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Full Paper

Half-Sandwich Guanidinates

Half-Sandwich Guanidinate–Osmium(II) Complexes: Synthesis and Application in the Selective Dehydration of Aldoximes

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Abstract: The novel guanidinate–osmium(II) complexes [OsCl{κ^2-(*N*,*N*′)-C(NR)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] [R = Ph (**3a**), 4-C_6H_4F (**3b**), 4-C_6H_4Cl (**3c**), 4-$C_6H_4CF_3$ (**3d**), 3-$C_6H_4CF_3$ (**3e**), 3,5-$C_6H_3(CF_3)_2$ (**3f**), 4-C_6H_4CN (**3g**), 4-C_6H_4Me (**3h**), 3-C_6H_4Me (**3i**), 2-C_6H_4Me (**3j**), 4-C_6H_4tBu (**3k**), 2,6-$C_6H_3i Pr_2$ (**3l**), 2,4,6-$C_6H_2Me_3$ (**3m**)] have been synthesized in high yields (70–88 %) by treatment of THF solutions of the dimeric precursor [{OsCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (**1**) with 4 equivalents of the corresponding guanidine (*i*PrHN)$_2$C=NR (**2a–m**) at room temperature. The easily separable guanidinium chloride salts [(*i*PrHN)$_2$C(NHR)]Cl (**4a–m**) were also formed in these reactions. The structures of **3a**, **3d**, and **3h** were unequivocally confirmed by X-ray diffraction methods. Complexes **3a**–**m** proved to be active in the catalytic dehydration of aldoximes. The best results were obtained with [OsCl{κ^2-(*N*,*N*′)-C(N-4-$C_6H_4CF_3$)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] (**3d**; 5 mol-%), which, in acetonitrile at 80 °C, was able to convert selectively a large variety of aromatic, heteroaromatic, α,β-unsaturated, and aliphatic aldoximes into the corresponding nitriles in high yields and short reaction times.

Introduction

Since the seminal work by Lappert and co-workers in 1970,[1] a large number of metal complexes containing guanidinate ligands have been described in the literature.[2] Notably, some of them have found utility in catalysis (e.g., polymerization of olefins, hydroamination of alkynes), as well as in materials science as precursors for chemical vapor deposition (CVD) and atom layer deposition (ALD) applications.[2] The easy generation of guanidinate mono- and dianions from readily available guanidines,[3] along with their high steric and electronic modulability, have allowed the coordination of these ligands to virtually all transition metals.[2] In this context, we recently reported the preparation of a series of ruthenium(II)– and ruthenium(IV)–guanidinate derivatives (see **A** and **B** in Figure 1), which proved to be very efficient catalysts for the base-free redox isomerization of allylic alcohols [turnover frequency (TOF) up to 1200 h^{-1}].[4] These complexes were easily obtained from the reactions of the dimeric precursors [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] and [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl), respectively, with an excess of the corresponding guanidine (*i*PrHN)$_2$C=NR.[4]

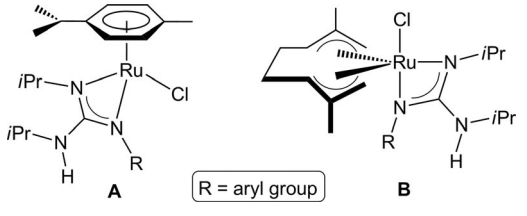

Figure 1. Structures of the ruthenium–guanidinate complexes **A** and **B**.

In addition to **A** and **B**, the synthesis of a significant number of other mono- and dinuclear ruthenium–guanidinate complexes have been reported,[5] and several iron representatives are known.[6] In marked contrast, within this group of the periodic table, little attention has been devoted to the chemistry of osmium compounds with this class of ligands. In fact, to the best of our knowledge, only four examples have been described so far in the literature (see Figure 2): 1) The mononuclear complexes **C** and **D**, containing a mono- and dianionic guanidinate ligand, respectively,[5c,5f] and 2) the dinuclear paddlewheel-type species **E** and **F**, in which anions of the bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine act as bridges in Os_2^{n+} cores (*n* = 6, 7).[7] Worthy of note, none of them has found applications in homogeneous catalysis.

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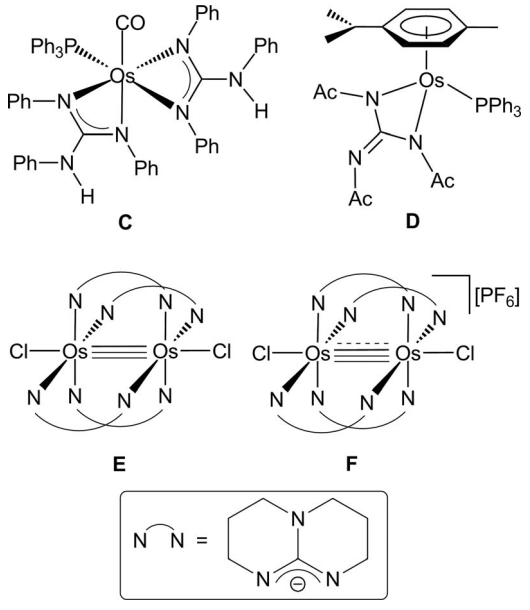
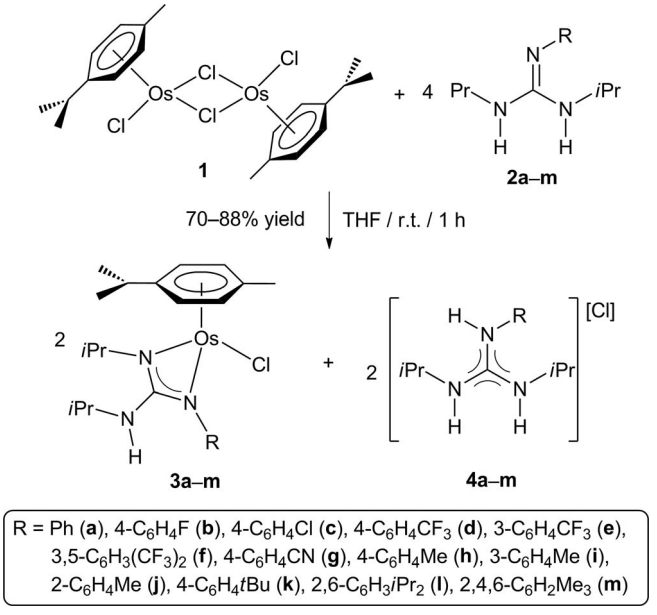


Figure 2. Structures of the known osmium–guanidinate complexes **C**–**F**.



Scheme 1. Synthesis of the novel osmium–guanidinate complexes **3a**–**m**.

With these precedents in mind, and as a continuation of our previous studies with ruthenium, we considered it of interest to prepare new examples of osmium–guanidinate complexes and explore their catalytic potential. As a result of this, we present herein the high-yielding synthesis of a family of half-sandwich osmium(II)–guanidinate complexes structurally related to **A**, that is, compounds [OsCl{κ^2-(*N*,*N*′)-C(NR)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] (R = Ar), and their successful application in the catalytic dehydration of aldoximes to generate nitriles.

Results and Discussion

Following the same synthetic procedure employed in the preparation of the ruthenium compounds **A** and **B** (Figure 1),[4] the novel osmium(II)–guanidinate complexes [OsCl{κ^2-(*N*,*N*′)-C(NR)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] [R = Ph (**3a**), 4-C_6H_4F (**3b**), 4-C_6H_4Cl (**3c**), 4-$C_6H_4CF_3$ (**3d**), 3-$C_6H_4CF_3$ (**3e**), 3,5-$C_6H_3(CF_3)_2$ (**3f**), 4-C_6H_4CN (**3g**), 4-C_6H_4Me (**3h**), 3-C_6H_4Me (**3i**), 2-C_6H_4Me (**3j**), 4-C_6H_4tBu (**3k**), 2,6-$C_6H_3iPr_2$ (**3l**), 2,4,6-$C_6H_2Me_3$ (**3m**)] were easily generated by treatment, at room temperature, of THF solutions of the dimeric precursor [{OsCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with 4 equivalents of the appropriate guanidine (*i*PrHN)$_2$C=NR (**2a**–**m**; Scheme 1). In these reactions, the corresponding guanidinium chloride salts [(*i*PrHN)$_2$C(NHR)][Cl] (**4a**–**m**) were also formed. Extraction of the crude reaction mixtures with pentane allowed the separation of complexes **3a**–**m** from these salts and their isolation in pure form (70–88 % yield) after crystallization (see details in the Exp. Sect.).

The air-stable complexes **3a**–**m** were characterized by elemental analysis, IR, and multinuclear NMR (^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H}) spectroscopy, the data obtained being fully consistent with the structural proposals (see the Exp. Sect. for details). The key spectroscopic features are as follows: 1) A characteristic ν(N–H) absorption band in the IR spectra in the 3315–3358 cm^{-1} region, 2) a doublet signal ($^3J_{H,H}$ = 10.2–11.1 Hz) at δ_H = 2.92–3.27 ppm for the NH proton in the ^{1}H NMR spectra, and 3) a downfield singlet for the central CN_3 carbon in the ^{13}C{^{1}H} NMR spectra at δ_C = 164.5–170.2 ppm. In accord with the stereogenic character of the osmium atom in **3a**–**m**, the NMR spectra also show four differentiated signals for the aromatic CH protons and carbon atoms of the η^6-coordinated cymene ring, along with two separated resonances for the methyl groups of its *i*Pr unit. In addition, as previously observed in the analogous ruthenium(II) complexes [RuCl{κ^2-(*N*,*N*′)-C(NR)(N*i*Pr)-NH*i*Pr}(η^6-*p*-cymene)] (R = 2,6-$C_6H_3iPr_2$, 2,4,6-$C_6H_2Me_3$),[4a] for complexes **3l**,**m**, the rotation of the *N*-aryl units is restricted in solution, as clearly evidenced by the chemical inequivalence in the NMR spectra of the Me and *i*Pr substituents located at *ortho* positions of the aromatic rings of the guanidinate ligands.

Compounds [OsCl{κ^2-(*N*,*N*′)-C(NR)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] [R = Ph (**3a**), 4-$C_6H_4CF_3$ (**3d**), 4-C_6H_4Me (**3h**)] were further characterized by single-crystal X-ray diffraction analysis. Diffraction-quality crystals were obtained in all cases by cooling a saturated solution of the complex in benzene. ORTEP-type views of the three structures are shown in Figure 3, and selected bond parameters are collected in Table 1.[8] We would like to note at this point that these are the first solid-state structures of mononuclear osmium–guanidinate complexes. Only the dinuclear complexes **E** and **F** (Figure 2), with which few comparisons can be made, have been previously studied by X-ray diffraction.[7] As shown in Figure 3, the three molecules exhibit the expected pseudo-octahedral three-legged piano-stool geometry with the *p*-cymene ligand in the usual η^6 coordination mode. Concerning the coordination of the guanidinate anions to osmium, despite the different electronic nature of the *N*-aryl groups present in these complexes, no significant structural differences are found (see Table 1). The Os–N1 and Os–N2 bond lengths, in the range 2.097(4)–2.138(4) Å, are longer than those in the crystal structures of the dinuclear species **E** and **F** (Os–N distances of ca. 2.040 Å).[7,9] The sum of the angles around the central car-

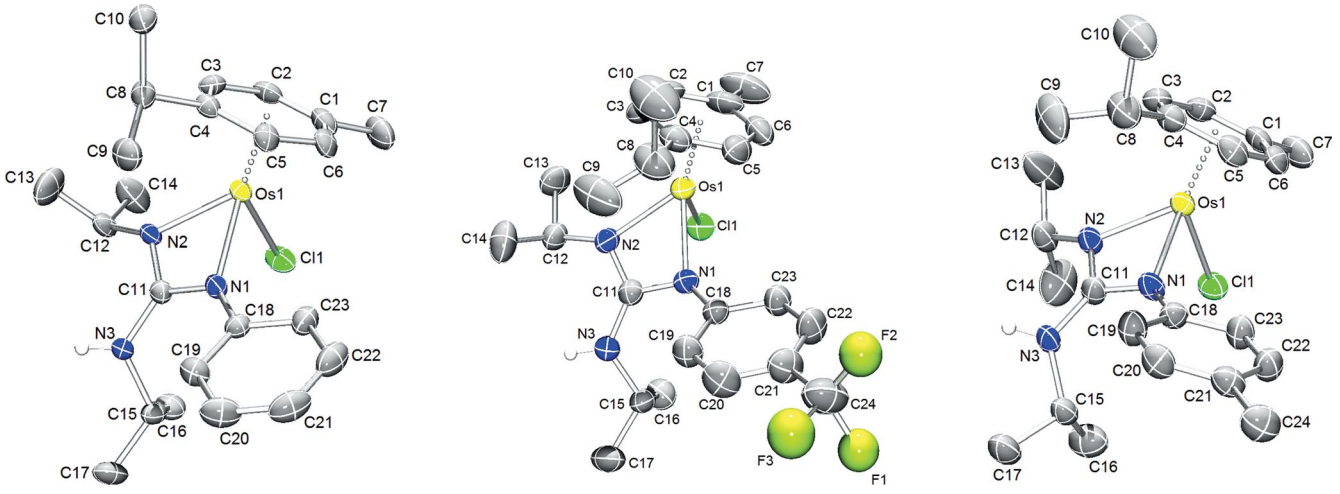


Figure 3. ORTEP-type views of the structures of the osmium(II)–guanidinate complexes **3a** (left), **3d** (center), and **3h** (right) showing the crystallographic labeling scheme. Hydrogen atoms, except those on the N3 atoms, have been omitted for clarity. Thermal ellipsoids are drawn at the 30 % probability level.

bon atom of the CN_3 skeletons (360°) indicates that the guanidinate anions are planar, with the resonance form **G** making an important contribution to their bonding (see Figure 4). This bonding description is supported by the shorter C11–N2 bond lengths [1.31(1)–1.317(6) Å] in comparison with those of C11–N1 and C11–N3 [1.345(6)–1.37(1) Å and 1.36(1)–1.376(6) Å, respectively].

Table 1. Selected bond lengths and angles for complexes **3a**, **3d**, and **3h**.

	3a	3d	3h
Bond lengths [Å]			
Os1–Cl1	2.407(2)	2.416(2)	2.411(1)
Os1–N1	2.108(4)	2.109(7)	2.097(4)
Os1–N2	2.138(4)	2.119(7)	2.130(4)
Os1–C*[a]	1.668(1)	1.665(1)	1.669(1)
C11–N1	1.345(6)	1.37(1)	1.353(6)
C11–N2	1.316(7)	1.31(1)	1.317(6)
C11–N3	1.376(6)	1.36(1)	1.364(6)
N1–C18	1.393(6)	1.38(1)	1.404(6)
N2–C12	1.448(7)	1.46(1)	1.459(6)
N3–C15	1.486(6)	1.47(1)	1.459(6)
Bond angles [°]			
C*–Os1–Cl1[a]	129.2(1)	129.9(1)	128.9(1)
C*–Os1–N1[a]	134.6(1)	137.1(1)	134.7(1)
C*–Os1–N2[a]	136.2(1)	135.7(1)	136.4(1)
Cl1–Os1–N1	83.5(1)	84.0(2)	85.2(2)
Cl1–Os1–N2	86.1(1)	83.3(2)	86.1(2)
N1–Os1–N2	61.3(2)	61.7(3)	61.2(2)
Os1–N1–C11	94.7(3)	93.9(5)	95.7(3)
Os1–N1–C18	134.6(3)	129.5(6)	131.6(3)
Os1–N2–C11	94.3(3)	95.5(5)	95.4(3)
Os1–N2–C12	137.1(3)	137.3(6)	137.4(3)
N1–C11–N2	109.0(4)	108.1(7)	107.5(4)
N1–C11–N3	125.5(5)	124.8(7)	125.3(4)
N2–C11–N3	125.5(5)	127.1(7)	127.2(4)

[a] C* denotes the centroid of the *p*-cymene ring (C1–C2–C3–C4–C5–C6).

Having characterized the complexes **3a**–**m**, we next explored their catalytic potential. In particular, given the good results obtained with the ruthenium–guanidinate derivatives **A** and **B** (Figure 1) in the redox isomerization of allylic alcohols, we initially focused on this catalytic transformation. It should be mentioned at this point that, although the osmium complexes have been much less studied than the ruthenium complexes,[10] the recent work of Esteruelas[11] and Baratta[12] and their co-workers has demonstrated that efficient catalysts can also be obtained from this metal (TOF up to 460 h^{-1}). However, the catalytic activities observed for **3a**–**m** in the isomerization of the model substrate 1-octen-3-ol were very disappointing. Thus, performing the reactions in THF at 80 °C with 1 mol-% of these complexes, a maximum conversion of 56 % was achieved with [OsCl{κ²-(*N*,*N*')-C(N-4-C_6H_4*t*Bu)(N*i*Pr)NH*i*Pr}(η⁶-*p*-cymene)] (**3k**) after 24 h. The addition of a base to the medium (2 mol-% of Cs_2CO_3) led to a slight improvement, but an incomplete reaction was again observed after 24 h (78 % GC yield of octan-3-one; TOF = 3 h^{-1}).

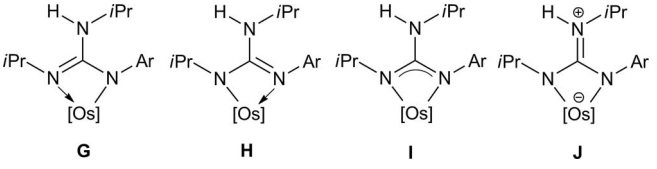


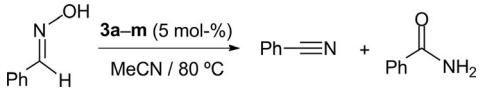
Figure 4. Limiting resonance forms of the guanidinate ligands coordinated to the [OsCl(η⁶-*p*-cymene)]⁺ fragment.

The low activities shown by **3a–m** in the isomerization of 1-octen-3-ol led us to explore other catalytic reactions, and, fortunately, we found that these complexes are useful for promoting the selective dehydration of aldoximes. This dehydration process represents a convenient and benign method for the synthesis of nitriles, because it avoids the use of the toxic cyanide sources commonly employed in the preparation of this important class of compounds (note that aldoximes are readily accessible from inexpensive aldehydes by condensation with hydroxylamine). Although the dehydration of aldoximes has been extensively studied and applied in synthetic organic chemistry for a long time, conventional protocols involve the use of stoichiometric amounts of reagents and suffer from limitations arising from the sensitivity of some functional groups to the reaction

conditions.[13] More appealing protocols have emerged in recent years employing metal catalysts, which usually operate under milder reaction conditions and with higher functional group compatibility. In this context, efficient catalytic systems involving Re,[14] Fe,[15] Ru,[16] Co,[17] Rh,[18] Ni,[19] Pd,[20] Cu,[21] Zn,[22] Ga,[23] and In[24] have been reported. To the best of our knowledge, complexes **3a**–**m** are the first examples of osmium compounds able to catalyze the dehydration of aldoximes.

As shown in Table 2, by employing 5 mol-% of these complexes and performing the reactions in acetonitrile, commercially available (*E*)-benzaldoxime could be transformed into benzonitrile in ≥87 % GC yield after 2–5 h of heating at 80 °C. Minor amounts of benzamide (1–3 %), a byproduct resulting from the formal rearrangement of the substrate,[25] were also formed in these reactions. Interestingly, the electronic nature of the *N*-aryl substituents of the guanidinate ligands plays a significant role in both the efficiency and selectivity of the process. Thus, the best results were obtained with complexes **3d**–**g** bearing the strong electron-withdrawing CF_3 and CN groups, which led to the almost quantitative consumption (≥96 % by GC) of the starting (*E*)-benzaldoxime after only 2 h (entries 4–7). By employing these complexes, the quantity of benzamide formed never exceeded 1 %. We would like to stress here that, contrary to other catalytic systems previously described in the literature, no additives or co-catalysts were needed.[26]

Table 2. Catalytic dehydration of (*E*)-benzaldoxime using the guanidinate–osmium(II) complexes [OsCl{κ^2-(*N*,*N*′)-C(NR)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] (**3a**–**m**).[a]

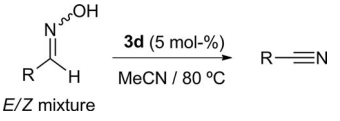


Entry	Catalyst	Time [h]	Conv.[b] [%]	Yield of benzonitrile[b] [%]
1	**3a**	4	95	92
2	**3b**	3	98	97
3	**3c**	3	98	96
4	**3d**	2	99	98
5	**3e**	2	98	97
6	**3f**	2	99	98
7	**3g**	2	96	95
8	**3h**	5	95	94
9	**3i**	5	96	94
10	**3j**	5	93	91
11	**3k**	5	95	94
12	**3l**	5	90	87
13	**3m**	5	92	90

[a] Reactions were performed under Ar with 0.5 mmol of (*E*)-benzaldoxime (0.33 M in acetonitrile). [b] Yield of benzonitrile determined by GC (uncorrected GC areas). The difference between GC conversion and yield corresponds to the amount of benzamide generated in the reactions.

By using one of the most active complexes, that is, [OsCl{κ^2-(*N*,*N*′)-C(N-4-$C_6H_4CF_3$)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] (**3d**), the scope of the process was next explored by carrying out the dehydration of differently substituted benzaldoximes (Table 3).[27] Thus, as observed for (*E*)-benzaldoxime (entry 1), all the substrates tested could be selectively transformed into the corresponding benzonitriles in high yields (≥96 % by GC; ≥82 % after chromatographic purification; entries 2–13) after 1–3 h of heating, regardless of their substitution pattern and electronic nature. As in the precedent case, the formation of only trace amounts of the respective benzamides (<2 %) was observed by GC in these reactions. Heteroaromatic (entries 14–15), aliphatic (entries 16–19), and α,β-unsaturated (entry 20) aldoximes were also successfully dehydrated, thus confirming the generality of this catalytic transformation. Again, they delivered the desired nitriles in high yields (99 % by GC; ≥81 % after chromatographic purification) and short reaction times (1–5 h). Notably, the chiral center of (*S*)-citronellaldoxime remained unaffected by the dehydration reaction (entry 19).

Table 3. Catalytic dehydration of aldoximes using the guanidinate–osmium(II) complex [OsCl{κ^2-(*N*,*N*′)-C(N-4-$C_6H_4CF_3$)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] (**3d**).[a]



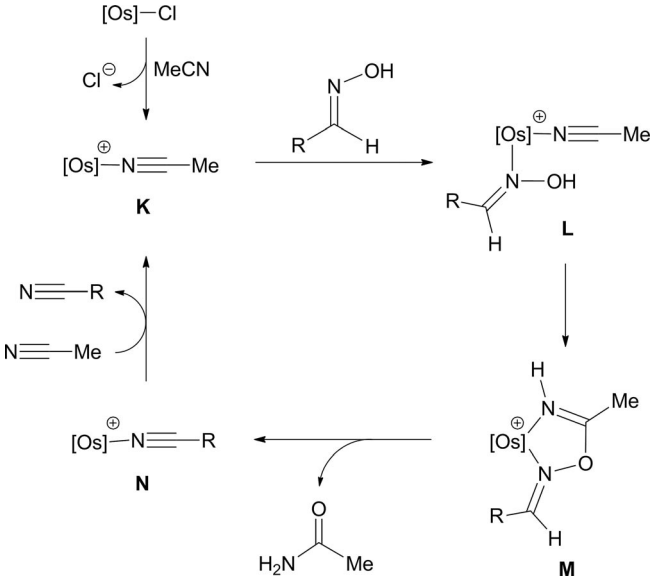
E/*Z* mixture

Entry	R	Time [h]	Conv.[b] [%]	Yield[b] [%]
1	Ph	2	99	98 (85)
2	2-C_6H_4Me	1	99	99 (86)
3	3-C_6H_4Me	2	>99	98 (88)
4	4-C_6H_4Me	2	>99	98 (87)
5	2-C_6H_4OMe	1	99	98 (84)
6	4-C_6H_4OMe	3	96	96 (85)
7	4-C_6H_4SMe	1	99	99 (86)
8	2-C_6H_4Cl	1	>99	99 (90)
9	4-C_6H_4F	2	99	98 (88)
10	2,4-$C_6H_3Cl_2$	1	>99	99 (86)
11	2,6-$C_6H_3Cl_2$	1	>99	99 (85)
12	2-Cl-6-C_6H_3F	1	99	99 (82)
13	2-$C_6H_4NO_2$	1	>99	98 (86)
14	3-furyl	1	>99	99 (89)
15	2-thienyl	1	>99	99 (85)
16	*n*-C_5H_{11}	3	>99	99 (83)
17	*n*-C_6H_{13}	5	>99	99 (81)
18	CH_2CH_2Ph	2	>99	99 (88)
19	(*S*)-citronellyl	2	>99	99 (86)
20	(*E*)-CH=CHPh	2	>99	99 (84)
21[c]	2,6-$C_6H_3Cl_2$	1.5	>99	99
22[d]	2,6-$C_6H_3Cl_2$	6	90	90

[a] Reactions were performed under Ar with 0.5 mmol of the corresponding aldoxime (0.33 M in acetonitrile). [b] Determined by GC (uncorrected GC areas); isolated yields after chromatographic work-up are given in parentheses. The difference between the GC conversion and yield corresponds to the primary amide present in the reaction mixture. [c] Reaction performed with 3 mol-% of complex **3d**. [d] Reaction performed with 1 mol-% of complex **3d**.

On the other hand, it is worth noting that the use of a lower catalyst loading was tolerated without a drastic increase in the reaction times. For example, by using 3 mol-% of **3d**, 2,6-dichlorobenzaldoxime was completely converted into 2,6-dichlorobenzonitrile after 1.5 h of heating (entry 21; to be compared with entry 11).[28] However, a further reduction of the osmium loading to 1 mol-% resulted in an incomplete transformation (entry 22). Also of note is the fact that the ^1H and $^{13}C\{^1H\}$ NMR spectra obtained from the crudes show the formation of an equimolar amount of acetamide with respect to the generated nitrile in all the reactions presented in Table 3. This fact, along with the low conversions obtained when using toluene as the reaction medium,[29] strongly suggests the active participation

of the acetonitrile solvent in the dehydration process. In this sense, a catalytic cycle similar to the one proposed by Tambara and Pantoş can be evoked to explain these observations (Scheme 2).[20b] In the first step, a molecule of the acetonitrile solvent coordinates to the metal with the dissociation of the chloride ligand to generate the catalytically active species **K**.[30] Subsequent coordination of the aldoxime to **K** generates the intermediate species **L**.[31] The coordinated aldoxime is dehydrated and the acetonitrile molecule converted into acetamide, via the five membered metallacyclic intermediate **M**, to give the nitrile-containing intermediate **N**. Final displacement of the nitrile by the acetonitrile solvent closes the catalytic cycle.[32]



Scheme 2. Proposed mechanism for the catalytic dehydration reactions.

Conclusions

A series of guanidinate–osmium(II) complexes **3a**–**m** of general composition [OsCl{κ²-(*N*,*N*′)-C(NR)(N*i*Pr)NH*i*Pr}(η⁶-*p*-cymene)] (R = Ar) have been synthesized by the reaction of the dimer [{OsCl(μ-Cl)(η⁶-*p*-cymene)}$_2$] (**1**) with an excess of the corresponding guanidine (*i*PrHN)$_2$C=NR (**2a–m**). These compounds represent the first examples of half-sandwich osmium complexes containing heteroallyl guanidinate monoanions as ligands reported to date, and the structures of three of these complexes have been unequivocally established by means of single-crystal diffraction techniques. In addition, their synthetic utility has been demonstrated through their ability to catalyze the selective dehydration of aldoximes. In particular, by using [OsCl{κ²-(*N*,*N*′)-C(N-4-C$_6$H$_4$CF$_3$)(N*i*Pr)NH*i*Pr}(η⁶-*p*-cymene)] (**3d**), a large variety of aromatic, heteroaromatic, α,β-unsaturated, and aliphatic aldoximes have been cleanly converted into the corresponding nitriles in high yields and short reaction times. Notably, to the best of our knowledge, no previous examples of osmium-based catalytic systems for this important transformation have been reported in the literature.

Experimental Section

General: The synthetic procedures were performed under dry argon by using vacuum-line and standard Schlenk or sealed-tube techniques. The solvents were dried by standard methods and distilled under argon before use. The complex [{OsCl(μ-Cl)(η⁶-*p*-cymene)}$_2$] (**1**),[33] the guanidines (*i*PrHN)$_2$C=NR (**2a–m**),[34] and all the aldoximes employed in the catalytic experiments,[35] except for (*E*)-benzaldoxime, were prepared by following the methods reported in the literature. IR spectra were recorded with a Perkin–Elmer 1720-XFT spectrometer. GC measurements were performed by using a Hewlett–Packard HP6890 apparatus (Supelco Beta-DexTM 120 column, 30 m length, 250 μm diameter). Elemental analyses were performed by the Analytical Service of the Instituto de Investigaciones Químicas (IIQ-CSIC) of Seville. The NMR spectra were recorded with a Bruker DPX300 or AV400 spectrometer. The chemical shifts are given in parts per million and are referenced to the residual peak of the deuteriated solvent employed (^{1}H and ^{13}C) or the $CFCl_3$ standard (^{19}F). DEPT experiments were carried out for all the compounds reported in this paper.

[OsCl{κ²-(*N*,*N*′)-C(NR)(N*i*Pr)NH*i*Pr}(η⁶-*p*-cymene)] [R = Ph (3a), 4-C$_6$H$_4$F (3b), 4-C$_6$H$_4$Cl (3c), 4-C$_6$H$_4$CF$_3$ (3d), 3-C$_6$H$_4$CF$_3$ (3e), 3,5-C$_6$H$_3$(CF$_3$)$_2$ (3f), 4-C$_6$H$_4$CN (3g), 4-C$_6$H$_4$Me (3h), 3-C$_6$H$_4$Me (3i), 2-C$_6$H$_4$Me (3j), 4-C$_6$H$_4$*t*Bu (3k), 2,6-C$_6$H$_3$*i*Pr$_2$ (3l), 2,4,6-C$_6$H$_2$Me$_3$ (3m)]: A solution of [{OsCl(μ-Cl)(η⁶-*p*-cymene)}$_2$] (**1**; 0.200 g, 0.253 mmol) in tetrahydrofuran (15 mL) was treated with the appropriate guanidine **2a**–**m** (1.012 mmol) at room temperature for 1 h. A rapid color change from orange to lemon-yellow was observed. After this time, the solvent was evaporated to dryness and pentane (20 mL) was added to the resulting oily residue, leading to the appearance of a white solid precipitate of the corresponding guanidinium chloride salt [(*i*PrHN)$_2$C(NHR)]Cl (**4a–m**).[4] The suspension was then filtered by using a cannula and the filtrate stored in a freezer at –10 °C for 48 h. Cooling led to the precipitation of [OsCl{κ²-(*N*,*N*′)-C(NR)(N*i*Pr)NH*i*Pr}(η⁶-*p*-cymene)] (**3a–m**) as yellow solids, which were separated, washed with cold pentane (3 mL), and dried under vacuum.

3a: Yield 0.231 g (79 %). IR (KBr): ṽ = 3317 (m, N–H) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ= 7.45–7.31 (m, 4 H, CH$_{arom}$), 6.99 (t, $^3J_{H,H}$ = 6.9 Hz, 1 H, CH$_{arom}$), 5.46 and 5.41 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H each, CH of cym), 5.17 and 5.13 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 3.53 and 3.37 (m, 1 H each, NC*H*Me$_2$), 3.04 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, NH), 2.47 (m, 1 H, C*H*Me$_2$ of cym), 2.31 (s, 3 H, Me of cym), 1.47 and 0.78 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.19 and 1.17 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.11 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.09 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ= 164.7 (s, CN$_3$), 149.5 (s, C$_{arom}$), 128.6, 122.0, and 120.5 (s, CH$_{arom}$), 89.9 and 89.1 (s, C of cym), 70.5, 69.8, 68.0, and 67.6 (s, CH of cym), 45.4 and 45.0 (s, NCHMe$_2$), 32.0 (s, *C*HMe$_2$ of cym), 25.6, 25.0, 24.3, 22.9, 22.5, and 22.4 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 18.9 (s, Me of cym) ppm. C$_{23}$H$_{34}$ClN$_3$Os (578.22): calcd. C 47.78, H 5.93, N 7.27; found C 47.90, H 6.02, N 7.33.

3b: Yield 0.247 g (82 %). IR (KBr): ṽ = 3319 (m, N–H) cm^{-1}. ^{19}F{^{1}H} NMR (C$_6$D$_6$): δ= –123.1 (s) ppm. ^{1}H NMR (C$_6$D$_6$): δ= 7.25 and 7.00 (m, 2 H each, CH$_{arom}$), 5.42 and 5.15 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 5.33 and 5.08 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H each, CH of cym), 3.45–3.30 (m, 2 H, NC*H*Me$_2$), 2.97 (d, $^3J_{H,H}$ = 10.5 Hz, 1 H, NH), 2.46 (m, 1 H, C*H*Me$_2$ of cym), 2.29 (s, 3 H, Me of cym), 1.44, 1.17, and 0.77 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.16, 1.11, and 1.08 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ= 164.8 (s, CN$_3$), 157.8 (d, $^1J_{C,F}$ = 238.8 Hz,

C_{arom}), 145.7 (d, $^4J_{C,F}$ = 2.2 Hz, C_{arom}), 123.1 (d, $^3J_{C,F}$ = 7.3 Hz, CH_{arom}), 115.0 (d, $^2J_{C,F}$ = 22.0 Hz, CH_{arom}), 89.8 and 89.2 (s, C of cym), 70.5, 69.7, 68.1, and 67.6 (s, CH of cym), 45.4 and 44.9 (s, NCHMe$_2$), 32.1 (s, CHMe$_2$ of cym), 25.6, 25.0, 24.2, 22.8, 22.6, and 22.5 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 18.9 (s, Me of cym) ppm. $C_{23}H_{33}ClFN_3Os$ (596.21): calcd. C 46.33, H 5.58, N 7.05; found C 46.25, H 5.66, N 7.09.

3c: Yield 0.270 g (87 %). IR (KBr): $\tilde{\nu}$ = 3313 (m, N–H) cm^{-1}. ^{1}H NMR (C_6D_6): δ= 7.31 and 7.20 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H each, CH_{arom}), 5.41 and 5.32 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 5.12 and 5.07 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H each, CH of cym), 3.43 and 3.36 (m, 1 H each, NC*H*Me$_2$), 2.96 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, NH), 2.43 (m, 1 H, C*H*Me$_2$ of cym), 2.27 (s, 3 H, Me of cym), 1.42 and 1.15 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.14 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.09 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.07 and 0.75 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 164.7 (s, CN_3), 148.3 and 125.0 (s, C_{arom}), 128.6 and 123.0 (s, CH_{arom}), 90.0 and 89.3 (s, C of cym), 70.4, 69.8, 68.0, and 67.4 (s, CH of cym), 45.4 and 45.1 (s, NCHMe$_2$), 32.0 (s, CHMe$_2$ of cym), 25.5, 24.9, 24.2, 22.8, 22.6, and 22.4 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 18.9 (s, Me of cym) ppm. $C_{23}H_{33}Cl_2N_3Os$ (612.66): calcd. C 45.09, H 5.43, N 6.86; found C 45.15, H 5.39, N 6.98.

3d: Yield 0.278 g (85 %). IR (KBr): $\tilde{\nu}$ = 3358 (m, N–H) cm^{-1}. ^{1}H NMR (C_6D_6): δ= 7.60 and 7.28 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H each, CH_{arom}), 5.41 and 5.32 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H each, CH of cym), 5.11 (d, $^3J_{H,H}$ = 5.1 Hz, 2 H, CH of cym), 3.41–3.27 (m, 2 H, NC*H*Me$_2$), 3.00 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, NH), 2.36 (m, 1 H, C*H*Me$_2$ of cym), 2.26 (s, 3 H, Me of cym), 1.40, 1.81, and 0.74 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.13 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.11 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.02 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 164.6 (s, CN_3), 152.8 (s, C_{arom}), 125.8 (q, $^3J_{C,F}$ = 3.3 Hz, CH_{arom}), 125.6 (q, $^1J_{C,F}$ = 270.7 Hz, CF_3), 121.5 (q, $^2J_{C,F}$ = 32.2 Hz, C_{arom}), 121.1 (s, CH_{arom}), 90.4 and 89.6 (s, C of cym), 70.3, 70.1, 68.0, and 67.3 (s, CH of cym), 45.6 and 45.5 (s, NCHMe$_2$), 32.1 (s, CHMe$_2$ of cym), 25.3, 24.7, 24.3, 22.7, 22.6, and 22.2 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 18.9 (s, Me of cym) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= –60.5 (s) ppm. $C_{24}H_{33}ClF_3N_3Os$ (646.21): calcd. C 44.61, H 5.15, N 6.50; found C 44.72, H 5.09, N 6.58.

3e: Yield 0.248 g (76 %). IR (KBr): $\tilde{\nu}$ = 3324 (m, N–H) cm^{-1}. ^{1}H NMR (C_6D_6): δ= 7.81 (s, 1 H, CH_{arom}), 7.40 (m, 1 H, CH_{arom}), 7.17 (m, 2 H, CH_{arom}), 5.43 and 5.35 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 5.14 and 5.12 (d, $^3J_{H,H}$ = 6.1 Hz, 1 H each, CH of cym), 3.45–3.27 (m, 2 H, NC*H*Me$_2$), 3.02 (d, $^3J_{H,H}$ = 10.5 Hz, 1 H, NH), 2.38 (m, 1 H, C*H*Me$_2$ of cym), 2.24 (s, 3 H, Me of cym), 1.39 and 0.81 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.14 and 1.05 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.11 and 1.03 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 164.7 (s, CN_3), 150.3 (s, C_{arom}), 130.8 (q, $^2J_{C,F}$ = 31.4 Hz, C_{arom}), 129.2 and 125.1 (s, CH_{arom}), 125.3 (q, $^1J_{C,F}$ = 272.3 Hz, CF_3), 117.5 (q, $^3J_{C,F}$ = 3.3 Hz, CH_{arom}), 116.2 (q, $^3J_{C,F}$ = 3.6 Hz, CH_{arom}), 89.9 and 89.7 (s, C of cym), 70.2, 70.0, 68.3, and 67.4 (s, CH of cym), 45.5 and 45.4 (s, NCHMe$_2$), 32.0 (s, CHMe$_2$ of cym), 25.4, 24.7, 24.2, 22.6, 22.5, and 22.2 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 18.9 (s, Me of cym) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= –62.0 (s) ppm. $C_{24}H_{33}ClF_3N_3Os$ (646.21): calcd. C 44.61, H 5.15, N 6.50; found C 44.68, H 5.30, N 6.61.

3f: Yield 0.318 g (88 %). IR (KBr): $\tilde{\nu}$ = 3324 (m, N–H) cm^{-1}. ^{1}H NMR (C_6D_6): δ= 7.79 (s, 2 H, CH_{arom}), 7.47 (m, 1 H, CH_{arom}), 5.41, 5.34, 5.16, and 5.04 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 3.31–3.16 (m, 2 H, NC*H*Me$_2$), 3.11 (d, $^3J_{H,H}$ = 11.1 Hz, 1 H, NH), 2.32 (m, 1 H, C*H*Me$_2$ of cym), 2.13 (s, 3 H, Me of cym), 1.29 and 1.07 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.04 and 0.95 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.94 and 0.81 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 164.7 (s, CN_3), 151.5 (s, C_{arom}), 131.8 (q, $^2J_{C,F}$ = 32.5 Hz, C_{arom}), 124.2 (q, $^1J_{C,F}$ = 272.6 Hz, CF_3), 120.7 and 111.9 (s, CH_{arom}), 90.4 and 89.9 (s, C of cym), 70.1, 69.9, 68.6, and 67.3 (s, CH of cym), 46.0 and 45.7 (s, NCHMe$_2$), 32.0 (s, CHMe$_2$ of cym), 25.1, 24.4, 24.0, 22.5, 22.2, and 22.0 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 18.8 (s, Me of cym) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ= –62.6 (s) ppm. $C_{25}H_{32}ClF_6N_3Os$ (714.21): calcd. C 42.04, H 4.52, N 5.88; found C 41.98, H 4.61, N 6.09.

3g: Yield 0.220 g (72 %). IR (KBr): $\tilde{\nu}$ = 3332 (m, N–H), 2212 (s, C≡N) cm^{-1}. ^{1}H NMR (C_6D_6): δ= 7.30 and 7.07 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H each, CH_{arom}), 5.40 and 5.29 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 5.08 and 5.06 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H each, CH of cym), 3.34–3.23 (m, 2 H, NC*H*Me$_2$), 3.00 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, NH), 2.31 (m, 1 H, C*H*Me$_2$ of cym), 2.23 (s, 3 H, Me of cym), 1.37 and 1.07 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.10 and 0.75 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.06 and 1.00 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 164.5 (s, CN_3), 153.4 and 102.2 (s, C_{arom}), 132.6 and 121.1 (s, CH_{arom}), 120.5 (s, C≡N), 90.7 and 89.7 (s, C of cym), 70.4, 70.1, 67.8, and 67.1 (s, CH of cym), 45.7 and 45.6 (s, NCHMe$_2$), 31.9 (s, CHMe$_2$ of cym), 25.2, 24.6, 24.3, 22.6, 22.5, and 22.1 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 18.8 (s, Me of cym) ppm. $C_{24}H_{33}ClN_4Os$ (603.23): calcd. C 47.79, H 5.51, N 9.29; found C 47.92, H 5.45, N 9.45.

3h: Yield 0.243 g (81 %). IR (KBr): $\tilde{\nu}$ = 3315 (m, N–H) cm^{-1}. ^{1}H NMR (C_6D_6): δ= 7.38 and 7.17 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H each, CH_{arom}), 5.46 and 5.43 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H each, CH of cym), 5.20 and 5.15 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 3.56 and 3.38 (m, 1 H each, NC*H*Me$_2$), 3.05 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, NH), 2.51 (m, 1 H, C*H*Me$_2$ of cym), 2.32 (s, 6 H, Ar*Me* and Me of cym), 1.48 and 1.21 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.19 and 1.12 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.13 (d, $^3J_{H,H}$ = 5.7 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.81 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 164.8 (s, CN_3), 147.1 and 129.6 (s, C_{arom}), 129.2 and 122.1 (s, CH_{arom}), 89.8 and 89.0 (s, C of cym), 70.6, 69.7, 68.1, and 67.7 (s, CH of cym), 45.4 and 44.8 (s, NCHMe$_2$), 32.0 (s, CHMe$_2$ of cym), 25.7, 25.1, 24.3, 23.0, and 22.5 (s, 2 C, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 20.7 and 19.0 (s, Ar*Me* and Me of cym) ppm. $C_{24}H_{36}ClN_3Os$ (592.25): calcd. C 48.67, H 6.13, N 7.10; found C 48.55, H 6.15, N 7.23.

3i: Yield 0.234 g (78 %). IR (KBr): $\tilde{\nu}$ = 3323 (m, N–H) cm^{-1}. ^{1}H NMR (C_6D_6): δ= 7.32–7.28 (m, 3 H, CH_{arom}), 6.84 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, CH_{arom}), 5.47 and 5.46 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H each, CH of cym), 5.20 and 5.18 (d, $^3J_{H,H}$ = 4.5 Hz, 1 H each, CH of cym), 3.58 and 3.37 (m, 1 H each, NC*H*Me$_2$), 3.06 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, NH), 2.51 (m, 1 H, C*H*Me$_2$ of cym), 2.36 and 2.32 (s, 3 H each, Ar*Me* and Me of cym), 1.48, 1.20 and 1.11 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.18 and 1.12 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.81 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ= 164.9 (s, CN_3), 149.5 and 137.9 (s, C_{arom}), 128.5, 122.7, 121.5, and 119.3 (s, CH_{arom}), 89.7 and 89.2 (s, C of cym), 70.5, 69.8, 68.2, and 67.7 (s, CH of cym), 45.4 and 45.0 (s, NCHMe$_2$), 32.0 (s, CHMe$_2$ of cym), 25.7, 25.1, 24.4, 22.9, 22.5, and 22.4 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 21.4 and 19.0 (s, Ar*Me* and Me of cym) ppm. $C_{24}H_{36}ClN_3Os$ (592.25): calcd. C 48.67, H 6.13, N 7.10; found C 48.78, H 6.09, N 6.98.

3j: Yield 0.216 g (72 %). IR (KBr): $\tilde{\nu}$ = 3332 (m, N–H) cm^{-1}. ^{1}H NMR (C_6D_6): δ= 7.36 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH_{arom}), 7.21 (m, 2 H, CH_{arom}), 7.07 (m, 1 H, CH_{arom}), 5.37 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H, CH of cym), 5.05 (m, 3 H, CH of cym), 3.37 and 3.26 (m, 1 H each, NC*H*Me$_2$), 3.05 (d,

$^3J_{H,H}$ = 10.2 Hz, 1 H, NH), 2.69 and 2.23 (s, 3 H each, Ar*Me* and Me of cym), 2.52 (m, 1 H, C*H*Me$_2$ of cym), 1.49 and 1.20 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.26, 1.17 and 1.14 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H each, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.65 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ= 166.6 (s, CN_3), 149.7 and 132.6 (s, C_{arom}), 131.1, 125.5, 122.0, and 121.9 (s, CH_{arom}), 90.6 and 87.3 (s, C of cym), 69.7, 69.4, 68.8, and 67.7 (s, CH of cym), 45.2 and 44.3 (s, NCHMe$_2$), 31.4 (s, *C*HMe$_2$ of cym), 25.7, 24.9, 24.0, 23.7, 22.5, and 22.2 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 19.7 and 18.7 (s, Ar*Me* and Me of cym) ppm. $C_{24}H_{36}ClN_3Os$ (592.25): calcd. C 48.67, H 6.13, N 7.10; found C 48.51, H 6.11, N 7.23.

3k: Yield 0.247 g (77 %). IR (KBr): $\tilde{\nu}$ = 3339 (m, N–H) cm^{-1}. ^1H NMR (C_6D_6): δ= 7.35 (br., 4 H, CH_{arom}), 5.37 and 5.35 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H each, CH of cym), 5.10 and 5.09 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H each, CH of cym), 3.47 and 3.30 (m, 1 H each, NC*H*Me$_2$), 2.95 (d, $^3J_{H,H}$ = 10.5 Hz, 1 H, NH), 2.42 (m, 1 H, C*H*Me$_2$ of cym), 2.22 (s, 3 H, Me of cym), 1.37 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.31 (s, 9 H, C*Me*$_3$), 1.10 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.08 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.00 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.98 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.70 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ= 164.8 (s, CN_3), 146.7 and 143.0 (s, C_{arom}), 125.3 and 121.9 (s, CH_{arom}), 89.9 and 89.2 (s, C of cym), 70.3, 69.9, 68.1, and 67.6 (s, CH of cym), 45.5 and 44.9 (s, NCHMe$_2$), 34.0 (s, *C*Me$_3$), 32.1 (s, *C*HMe$_2$ of cym), 31.5 (s, *C*Me$_3$), 25.7, 25.1, 24.3, 22.8, and 22.6 (s, 2 C, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 19.0 (s, Me of cym) ppm. $C_{27}H_{42}ClN_3Os$ (634.33): calcd. C 51.12, H 6.67, N 6.62; found C 51.20, H 6.81, N 6.79.

3l: Yield 0.234 g (70 %). IR (KBr): $\tilde{\nu}$ = 3329 (m, N–H) cm^{-1}. ^1H NMR (C_6D_6): δ= 7.36–7.22 (m, 3 H, CH_{arom}), 5.41 and 5.22 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H each, CH of cym), 5.36 and 5.27 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 4.46, 3.52, 3.33, and 3.10 (m, 1 H each, NC*H*Me$_2$ and C*H*Me$_2$ of Ar), 2.92 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, NH), 2.83 (m, 1 H, C*H*Me$_2$ of cym), 2.15 (s, 3 H, Me of cym), 1.58, 1.55, 1.50, 1.47, and 1.41 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H each, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar), 1.36 and 1.33 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H each, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar), 1.24, 1.21, and 0.56 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H each, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ= 170.2 (s, CN_3), 146.1, 144.2, and 143.5 (s, C_{arom}), 124.8, 124.4, and 124.0 (s, CH_{arom}), 92.2 and 83.9 (s, C of cym), 70.2, 69.1, 68.9, and 67.0 (s, CH of cym), 45.2 and 44.4 (s, NCHMe$_2$), 31.9 (s, *C*HMe$_2$ of cym), 27.6 and 27.2 (s, *C*HMe$_2$ of Ar), 26.2, 25.5, 25.4, 24.5, 24.4, 23.6, 23.5, 23.2, 22.6, and 22.5 (s, NCH*Me*$_2$, CH*Me*$_2$ of cym and CH*Me*$_2$ of Ar), 18.7 (s, Me of cym) ppm. $C_{29}H_{46}ClN_3Os$ (662.38): calcd. C 52.58, H 7.00, N 6.34; found C 52.71, H 7.11, N 6.53.

3m: Yield 0.235 g (75 %). IR (KBr): $\tilde{\nu}$ = 3324 (m, N–H) cm^{-1}. ^1H NMR (C_6D_6): δ= 7.06 and 6.98 (s, 1 H each, CH_{arom}), 5.32 and 5.27 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H each, CH of cym), 5.19 and 5.09 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H each, CH of cym), 3.45 and 3.09 (m, 1 H each, NC*H*Me$_2$), 3.27 (d, $^3J_{H,H}$ = 10.2 Hz, 1 H, NH), 2.79 (m, 1 H, C*H*Me$_2$ of cym), 2.75, 2.42, and 2.35 (s, 3 H each, Ar*Me*), 2.10 (s, 3 H, Me of cym), 1.54 and 1.24 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.31 and 1.27 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.15 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.59 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ= 167.7 (s, CN_3), 143.9, 134.3, 132.2, and 131.8 (s, C_{arom}), 129.7 and 128.7 (s, CH_{arom}), 92.0 and 84.0 (s, C of cym), 69.6, 69.4, and 68.5 (s, 2 C, CH of cym), 45.0 and 44.1 (s, NCHMe$_2$), 31.8 (s, *C*HMe$_2$ of cym), 25.8, 25.4, 24.5, 23.7, 22.8, and 22.5 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 20.9, 20.7, 19.2, and 18.8 (s, Ar*Me* and Me of cym) ppm. $C_{26}H_{40}ClN_3Os$ (620.30): calcd. C 50.34, H 6.50, N 6.77; found C 50.45, H 6.43, N 6.90.

The characterization data for the novel guanidinium chloride salts [(*i*PrHN)$_2$C(NHR)]Cl [R = 4-$C_6H_4CF_3$ (**4d**), 3-$C_6H_4CF_3$ (**4e**), 3,5-$C_6H_3(CF_3)_2$ (**4f**), 2-C_6H_4Me (**4j**)] are as follows:

4d: Yield 0.116 g (71 %). IR (KBr): $\tilde{\nu}$ = 3240 (s, N–H), 3178 (s, N–H) cm^{-1}. ^1H NMR ($CDCl_3$): δ= 10.31 (br. s, 1 H, NH), 7.99 (br. s, 2 H, NH), 7.56 and 7.39 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H each, CH_{arom}), 3.97 (br. s, 2 H, C*H*Me$_2$), 1.20 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ= 154.6 (s, CN_3), 141.0 (s, C_{arom}), 126.8 (q, $^2J_{C,F}$ = 34.0 Hz, C_{arom}), 126.7 and 122.0 (s, CH_{arom}), 123.8 (q, $^1J_{C,F}$ = 271.6 Hz, CF_3), 46.4 (s, *C*HMe$_2$), 22.5 (s, CH*Me*$_2$) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ= –62.3 (s) ppm. $C_{14}H_{21}ClF_3N_3$ (323.78): calcd. C 51.93, H 6.54, N 12.98; found C 52.06, H 6.47, N 13.11.

4e: Yield 0.126 g (77 %). IR (KBr): $\tilde{\nu}$ = 3198 (s, N–H), 3180 (s, N–H) cm^{-1}. ^1H NMR ($CDCl_3$): δ= 10.19 (br. s, 1 H, NH), 7.86 (br. s, 2 H, NH), 7.41–7.29 (m, 4 H, CH_{arom}), 3.86 (br. s, 2 H, C*H*Me$_2$), 1.09 (d, $^3J_{H,H}$ = 6.1 Hz, 12 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ= 154.5 (s, CN_3), 138.3 (s, C_{arom}), 131.7 (q, $^2J_{C,F}$ = 32.4 Hz, C_{arom}), 130.0, 124.9, 121.6, and 118.2 (s, CH_{arom}), 123.4 (q, $^1J_{C,F}$ = 272.5 Hz, CF_3), 46.2 (s, *C*HMe$_2$), 22.3 (s, CH*Me*$_2$) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ= –63.0 (s) ppm. $C_{14}H_{21}ClF_3N_3$ (323.78): calcd. C 51.93, H 6.54, N 12.98; found C 51.80, H 6.63, N 13.09.

4f: Yield 0.158 g (80 %). IR (KBr): $\tilde{\nu}$ = 3195 (s, N–H), 3066 (s, N–H) cm^{-1}. ^1H NMR ($CDCl_3$): δ= 10.59 (br. s, 1 H, NH), 8.14 (br. s, 2 H, NH), 7.79 (s, 2 H, CH_{arom}), 7.60 (s, 1 H, CH_{arom}), 3.95 (br. s, 2 H, C*H*Me$_2$), 1.24 (d, $^3J_{H,H}$ = 6.2 Hz, 12 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ= 154.4 (s, CN_3), 139.7 (s, C_{arom}), 132.8 (q, $^2J_{C,F}$ = 33.9 Hz, C_{arom}), 122.7 (q, $^1J_{C,F}$ = 272.8 Hz, CF_3), 120.6 and 118.0 (br. s, CH_{arom}), 46.9 (s, *C*HMe$_2$), 22.4 (s, CH*Me*$_2$) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ= –63.2 (s) ppm. $C_{15}H_{20}ClF_6N_3$ (391.78): calcd. C 45.98, H 5.15, N 10.73; found C 46.12, H 5.18, N 10.85.

4j: Yield 0.101 g (74 %). IR (KBr): $\tilde{\nu}$ = 3215 (s, N–H), 3199 (s, N–H) cm^{-1}. ^1H NMR ($CDCl_3$): δ= 9.48 (br. s, 1 H, NH), 7.34 (br. s, 2 H, NH), 7.14–5.98 (m, 4 H, CH_{arom}), 3.89 (br. s, 2 H, C*H*Me$_2$), 2.21 (s, 3 H, Ar*Me*), 1.05 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ= 154.5 (s, CN_3), 135.3 and 133.7 (s, C_{arom}), 131.2, 127.0, 126.9, and 125.3 (s, CH_{arom}), 45.5 (s, *C*HMe$_2$), 22.5 (s, CH*Me*$_2$), 18.1 (s, Ar*Me*) ppm. $C_{14}H_{24}ClN_3$ (269.81): calcd. C 62.32, H 8.97, N 15.57; found C 62.46, H 9.03, N 15.69.

General Procedure for the Catalytic Dehydration of Aldoximes Employing the Osmium–Guanidinate Complex [OsCl{κ^2-(*N*,*N*′)-C(N-4-$C_6H_4CF_3$)(N*i*Pr)NH*i*Pr}(η^6-*p*-cymene)] (3d): The aldoxime (0.5 mmol), acetonitrile (1.5 mL), and osmium(II) complex **3d** (0.016 g, 0.025 mmol) were introduced into a Teflon-capped sealed tube, and the reaction mixture stirred at 80 °C for the indicated time (see Table 3). The course of the reaction was monitored by regularly taking samples of around 20 μL, which, after extraction with CH_2Cl_2 (3 mL), were analyzed by GC. To isolate the nitrile products, the identities of which were assessed by comparison of their NMR data with those reported in the literature (copies of the NMR spectra are given in the Supporting Information), the solvent was eliminated under reduced pressure and the crude reaction mixture purified by column chromatography on silica gel using an ethyl acetate/hexane mixture (40:60, v/v) as eluent.

X-ray Crystal Structure Determinations of Complexes 3a, 3d, and 3h: Crystals of **3a**, **3d**, and **3h** suitable for X-ray diffraction analysis were obtained by cooling a saturated solution of the corresponding complex in benzene. The most relevant crystal and refinement data are collected in Table 4. In all the cases, data collection was performed with a Rigaku-Oxford Diffraction Xcalibur Onyx Nova single-crystal diffractometer using Cu-K_α radiation (λ = 1.5418 Å). Images were collected at a fixed crystal-detector distance

of 62 mm by using the oscillation method with 1.20° oscillation for **3a**, 1.00° for **3d**, and 1.20° for **3h**, and 1.25–2.50 s variable exposure time per image for **3a**, 10.00–60.03 s for **3d**, and 3.50–11.00 s for **3h**. The data collection strategy was determined by using the program CrysAlis^{Pro}.[36] Data reduction and cell refinement were also performed with the program CrysAlis^{Pro}[36] and an empirical absorption correction was applied by using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis^{Pro}.[36] The presence of osmium atoms remarkably increases the absorption coefficients (11.138, 9.357, and 10.668 mm^{-1} for **3a**, **3d**, and **3h**, respectively). To prevent errors due to different path lengths through the crystal for different reflections, an additional numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied also by using the SCALE3 ABSPACK algorithm. All the structures were solved by Patterson interpretation and phase expansion using DIRDIF2008.[37] Isotropic least-squares refinements were performed on F^2 by using SHELXL2014[38]. During the final stages of the refinements, all the positional and anisotropic displacement parameters of all non-hydrogen atoms were refined (except fluorine atoms of a highly disordered trifluoromethyl group found in complex **3d**; these fluorine atoms were isotropically refined, with the help of appropriate restraints, by using the two possible sites suggested by SHELXL2014). The hydrogen atoms were geometrically located and their coordinates were refined riding on their parent atoms. Four molecules per unit cell of benzene were found in the crystals of complex **3d**. Restraints on distances and displacement parameters were used to improve the convergence of the refinement. The PLATON[39] TwinRotMat algorithm proposed a twin law [a rotation axis (0 0 1) in reciprocal space] for the crystals of this complex, most likely because the *b* and *c* axes are almost equal. Although the fractional contribution of one of the domains is small (2.4 %), the use of the twin law significantly improved the results, especially in the analysis of the variance. *K*, defined as mean(F_o^2)/mean(F_c^2), differs markedly from unity for the weak reflections if the twin law is suppressed. In all cases, the maximum residual electron density is located near to osmium atoms. Complex **3d** deserves special attention. Four peaks greater than 1 e $Å^{-3}$ were found (3.62, 3.41, 2.57, and 1.48 e $Å^{-3}$). These values are certainly not too high for a heavy atom structure. The last two peaks are very close to osmium and can be discarded without further consideration, but the first two are quite distant. A careful analysis showed that the four peaks are aligned (parallel to the *a* axis) between two osmium atoms of different unit cells. Inspection of the *R* value statistics as a function of resolution confirmed that, in this crystal structure, the strong reflections are much more affected by errors than the rest (this fact does not occur in the other two structures). Both observations, and the lack of a reasonable chemical interpretation, led to the conclusion that these are spurious peaks (ripples), caused by the inaccuracy of the strong reflections when introduced into the Fourier synthesis to obtain the electron density function. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, in which $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (*a* and *b* values are given in Table 4) with $\sigma(F_o^2)$ from counting statistics and $P = [\max(F_o^2,0) + 2F_c^2]/3$. Atomic scattering factors were taken from International Tables for

Table 4. Crystal data and structure refinement details for **3a**, **3d**, and **3h**.

	3a	**3d**	**3h**
Chemical formula	$OsC_{23}H_{34}N_3Cl$	$OsC_{24}H_{33}F_3N_3Cl{\cdot}1/2C_6H_6$	$OsC_{24}H_{36}N_3Cl$
M_r	578.18	685.24	592.21
T [K]	293(2)	293(2)	293(2)
Wavelength [Å]	1.5418	1.5418	1.5418
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	*I*2/*a*	$P\bar{1}$
Crystal size [mm]	0.35 × 0.24 × 0.18	0.20 × 0.06 × 0.02	0.22 × 0.12 × 0.04
a [Å]	12.0265(4)	11.5298(3)	11.9464(5)
b [Å]	12.4358(5)	22.9365(5)	12.8170(5)
c [Å]	17.2701(6)	22.5089(4)	17.6562(6)
α[°]	70.253(3)	90	70.005(4)
β[°]	87.880(3)	99.301(2)	87.315(3)
γ[°]	81.011(3)	90	81.120(3)
Z	4	8	4
V [Å^3]	2400.8(2)	5874.3(2)	2510.0(2)
$\varrho_{calcd.}$ [g cm^{-3}]	1.600	1.550	1.567
μ[mm^{-1}]	11.138	9.357	10.668
F(000)	1144	2712	1176
θrange [°]	3.72 to 69.56	3.85 to 69.67	3.71 to 69.67
Index ranges	$-14 \le h \le 13$	$-13 \le h \le 13$	$-14 \le h \le 12$
	$-14 \le k \le 15$	$-19 \le k \le 27$	$-14 \le k \le 15$
	$-19 \le l \le 20$	$-27 \le l \le 26$	$-18 \le l \le 21$
Completeness to θ_{max} [%]	98.1	96.2	98.1
Number of data collected	20881	15656	22231
Number of unique data	8866 (R_{int} = 0.0454)	5448 (R_{int} = 0.0363)	9301 (R_{int} = 0.0363)
Number parameters/restraints	541/0	322/38	539/0
Refinement method		Full-matrix least-squares on F^2	
Goodness of fit on F^2	1.062	1.099	1.017
Weight function (*a*, *b*)	0.0788, 0.0000	0.1453, 20.7181	0.0483, 0.0000
R [$F^2 > 2\sigma(F^2)$][a]	0.0448	0.0635	0.0321
$wR(F^2)$ [$F^2 > 2\sigma(F^2)$][a]	0.1122	0.2038	0.0809
R (all data)	0.0475	0.0680	0.0390
$wR(F^2)$ (all data)	0.1156	0.2133	0.0866
Largest diff peak and hole [e $Å^{-3}$]	2.130 and −2.483	3.624 and −0.987	1.374 and −1.237

[a] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Crystallography, Volume C.[40] Geometrical calculations were carried out by using PLATON.[39] The crystallographic plots were drawn by using ORTEP3.[41]

CCDC 1432851 (for **3a**), 1432852 (for **3d**), and 1432853 (for **3h**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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media, to trap the water released in the process, was needed to achieve good conversions and selectivity (see ref.[16]).

[27] Most of the aldoximes included in Table 3 were synthesized as mixtures of the corresponding *E* and *Z* isomers in ratios ranging from 95:5 to 30:70. Differences in the reactivity of the two stereoisomers were not observed. Monitoring of the reactions by GC showed that *E* and *Z* isomers are consumed at similar rates.

[28] Although complex **3d** is not the most efficient catalyst described to date for this catalytic transformation, its activity is comparable or surpasses that of the known Ru-, Pd-, Cu-, Zn-, or Ga-based systems, which require metal loadings of 4–10 mol-% to deliver the nitriles in high yields.

[29] As a representative example, when the model (*E*)-benzaldoxime was dehydrated in toluene with 5 mol-% of **3d**, only 36 % of benzonitrile was formed after 24 h of heating at 80 °C.

[30] The NMR spectra of **3a**–**m** recorded in [D_3]acetonitrile indicate that an equilibrium between these complexes and the corresponding solvates **K** is established in solution.

[31] The vacant coordination site for the coordination of the aldoxime is most probably generated by a change in the coordination mode of the guanidinate ligand [from κ^2-(*N*,*N*′) to κ^1-(*N*)]. Dissociation of the *p*-cymene ligand seems unlikely because the catalytic reactions are not affected when carried out in the presence of an excess of free *p*-cymene (100 equiv. per Os). The Hg^0 test also ruled out the formation of catalytically active nanoparticles. Examples of changes in the hapticity of coordinated guanidinate ligands can be found, among others, in ref.[5l,5m] and: a) S. M. Mullins, A. P. Duncan, R. G. Bergman, J. Arnold, *Inorg. Chem.* **2001**, *40*, 6952–6963; b) R. Fernández-Galán, A. Antiñolo, F. Carrillo-Hermosilla, I. López-Solera, A. Otero, A. Serrano-Laguna, E. Villaseñor, *J. Organomet. Chem.* **2012**, *711*, 35–42.

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