. The counter-cation in **1** is tetrabutylammonium $[NnBu_4]^+$, as could be expected. However, we were surprised to find that **2** took $[2,6\text{-}Me_2PyH]^+$ (which was generated during the reaction) as a counter-cation, as revealed by ^1H NMR measurements (see below). This might result from a supramolecular interaction/recognition between $[M^{VI}N(DBCat)_2]^-$ and $[2,6\text{-}Me_2PyH]^+$ ions or from a low solubility of the $[2,6\text{-}Me_2PyH]^+$ salts of $[M^{VI}N(DBCat)_2]^-$ in methanol.



Scheme 1. Syntheses of **1** and **2**

Complexes **1a**, **1b**, **2a** and **2b** are diamagnetic, air-stable solids, having good solubility in common organic solvents, such as dichloromethane, acetonitrile, and tetrahydrofuran. In solution at room temperature, **1a** and **1b** are stable for months. The solutions of **2a** and **2b** can be stored at −20 °C for several weeks.

The ^1H NMR spectra of **1a** and **1b** both show two well-resolved multiplets with δ = 6.62, 6.89 ppm (for **1a**) and 6.71, 7.00 ppm (for **1b**), together with the normal signals of $[NnBu_4]^+$. The spectrum of **1a** is shown in Figure 1a as an example. There are no $[NnBu_4]^+$ signals in the ^1H NMR spectra of **2a** and **2b**. Instead, a set of signals at δ = 2.8, 7.5, and 8.2 ppm, assignable to $[2,6\text{-}Me_2PyH]^+$, was observed (see Figure 1b,c). Note that although **2a/2b** may have two geometric isomers (with C_s and C_2 symmetries, respectively), only a single set of the coordinated catecholate signals was located in the spectrum. Probably, only one of the isomers is present in solution, or the signals of the two isomers are not different enough to be clearly resolved.

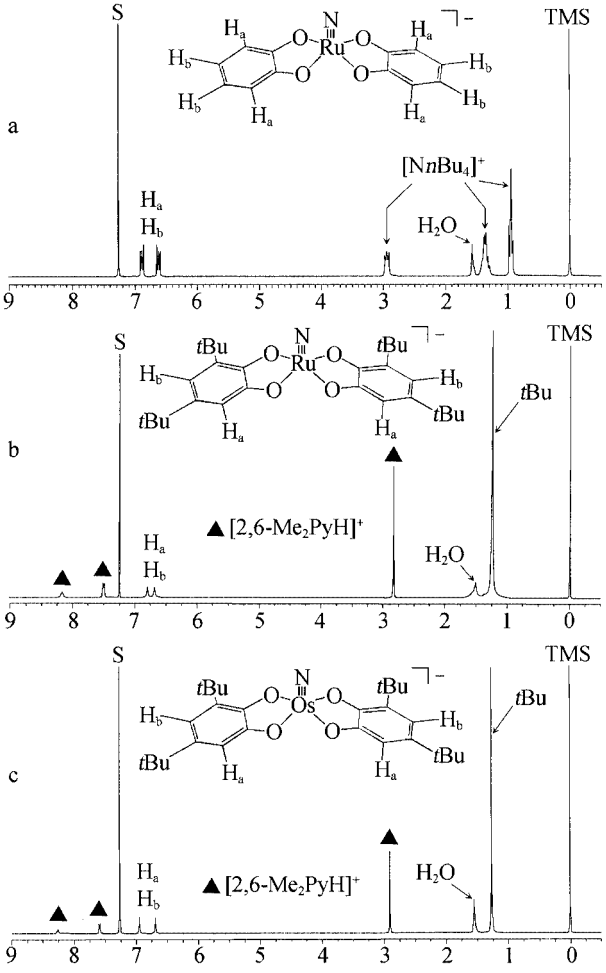


Figure 1. ^1H NMR spectra of a) **1a**, b) **2a**, and c) **2b** in $CDCl_3$; the water is mainly from the $CDCl_3$ solvent

Negative-ion FAB mass spectra of **1a**, **1b**, **2a** and **2b** show intense cluster peaks assignable to $[M^{VI}N(Cat)_2]^-$ or

$[M^{VI}N(DBCat)_2]^-$; the observed and simulated isotope-distribution patterns are virtually identical.

In the IR spectra of **1a**, **1b**, **2a** and **2b**, sharp and intense bands, ascribable to $\nu_{Ru\equiv N}/\nu_{Os\equiv N}$ appear at 1049 (**1a**) and 1051 cm^{-1} (**2a**) for the ruthenium species and at 1093 (**1b**) and 1097 cm^{-1} (**2b**) for the osmium species. The $\nu_{M\equiv N}$ frequency of **1a**/**1b** is appreciably higher than the corresponding frequency of the sulfur analogues $[NnBu_4][M^{VI}N(S_2C_6H_4)_2]$ (M = Ru, Os; $S_2C_6H_4$ = 1,2-benzenedithiolate; $\nu_{Ru\equiv N}$ = 1024 cm^{-1}, $\nu_{Os\equiv N}$ = 1063 cm^{-1}) reported by Sellmann and co-workers.[10] The study of the effect of catecholate auxiliaries on the M≡N bond by comparing the $\nu_{M\equiv N}$ frequencies of **1a** and **2a**, or **1b** and **2b**, is complicated by the different counter-cations in the nitrido complexes.

Structures of $[NnBu_4][M^{VI}N(Cat)_2]$ (M = Ru, Os)

Complexes **1a** and **1b** are isostructural and they both crystallize in the monoclinic space group *C*2/*c*, with very similar unit-cell dimensions (see Table 1). This resembles their sulfur analogues $[NnBu_4][M^{VI}N(S_2C_6H_4)_2]$ (M = Ru, Os),[10] which are also isostructural and have similar unit-cell dimensions, except that the 1,2-benzenedithiolate complexes both crystallize in the orthorhombic space group $Pna2_1$. Figure 2 shows the ORTEP drawings of the $[M^{VI}N(Cat)_2]^-$ anions of **1a** and **1b** with atom-numbering schemes. Selected bond lengths and angles for the two (nitrido)metal catecholate complexes are given in Table 2.

As shown in Figure 2 and Table 2, the $[M^{VI}N(Cat)_2]^-$ anions of **1a** and **1b** feature a slightly distorted square-pyramidal coordination geometry with the nitrido group situated at the apical position (ca. 0.62 Å above the basal plane constituted by the four oxygen atoms of the catecholate ligands) as in their sulfur analogues $[M^{VI}N(S_2C_6H_4)_2]^-$ (M = Ru, Os; the nitrido groups are ca. 0.69 Å above the basal plane).[10] However, contrary to the lack of symmetry of $[Ru^{VI}N(S_2C_6H_4)_2]^-$ and $[Os^{VI}N(S_2C_6H_4)_2]^-$ in the corresponding crystal structures, the structures of **1a** and **1b** have a C_2 axis along the M≡N bond of $[M^{VI}N(Cat)_2]^-$. The

Table 1. Crystal data for **1a**, **1b** and **3**

	1a	**1b**	**3**
Formula	$C_{28}H_{44}N_2O_4Ru$	$C_{28}H_{44}N_2O_4Os$	$C_{64}H_{70}NO_4OsP_2$
Cryst. system	monoclinic	monoclinic	orthorhombic
Fw	573.72	662.85	1169.35
Space group	*C*2/*c*	*C*2/*c*	$Pna2_1$
a (Å)	10.357(2)	10.330(2)	18.771(4)
b (Å)	14.014(3)	14.039(3)	14.644(3)
c (Å)	20.748(4)	20.766(4)	20.851(4)
α (deg)	90	90	90
β (deg)	100.74(3)	100.55(3)	90
γ (deg)	90	90	90
V ($Å^3$)	2959(1)	2961(1)	5732(2)
Z	4	4	4
ρ_{calc} (g cm^{-3})	1.288	1.487	1.355
2θ range (deg)	51.02	50.66	50.92
GOF	0.99	0.98	0.98
*R*1	0.032	0.035	0.026
*wR*2	0.075	0.073	0.071

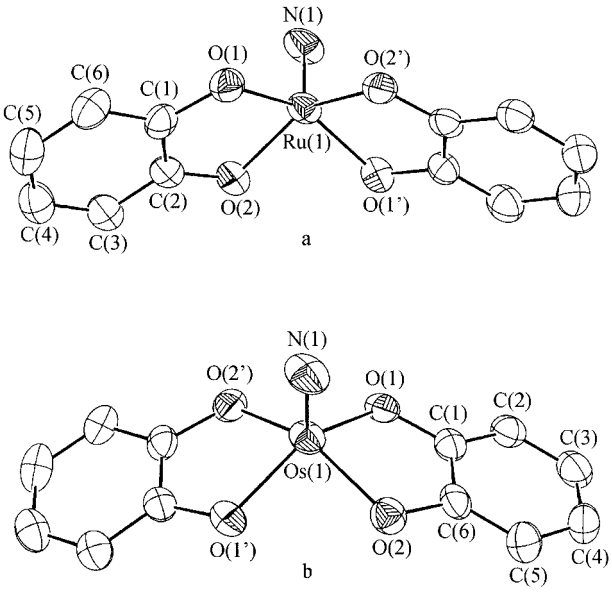


Figure 2. ORTEP drawings of a) **1a** and b) **1b** with omission of hydrogen atoms and counter-cations (thermal ellipsoid probability level: 30 %)

Table 2. Selected bond lengths (Å) and angles (deg) of **1a** and **1b**

	1a [M = Ru]	**1b** [M = Os]
M(1)−O(1)	1.954(3)	1.971(4)
M(1)−O(2)	1.962(2)	1.971(4)
M(1)−N(1)	1.603(4)	1.641(8)
C(1)−O(1)	1.366(4)	1.374(7)
C(2)−O(2)	1.352(4)	1.370(7)[a]
C(1)−C(2)	1.386(5)	1.373(9)
C(2)−C(3)	1.389(5)	1.374(9)
C(3)−C(4)	1.375(5)	1.379(10)
C(4)−C(5)	1.359(6)	1.387(10)
C(5)−C(6)	1.405(6)	1.360(9)
C(6)−C(1)	1.366(5)	1.386(8)
N(1)−M(1)−O(1)	107.08(8)	109.7(1)
N(1)−M(1)−O(2)	109.56(7)	107.6(1)
M(1)−O(1)−C(1)	111.6(2)	112.3(3)
M(1)−O(2)−C(2)	111.7(2)	112.4(4)[b]
O(1)−M(1)−O(2)	82.9(1)	82.2(2)
O(1)−M(1)−O(2′)	85.8(1)	86.1(2)
O(1)−M(1)−O(1′)	145.8(2)	140.7(2)
O(2)−M(1)−O(2′)	140.9(1)	144.9(3)

[a] C(6)−O(2). [b] Os(1)−O(2)−C(6).

Ru≡N distance in **1a** is 1.603(4) Å, slightly shorter than the Os≡N distance in **1b** [1.641(8) Å]. These Ru≡N/Os≡N distances are similar to those reported for $[NnBu_4][Ru^{VI}N(S_2C_6H_4)_2]$ [1.613(5) Å] and $[NnBu_4][Os^{VI}N(S_2C_6H_4)_2]$ [1.64(1) Å].[10] The average values of the N−M−O angles in **1a** and **1b** are 108.3 and 108.7°, respectively and are larger than the average N−M−S values in $[NnBu_4][Ru^{VI}N(S_2C_6H_4)_2]$ (107.6°) and $[NnBu_4][Os^{VI}N(S_2C_6H_4)_2]$ (107.2°), suggesting a greater repulsion between the π-electrons of the M≡N bond and the bonding electrons of the M−O bonds.[10]

The M−O distances in **1a** [1.954(3) and 1.962(2) Å] and **1b** [1.971(4) Å] fall in a narrower range than those in

[Ru(DBCat)$_3$] [1.941(10)−1.997(10) Å] and [Os(DBCat)$_3$] [1.947(7)−1.984(7) Å], reported by Pierpont and co-workers.[40] The C−O distances of **1a** [1.352(4), 1.366(4) Å] and **1b** [1.370(7), 1.374(7) Å] are significantly longer than those in the [Ru(DBCat)$_3$] [1.299(5), 1.319(6) Å] and [Os(DBCat)$_3$] [1.32(1) Å] complexes.[40] Since metal catecholate complexes typically feature C−O distances of, for example, 1.281(3) and 1.334(13) Å when the coordinated catecholate ligands adopt the semiquinonate(1−) and catecholate(2−) states, respectively,[40] the long C−O distances in **1a** and **1b**, together with their short M−O distances, should reveal a clear charge distribution in the two nitrido complexes, that is, the coordinated catecholate ligands are all in the catecholate(2−) state and their ruthenium and osmium ions are both in an oxidation state of +6.

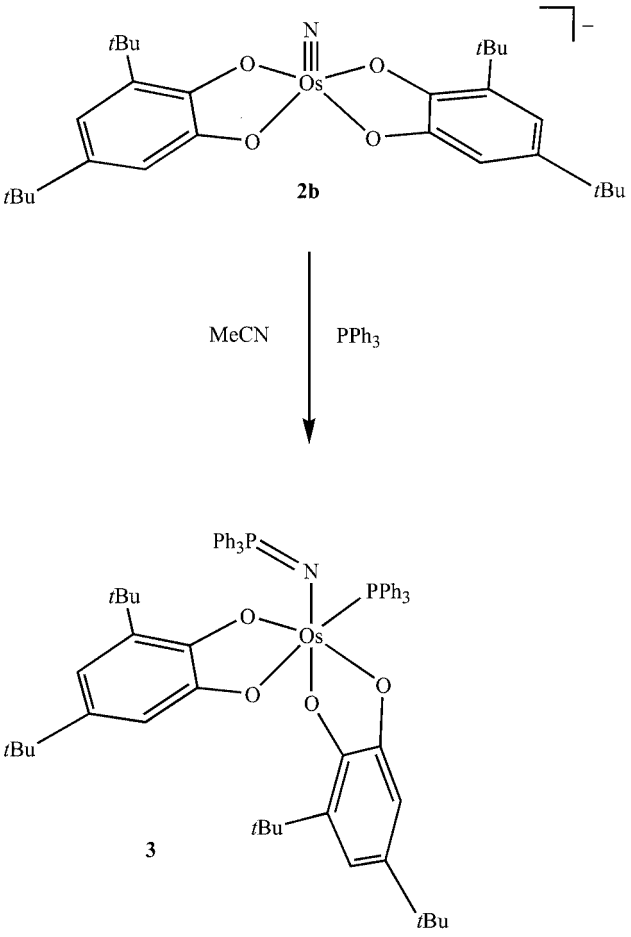
Note that high-valent ruthenium(VI)/osmium(VI) catecholate complexes are still sparse. Besides the Os^{VI} species [Os(Cat)$_3$] and [Os(DBCat)$_3$],[39,40] several (oxo)osmium(VI) complexes bearing catecholate auxiliaries have been prepared and characterized by Griffith and co-worker through spectroscopic means.[43] Complexes **1a** and **1b** reported in this work are, to the best of our knowledge, the only ruthenium(VI)/osmium(VI) complexes with catecholate ligands whose charge distribution has been confirmed by X-ray structure determination.

Reaction of $[Os^{VI}N(DBCat)_2]^-$ with Triphenylphosphane to Form $[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$

The (nitrido)ruthenium/osmium complexes **1a**, **1b**, **2a** and **2b** are reactive toward PPh_3. Treatment of **2b** with PPh_3 in acetonitrile at room temperature for 0.5 h afforded the (phosphoraniminato)osmium(V) complex $[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$ (**3**) in 90 % yield (see Scheme 2). However, the products of the reactions of **1a**, **1b** and **2a** with PPh_3 remain to be identified.

Complex **3** is a paramagnetic solid, stable toward moist air both in solid state and in solution. The ESR spectrum of **3** in solid state shows a single signal with a *g* value of 1.99, resembling the spectrum of a ruthenium(V) species (g = 2.11).[44] This indicates that the osmium(V) in **3** adopts a low-spin state, as is usual for heavy transition-metals.[44] The positive-ion FAB mass spectrum of **3** is dominated by an intense cluster peak at m/z = 1172, which can be attributed to the protonated parent ion ($[M + H]^+$).

The formation of a (phosphoraniminato)osmium(V) complex from the reaction of a (nitrido)osmium(VI) complex with phosphane is unusual. Previous reactions of (nitrido)osmium(VI) complexes, such as $[Os^{VI}NX_4]^-$ (X = Cl, Br),[3,4] $[Os^{VI}N(tpy)Cl_2]^+$ (tpy = 2,2′:6′,2′′-terpyridine),[45] $[Os^{VI}N(L)Cl]$ (L = salen and its derivatives),[32] and $[Os^{VI}N(L)Cl_2]$ (L = $[Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3]^-$)[31,46] all gave (phosphoraniminato)osmium(IV) and, much less frequently, (phosphoraniminato)osmium(III) complexes. Meyer and co-workers reported that electrochemical oxidation of *trans*-$[Os^{IV}(NPPh_3)(tpy)Cl_2]^+$ presumably gave *trans*-$[Os^{V}(NPPh_3)(tpy)Cl_2]^{2+}$ but this (phosphoraniminato)osmium(V) species was not isolated or characterized. The remarkable stability of complex **3** might arise from the unique binding behavior of the 3,5-di-*tert*-butylcatecholate ligands.



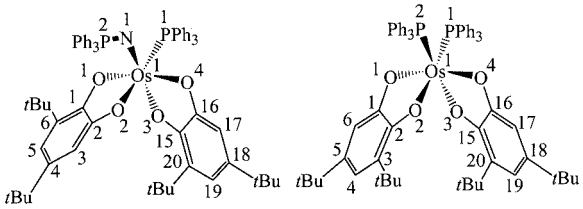
Scheme 2. Reaction of **2b** to form **3**

Stable osmium(V) complexes are not unprecedented in the literature.[1] We once isolated and structurally characterized several (oxo)osmium(V) complexes.[1] Recently, Meyer and co-workers prepared and characterized the (imido)osmium(V) complex $[Os^{V}(NH)(Tp)Cl_2]$ [Tp = hydrotris(pyrazol-1-yl)borate].[47] The coordination of phosphanes to high-valent osmium, as in the case of **3**, is much less common than that to low-valent osmium. A few (dioxo)osmium(VI) complexes, *trans*-$[Os^{VI}O_2X_2(PR_3)_2]$, were prepared by Walton and co-workers in early 1980s.[48]

Structure of $[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$

Complex **3** crystallized in the orthorhombic space group $Pna2_1$. The ORTEP drawing of the complex is depicted in Figure 3. A surprising feature in this structure is the helical Os(DBCat)$_2$ arrangement, coupled with the *cis* arrangement of the $NPPh_3$ and PPh_3 groups. Such groups are expected to be *trans* to each other according to the structure of the nitrido precursor **2b** (which we were unable to determine by X-ray crystallography but should be similar to the structure of **1b**, shown in Figure 2). Probably, a *trans* arrangement of the $NPPh_3$ and PPh_3 groups would suffer

Table 3. Selected bond lengths (Å) and angles (deg) of $[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$ (**3**) compared with those of $[Os^{IV}(DBCat)_2(PPh_3)_2]$



3 $[Os^{IV}(DBCat)_2(PPh_3)_2]$

Os(1)−O(1)	1.962(3) [1.982(4)][a]	Os(1)−O(2)	2.061(2) [2.042(4)]
Os(1)−O(3)	2.000(3) [2.048(5)]	Os(1)−O(4)	2.008(3) [2.001(4)]
Os(1)−N(1)	2.077(3) [2.350(2)][b]	Os(1)−P(1)	2.297(1) [2.357(2)]
N(1)−P(2)	1.616(3)	C(1)−O(1)	1.342(5) [1.341(8)]
C(2)−O(2)	1.343(4) [1.333(7)]	C(15)−O(3)	1.351(4) [1.321(7)]
C(16)−O(4)	1.341(4) [1.326(8)]	C(1)−C(2)	1.418(5) [1.422(9)]
C(2)−C(3)	1.373(6) [1.414(9)]	C(3)−C(4)	1.368(6) [1.394(9)]
C(4)−C(5)	1.407(6) [1.390(9)]	C(5)−C(6)	1.371(6) [1.380(10)]
C(6)−C(1)	1.419(5) [1.396(9)]	C(15)−C(16)	1.430(6) [1.407(8)]
C(16)−C(17)	1.375(6) [1.402(9)]	C(17)−C(18)	1.389(6) [1.378(11)]
C(18)−C(19)	1.400(6) [1.409(10)]	C(19)−C(20)	1.386(6) [1.365(9)]
C(20)−C(15)	1.386(5) [1.423(10)]		
O(1)−Os(1)−O(2)	81.2(1) [80.3(2)]	O(1)−Os(1)−O(4)	167.2(1) [166.5(2)]
O(3)−Os(1)−O(4)	80.3(1) [79.4(2)]	O(3)−Os(1)−O(2)	85.6(1) [83.5(2)]
O(1)−Os(1)−O(3)	87.6(1) [91.6(2)]	O(2)−Os(1)−O(4)	93.7(1) [88.6(2)]
P(1)−Os(1)−O(2)	175.96(8) [164.7(1)]	N(1)−Os(1)−O(1)	96.9(1) [101.0(1)]
N(1)−Os(1)−O(2)	88.2(1) [90.1(1)]	N(1)−Os(1)−O(3)	171.6(1) [164.6(1)]
N(1)−Os(1)−O(4)	94.6(1) [86.6(1)]	Os(1)−N(1)−P(2)	128.7(2)

[a] The values for $[Os^{IV}(DBCat)_2(PPh_3)_2]$ (from ref.[49]) are in square brackets. [b] Os(1)−P(2).

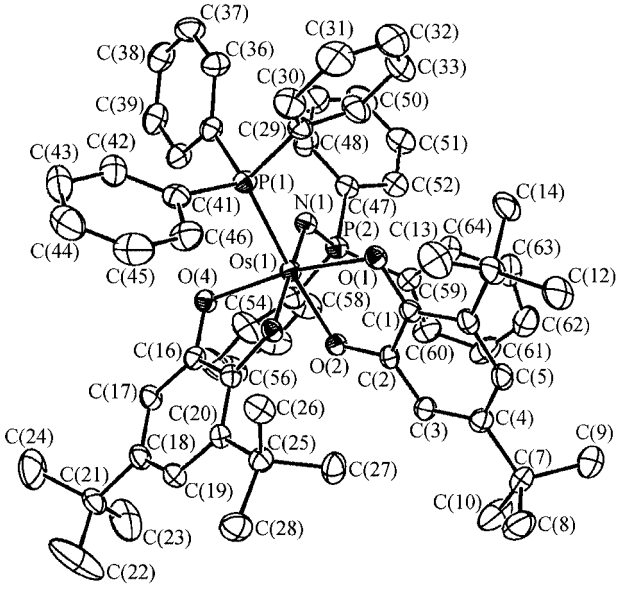


Figure 3. ORTEP drawing of **3** with omission of hydrogen atoms (thermal ellipsoid probability level: 30 %)

from significant steric interaction between the coordinated PPh_3 group and the *t*Bu groups of the bound catecholate ligands. Indeed, the structure of $[Os^{IV}(DBCat)_2(PPh_3)_2]$, reported by Pierpont and co-workers,[49] has also a helical $Os(DBCat)_2$ arrangement and *cis* PPh_3 ligands. Table 3 shows the selected bond lengths and angles for **3**; the corresponding geometric parameters of $[Os^{IV}(DBCat)_2(PPh_3)_2]$ are also given in the table for comparison.

It can be seen that both **3** and $[Os^{IV}(DBCat)_2(PPh_3)_2]$ have an $[Os(DBCat)_2(PPh_3)]$ moiety. However, the orientations of the coordinated catecholate ligands in the two complexes are different (see Table 3). A comparison between the geometrical parameters of **3** and $[Os^{IV}(DBCat)_2(PPh_3)_2]$ reveals additional differences in the $[Os(DBCat)_2(PPh_3)]$ moieties of the two structures. First, the Os−P(phosphane) distance in **3** is appreciably shorter than that in $[Os^{IV}(DBCat)_2(PPh_3)_2]$ [2.297(1) vs. 2.357(2) Å]. Second, the P(1)−Os(1)−O(2) moiety in $[Os^{IV}(DBCat)_2(PPh_3)_2]$ is more bent than that in **3** [164.7(1) vs. 175.96(8)°].

The OsO_4NP core in **3** can be best described as a distorted octahedron with the P(1) and O(2) atoms situated at the axial positions. The Os(1) atom and the four equatorial atoms O(1), O(3), O(4), and N(1) are basically co-planar, and the axial P(1)−Os(1)−O(2) moiety is almost linear [with an angle of 175.96(8)°]. One of the major distortions of the OsO_4NP core from a regular octahedron lies in a significant lengthening of the axial bond at the P(1) side [cf. Os(1)−P(1) 2.297(1) Å, Os(1)−O(2) 2.061(2) Å].

The Os−O distances in **3** range from 1.962(3) to 2.061(2) Å, which compare well with those in $[Os^{IV}(DBCat)_2(PPh_3)_2]$ [1.982(4)−2.048(5) Å], except that the average distance in **3** [2.008(3) Å] is slightly shorter than that in $[Os^{IV}(DBCat)_2(PPh_3)_2]$ [2.018(5) Å]. The C−O distances in **3** [1.341(4)−1.351(4) Å] are similar to, or even longer than,

Table 4. Key bond lengths (Å) and angles (deg) of (phosphoraniminato)osmium complexes

Complex	Os−N	N−P	Os-*N*−P	ref.
trans-$[Os^{IV}(NPPh_3)(tpy)Cl_2]PF_6$	2.093(5)	1.618(5)	132.5(3)	[45]
cis-$[Os^{IV}(NPPh_2Me)(tpy)Cl_2]PF_6$	2.061(6)	1.619(6)	132.2(4)	[45]
$[Os^{IV}(NPPh_3)(salophen)Cl]$[a]	1.92(1)	1.56(1)	149.6(10)	[32]
$[Os^{IV}(NPPh_3)(L)Cl_2]$[b]	1.893(5)	1.575(5)	137.5(3)	[46]
$[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$ (**3**)	2.077(3)	1.616(3)	128.7(2)	This work

[a] salophen = *N*,*N*′-bis(salicylidene)*o*-phenylenediamine dianion. [b] L = $[Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3]^-$

those in $[Os^{IV}(DBCat)_2(PPh_3)_2]$ [1.321(7)−1.341(8) Å], consistent with the $DBCat^{2-}$ state of the coordinated catecholate ligands in **3**.

Complex **3** has an Os(1)−N(1) distance of 2.077(3) Å and an N(1)−P(2) distance of 1.616(3) Å. These Os−N(phosphoraniminato) and N−P distances are similar to those in *trans*-$[Os^{IV}(NPPh_3)(tpy)Cl_2]PF_6$ and *cis*-$[Os^{IV}(NPPh_2Me)(tpy)Cl_2]PF_6$,[45] but considerably longer than those in $[Os^{IV}(NPPh_3)(salophen)Cl]$[32] and $[Os^{IV}(NPPh_3)(L)Cl_2]$[46] (see Table 4). The Os−*N*−PPh_3 angle in **3** is 128.7(2)°. As shown in Table 4, this is the smallest Os−*N*−PR_3 angle ever found in the crystal structures of (phosphoraniminato)osmium complexes.

Conclusion

We have prepared several (nitrido)ruthenium(VI) and -osmium(VI) complexes bearing catecholate auxiliaries, which constitute a new class of mononuclear (nitrido)metal complexes. X-ray structure determinations on $[NnBu_4][Ru^{VI}N(Cat)_2]$ and $[NnBu_4][Os^{VI}N(Cat)_2]$ confirm that the catecholate ligands in these (nitrido)ruthenium(VI) and -osmium(VI) complexes all adopt the catecholate(2−) state, rather than the semiquinonate(1−) or quinone states. The structure determinations on $[NnBu_4][Ru^{VI}N(Cat)_2]$ and $[NnBu_4][Os^{VI}N(Cat)_2]$, together with those on their 1,2-benzenedithiolate counterparts reported by Sellmann and co-workers,[10] allow for a direct comparison between the effects of oxygen and sulfur donors on the structures of (nitrido)metal complexes. Incorporation of 3,5-di-*tert*-butylcatecholate auxiliaries into a (nitrido)osmium species results in an unusual reactivity of the nitrido complex toward tertiary phosphane, affording an unprecedented (phosphoraniminato)osmium(V) complex.

Experimental Section

General Remarks: All solvents were purified by standard methods before use. Catechol, 3,5-di-*tert*-butylcatechol, 2,6-dimethylpyridine, and triphenylphosphane (Aldrich) were used as received. $[NnBu_4][M^{VI}NCl_4]$ (M = Ru, Os) were prepared according to the reported procedures.[2] ^{1}H NMR spectra were recorded on a Bruker DPX-300 or −400 FT-IR spectrometer (chemical shifts, δ, are relative to tetramethylsilane). Infrared spectra were recorded on a Bio-Rad FTS-165 spectrometer. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer. The ESR spectrum was recorded on a Bruker EMX100 ESR spectrometer. Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences.

Preparation of $[NnBu_4][M^{VI}N(Cat)_2]$ (M = Ru 1a, Os 1b): Several drops of 2,6-dimethylpyridine were added under nitrogen to a solution of H_2Cat (22 mg, 0.2 mmol) in methanol (5 mL). After being stirred for 0.5 h, the mixture was treated with $[NnBu_4][M^{VI}NCl_4]$ (0.1 mmol) and further stirred for 0.5 h. Slow evaporation of the solvent led to precipitation of the desired product as a microcrystalline solid, which was collected by filtration, washed with diethyl ether, and dried in vacuo.

$[NnBu_4][Ru^{VI}N(Cat)_2]$ (1a): Yield: 48.8 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, 12 H), 1.34 (m, 16 H), 2.92 (t, 8 H), 6.62 (m, 4 H), 6.89 (m, 4 H) ppm. IR (Nujol): 1049 cm^{-1} ($\nu_{Ru\equiv N}$). FAB MS: *m*/*z* = 332 $[Ru^{VI}N(Cat)_2]^-$. $C_{28}H_{44}N_2O_4Ru$ (573.7): calcd. C 58.62, H 7.73, N 4.88; found C 58.20, H 7.42, N 4.53.

$[NnBu_4][Os^{VI}N(Cat)_2]$ (1b): Yield: 49.7 mg (75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, 12 H), 1.46 (m, 16 H), 3.15 (t, 8 H), 6.71 (m, 4 H), 7.00 (m, 4 H) ppm. IR (Nujol): 1093 cm^{-1} ($\nu_{Os\equiv N}$). FAB MS: *m*/*z* = 422 $[Os^{VI}N(Cat)_2]^-$. $C_{28}H_{44}N_2O_4Os{\cdot}H_2O$ (680.9): calcd. C 49.39, H 6.81, N 4.11; found C 49.79, H 6.50, N 3.91.

Preparation of $[2,6\text{-}Me_2PyH][M^{VI}N(DBCat)_2]$ (M = Ru 2a, Os 2b): Several drops of 2,6-dimethylpyridine were added under nitrogen to a solution of H_2DBCat (445 mg, 2 mmol) in methanol (20 mL). After being stirred for 0.5 h, the mixture was treated with $[NnBu_4][M^{VI}NCl_4]$ (1 mmol), which resulted in precipitation of the desired product immediately. The precipitate was collected by filtration, washed with diethyl ether, and dried in vacuo.

$[2,6\text{-}Me_2PyH][Ru^{VI}N(DBCat)_2]$ (2a): Yield: 598 mg (90 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 36 H), 2.84 (s, 6 H), 6.69 (s, 2 H), 6.80 (s, 2 H), 7.51 (d, 2 H), 8.18 (t, 1 H) ppm. IR (Nujol): 1051 cm^{-1} ($\nu_{Ru\equiv N}$). FAB MS: *m*/*z* = 556 $[Ru^{VI}N(DBCat)_2]^-$. $C_{35}H_{50}N_2O_4Ru{\cdot}0.5CHCl_3$ (723.5; a sample recrystallized from chloroform/diethyl ether): calcd. C 58.93, H 7.03, N 3.87; found C 59.36, H 6.88, N 4.15.

$[2,6\text{-}Me_2PyH][Os^{VI}N(DBCat)_2]$ (2b): Yield: 602 mg (80 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (d, 36 H), 2.89 (s, 6 H), 6.69 (d, 2 H), 6.94 (d, 2 H), 7.58 (d, 2 H), 8.25 (t, 1 H) ppm. IR (Nujol): 1097 cm^{-1} ($\nu_{Os\equiv N}$). FAB MS: *m*/*z* = 646 $[Os^{VI}N(DBCat)_2]^-$. $C_{35}H_{50}N_2O_4Os{\cdot}H_2O$ (771.0): calcd. C 54.52, H 6.80, N 3.63; found C 54.55, H 6.44, N 3.80.

Reaction of $[2,6\text{-}Me_2PyH][Os^{VI}N(DBCat)_2]$ (2b) with Triphenylphosphane: A mixture of **2b** (180 mg, 0.2 mmol) and PPh_3 (130 mg, 0.5 mmol) in acetonitrile (10 mL) was stirred for 0.5 h and gave a purple-red solution. After removal of the solvent, the residue

was transferred onto an alumina column with dichloromethane as an eluent. The purple-red band was collected and concentrated to dryness by rotary evaporation to give a purple-red solid, which was identified as $[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$ (**3**).

$[Os^{V}(NPPh_3)(DBCat)_2(PPh_3)]$ (3): Yield: 210 mg (90 %). FAB MS: m/z = 1172 $[M + H]^+$. $C_{64}H_{70}NO_4OsP_2$ (1169.4): calcd. C 65.73, H 6.03, N 1.20; found C 65.77, H 5.92, N 1.05.

X-ray Crystallographic Study: Diffraction-quality crystals of **1a** and **1b** were obtained by slow evaporation of their methanol solutions at room temperature, whereas those of **3** were obtained by slow evaporation of its acetonitrile/diethyl ether (3:1, v/v) solution at −20 °C. Crystals of the dimensions of 0.6 × 0.2 × 0.1 (**1a**), 0.2 × 0.15 × 0.1 (**1b**), and 0.7 × 0.5 × 0.4 mm (**3**) mounted in glass capillaries were used for data collection at −20 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). The data were collected with 2.5° (**1a**), 3° (**1b**), and 1.5° (**3**) oscillation steps of φ, 480 s (**1a** and **1b**) and 240 s (**3**) exposure time and 120 mm scanner distance. Eighty (**1a**), 50 (**1b**), and 123 (**3**) images were collected. The images were interpreted and intensities integrated using the DENZO[50] program. The structures were solved by direct methods by employing the SIR-97[51] program on PC. The ruthenium/osmium and many other non-hydrogen atoms were located according to the direct methods and the successive least-square Fourier cycles. The positions of the remaining non-hydrogen atoms were found after successful refinement by full-matrix least-squares using the SHELXL-97[52] program on PC. In the case of **1a**, one methyl group of the *n*Bu moiety was disordered into two positions.

CCDC-216402 (**1a**), CCDC-216401 (**1b**), CCDC-216403 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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