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Selective Hydration of Nitriles to Amides Promoted by an Os–NHC Catalyst: Formation and X-ray Characterization of κ^2-Amidate Intermediates

María L. Buil,[†] Victorio Cadierno,[‡] Miguel A. Esteruelas,*[,†] José Gimeno,*[,‡] Juana Herrero,[§] Susana Izquierdo,[†] and Enrique Oñate[†]

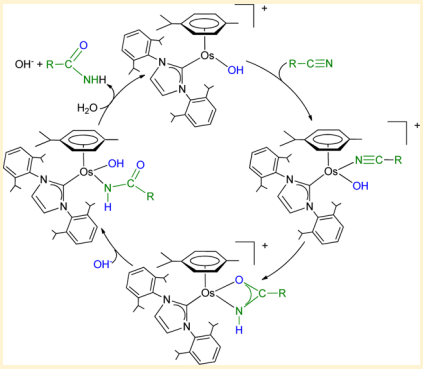
[†]Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

[‡]Laboratorio de Compuestos Organometálicos y Catálisis (Unidad Asociada al CSIC), Departamento de Química Orgánica e Inorgánica, IUQOEM, Universidad de Oviedo, 33006 Oviedo, Spain

[§]Departamento de Ingeniería Química y Química Inorgánica, ETSIIYT, Universidad de Cantabria, 39005 Santander, Spain

Supporting Information

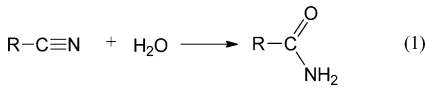
ABSTRACT: The complex [Os(η^6-*p*-cymene)(OH)IPr]OTf (**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene; OTf = CF_3SO_3) reacts with benzonitrile and acetonitrile to afford the κ^2-amidate derivatives [Os(η^6-*p*-cymene){κ^2*O*,*N*-NHC(O)-R}IPr]OTf (R = Ph (**2**), CH_3 (**3**)). Their formation has been investigated by DFT calculations (B3PWP1), starting from the model intermediate [Os(η^6-benzene)-(OH)(CH_3CN)IMe]$^+$ (IMe = 1,3-bis(2,6-dimethylphenyl)imidazolylidene). Complex **2** has been characterized by X-ray diffraction analysis. In the presence of water, the κ^2-amidate species release the corresponding amides and regenerate **1**. In agreement with this, complex **1** has been found to be an efficient catalyst for the selective hydration of a wide range of aromatic and aliphatic nitriles to amides, including substituted benzonitriles, cyanopyridines, acetonitrile, and 2-(4-isobutylphenyl)propionitrile among others. The mechanism of the catalysis is also discussed.



INTRODUCTION

N-heterocyclic carbenes (NHCs) are versatile and easy-to-make ancillary ligands, which are receiving a great deal of attention in homogeneous catalysis due to their ability to stabilize a variety of complexes with high activities in a wide range of organic reactions.[1]

Osmium–NHC derivatives are scarce in comparison with the species of this type in the iron triad.[2] Furthermore, osmium complexes are usually viewed as stable models of reactive intermediates proposed in catalytic transformations with ruthenium.[3] It is therefore not surprising that osmium–NHC catalysis had attracted very little attention. In 2005, in agreement with recent findings demonstrating that osmium is certainly a promising alternative to the classical metal catalysts for promoting some organic reactions,[4] we reported the synthesis of the complexes [Os(η^6-*p*-cymene)Cl(=CHPh)-IPr]OTf and [Os(η^6-*p*-cymene)Cl(=CHPh)IMes]OTf (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene, IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazolylidene; OTf = CF_3SO_3), which were the first osmium–NHC catalysts.[5] They are active in the ring-closing metathesis of diallyl diethylmalonate, the ring-opening metathesis polymerization of cyclooctene, and a variety of olefin cross-metatheses. Following this report, we subsequently synthesized [Os(η^6-*p*-cymene)(OH)IPr]OTf, which was found to be an efficient catalyst precursor for the hydrogen transfer reaction from 2-propanol to numerous aromatic and aliphatic aldehydes.[6] Now, we show that this hydroxo derivative also promotes the hydration of a wide range of nitriles to amides (eq 1).



$$R{-}C{\equiv}N + H_2O \longrightarrow R{-}C(=O){-}NH_2 \qquad (1)$$

The conversion of nitriles to amides by conventional acid/base strategies affords low yields and requires harsh conditions.[7] Furthermore, it takes place with low selectivity, since the rate of hydrolysis of the amide to the corresponding carboxylic acid is usually greater than that of the nitrile precursor to the amide.[8] In contrast to the conventional methods, the catalytic hydration of nitriles is an atom-economical reaction, which has been achieved using enzymes[9] as well as a broad spectrum of late transition metals,[10] including a few osmium catalysts of modest activity (TOF = 0.6–17 h^{-1}) and versatility.[11]

One of the mechanisms usually evoked in the literature involves the nucleophilic attack of a hydroxide ligand to the carbon atom of the coordinated nitrile to afford a κ^2-amidate

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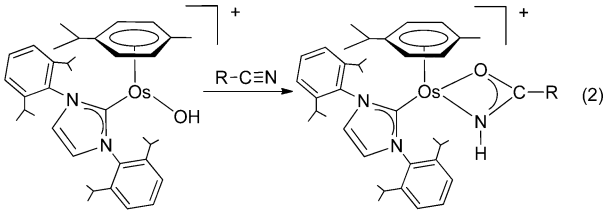
intermediate, which subsequently undergoes water addition to give the amide and regenerate the catalyst.[12] This type of four-membered heterometallacycle intermediate has been suggested for reactions catalyzed by Mo,[12c] Ru,[13] Rh,[14] Pd,[15] and Pt[16] complexes among others. However, it has only been trapped with the $[Co(cyclen)(H_2O)_2]^{3+}$ (cyclen = 1,4,7,11-tetraazacyclododecane) catalyst.[17]

This paper reports the isolation and X-ray characterization of κ^2-amidate intermediates and DFT calculations on their formation, in addition to the most active and versatile osmium catalyst described so far.

RESULTS AND DISCUSSION

1. Formation and Characterization of κ^2-Amidate Intermediates. Stirring of the hydroxide complex $[Os(\eta^6\text{-}p\text{-cymene})(OH)IPr]OTf$ (**1**) in benzonitrile and acetonitrile, at room temperature for 2.5 h, gave rise to the respective κ^2-amidate derivatives $[Os(\eta^6\text{-}p\text{-cymene})\{\kappa^2O,N\text{-NHC(O)R}\}IPr]OTf$ (R = Ph (**2**), CH_3 (**3**)), as a result of the formal insertion of the C−N triple bond of the solvents into the O−H bond of the organometallic starting compound (eq 2). The behavior of



1 is consistent with that previously observed for the bisphosphine complexes $OsH(EH)(CO)(P^iPr_3)_2$ (E = O,[18] S[19]), which react with dimethyl acetylenedicarboxylate and heterocumulenes to afford products resulting from the insertion of the C−C triple and C−N and C−O double bonds of the substrates into the E−H bonds of the carbonyl compounds.

Complexes **2** and **3** were isolated as yellow solids in 55% and 72% yields, respectively, and characterized by elemental analysis and IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **2** was further characterized by X-ray diffraction analysis. Figure 1 gives a view of the cation of the salt. The geometry around the metal center is close to octahedral, with the arene occupying three sites of a face. The angles formed by the NHC ligand and the N(1) and O(1) atoms of the four-membered heterometallacycle are close to 91°, while the N(1)−Os−O(1) bite angle of the amidate group is 60.31(9)°. The Os−C(8) bond length of 2.105(3) Å agrees well with those previously reported for Os−NHC compounds with normal coordination of the NHC unit,[2,5,6] whereas the Os−N(1) and Os−O(1) distances of 2.105(3) and 2.1465(19) Å, respectively, are within the expected ranges for single bonds.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** and **3**, in dichloromethane-d_2, at room temperature are consistent with the structure shown in Figure 1. In the ^1H NMR spectra, the most noticeable resonances are those corresponding to the NH hydrogen atoms of the amidate groups, which are observed at 6.51 (**2**) and 5.95 ppm (**3**). In the $^{13}C\{^1H\}$ NMR spectra, the NHC OsC resonances appear at 164.0 (**2**) and 167.8 ppm (**3**), whereas the NCO signals of the amidate groups are observed at 182.0 (**2**) and 185.5 ppm (**3**).

The formation of **2** and **3** can be rationalized according to Scheme 1. The formal insertion of the C−N triple bond of the

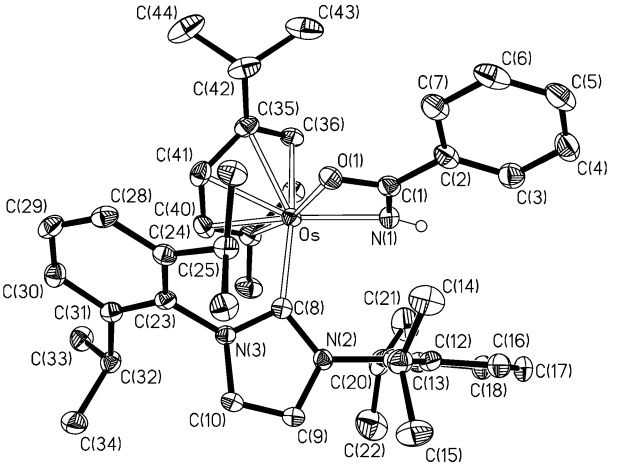
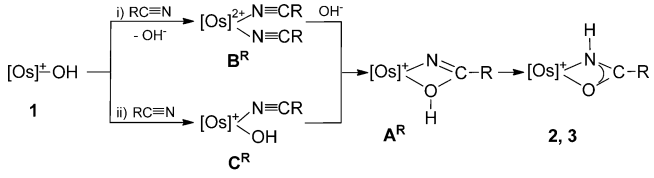


Figure 1. Molecular diagram of the cation of **2**. Selected bond lengths (Å) and angles (deg): Os−C(8), 2.105(3); Os−N(1), 2.105(3); Os−O(1), 2.1465(19); O(1)−C(1), 1.283(4); N(1)−C(1), 1.296(4); N(1)−H(1), 0.84(4); C(8)−Os−O(1), 90.51(9); C(8)−Os−N(1), 91.78(10); N(1)−Os−O(1), 60.31(9).

Scheme 1



$[Os]^+ \equiv [Os(\eta^6\text{-}p\text{-cymene})IPr]^+$; R = Ph, Me

nitriles into the O−H bond of the hydroxide ligand of **1** should involve the attack of the oxygen at the C(sp) atom of the substrates to afford intermediates of the type $\mathbf{A^R}$, followed by hydrogen migration from the oxygen to the nitrogen atom. The attack of the hydroxide ligand at the nitriles could be, at first glance, an intermolecular process (pathway i), which should take place by means of the initial displacement of the OH^- group by solvent molecules to give the bis-nitrile intermediates $\mathbf{B^R}$. Thus, the subsequent external attack of the dissociated hydroxide ligand at the C(sp) atom of a coordinated nitrile molecule should lead to $\mathbf{A^R}$. The latter could be alternatively generated through an intramolecular process (pathway ii) on the hydroxide−acetonitrile intermediate $\mathbf{C^R}$. In order to analyze the feasibility of the intermolecular mechanism, we stirred the previously reported[2x] bis-solvento compound $[Os(\eta^6\text{-}p\text{-cymene})(CH_3CN)_2IPr](BF_4)_2$ ($\mathbf{B^{Me}}$) with 2.3 equiv of KOH, in acetonitrile as solvent, which prevents the dissociation of the nitrile, at room temperature. Under these conditions, after 24 h, complex $\mathbf{B^{Me}}$ was recovered unchanged. This proves that the formation of **2** and **3** does not take place through an intermolecular mechanism involving the external attack of a hydroxide ligand to a coordinated nitrile molecule. To obtain information about the intramolecular process, we performed DFT calculations (B3PWP1) on the transformation from the model hydroxo−acetonitrile intermediate $[Os(\eta^6\text{-benzene})(OH)(CH_3CN)IMe]^+$ ($\mathbf{C^{Me}}$) into the $[Os(\eta^6\text{-benzene})\{\kappa^2O,N\text{-NC(OH)CH}_3\}IMe]^+$ ($\mathbf{A^{Me}}$) species. The changes in the free energy ΔG were computed at 298.15 K and P = 1 atm. Figure 2 gives the energy profile.

The species $\mathbf{A^{Me}}$ is 11.7 kcal mol^{-1} less stable than the intermediate $\mathbf{C^{Me}}$. The transformation takes place via the

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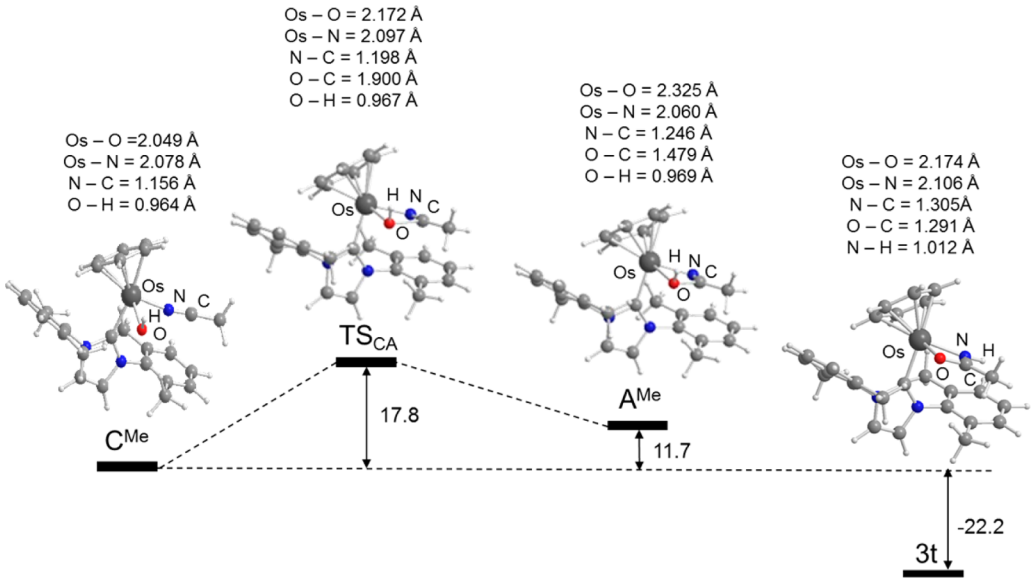


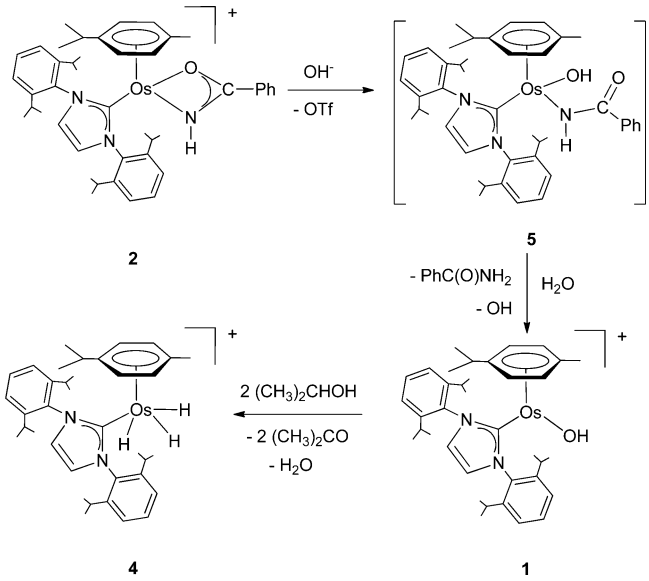
Figure 2. Energy profile (ΔG (kcal mol^{-1})) for the transformation of $\mathbf{C}^{\mathbf{Me}}$ to $\mathbf{A}^{\mathbf{Me}}$ and **3t**.

transition state $\mathbf{TS}_{\mathbf{CA}}$, which lies 17.8 kcal mol^{-1} above $\mathbf{C}^{\mathbf{Me}}$. Its formation results from the approach of the oxygen atom to the C(sp) atom of the nitrile (O−C = 1.900 Å). The process provokes the elongation of the Os−O, Os−N, and N−C bonds, from 2.049, 2.078, and 1.156 Å in $\mathbf{C}^{\mathbf{Me}}$ to 2.172, 2.097, and 1.198 Å in $\mathbf{TS}_{\mathbf{CA}}$. As expected, as a consequence of the formation of $\mathbf{A}^{\mathbf{Me}}$, the distances O−C (1.479 Å) and Os−N (2.060 Å) decrease, while the Os−O (2.325 Å) and C−N (1.246 Å) bond lengths increase. The hydrogen migration from the oxygen to the nitrogen atom is an exothermic process by 33.9 kcal mol^{-1}.

2. κ^2-Amidate Complexes as Intermediates in the Catalytic Hydration of Nitriles. Complex **2** releases benzamide and generates acetone and the trihydride derivative [OsH_3(η^6-*p*-cymene)IPr]OTf (**4**) in 1/1 water/2-propanol solvent mixtures. The OH^- group catalyzes the transformation. Thus, the addition of 10 mol % of KOH to the mixture produces a significant increase of the reaction rate. These observations can be rationalized according to Scheme 2. The coordination of a hydroxide group to the osmium atom of **2** should promote the κ^2O,N to κ^1N transformation of the amidate ligand, affording a neutral Os(η^6-*p*-cymene){κ^1*N*-NHC(O)Ph}(OH)IPr (**5**) species. Then, this intermediate could undergo hydrolysis to yield the amide and to regenerate the hydroxo catalyst **1**. As has been previously shown, in the absence of nitrile, the reaction of **1** with 2-propanol leads to **4** and acetone.[6]

Complexes **1** and **2** both promote the formation of amides from nitriles, as expected, since the formation of **2** according to eq 2 and its hydrolysis according to Scheme 2 constitute a cycle for the catalytic hydration of benzonitrile to benzamide (Scheme 3). The reactions were performed at 120 °C under an argon atmosphere, using a nitrile concentration of 0.33 M and catalyst/substrate and KOH/substrate molar ratios of 0.03 and 0.1, respectively. Under these conditions benzamide was obtained in 99% yield after 4 h. Lower reaction rates were observed for KOH/substrate molar ratios lower than 0.05 and higher than 0.1. However, the use of 2-methylpropanol instead of 2-propanol did not produce any change in the reaction rate or in the yield of obtained product, indicating that the alcohol is not directly involved in the catalysis. Since the hydration rate changes with the KOH/substrate molar ratio and the hydrolysis of the κ^2*O,N*-amidate intermediate is catalyzed by OH^-, the latter appears to be the rate-determining step of the hydration process.

Scheme 2



3. Scope of the Catalyst. Complex **1** is an efficient catalyst for the selective hydration of a wide range of aromatic and aliphatic nitriles to the corresponding amides, which are obtained in high yield within a short time in all cases (Table 1).

Benzonitriles with electron-withdrawing and -donating substituents at different positions (runs 2−5) are converted into the amides in 63−98% yields with turnover frequencies at 50% conversion ($TOF_{50\%}$) of 2−22 h^{-1}, under the experimental conditions previously mentioned for benzonitrile (run 1). The withdrawing chlorine substituent (run 2) increases the hydration rate with regard to benzonitrile, while the donating methyl substituent diminishes the turnover frequency, as expected for a marked dependence of the reaction on the

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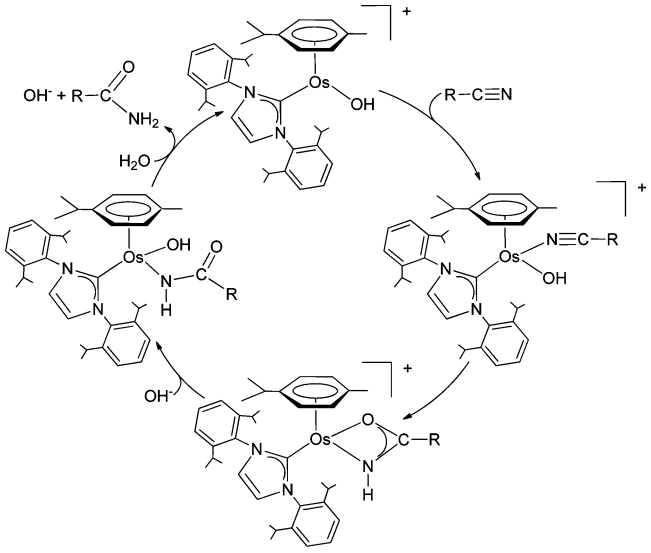
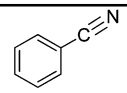
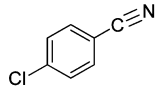
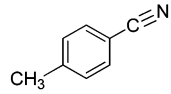
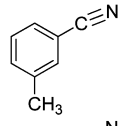
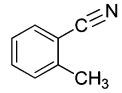
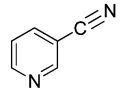
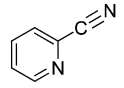
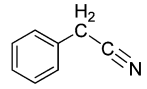
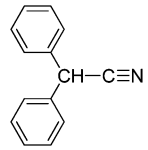
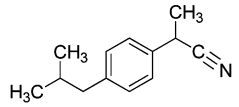
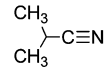
Scheme 3



electrophilicity of the C(sp) atom of the nitrile. Thus, the $TOF_{50\%}$ values decrease in the sequence 4-Cl > Ph > 4-Me (runs 2 > 1 > 3). The position of the substituent also has a clear influence on the reaction rate, increasing as the substituent is away from the functional CN group. In agreement with this, the $TOF_{50\%}$ values for methyl-substituted benzonitriles decrease in the sequence para > meta > ortho (runs 3 > 4 > 5). Interestingly, rates about 10 times faster are obtained for the hydration of cyanopyridines (runs 6 and 7), showing that the competitive coordination of the pyridine nitrogen atom does not prevent the catalysis. Nicotinamide,[20] a water-soluble member of the vitamin B family with wide use in medicine, is formed in 99% yield and isolated in 91% yield, with a $TOF_{50\%}$ value of 186 h^{-1}. In contrast to the case for the methyl-substituted benzonitriles, the reaction rate appears to increase as the CN group is closer to the pyridinic nitrogen atom. Thus, the hydration of 2-cyanopyridine is faster than that of 3-cyanopyridine. The presence of the basic pyridinic nitrogen atom at position 2 of the heterocycle seems to favor the hydrolysis of the amidate group, which may be related to the formation of hydrogen bonds between both nitrogen atoms and water molecules.

Less reactive aliphatic nitriles are also efficiently converted into the corresponding amides (runs 8−12). Acetamide is formed in 97% yield and isolated in 96% yield, with a $TOF_{50\%}$ value of 15 h^{-1} (run 8). The replacement of a hydrogen atom of acetonitrile by a phenyl group produces an increase in the reaction rate. Benzylnitrile (run 9) is hydrated with a $TOF_{50\%}$ value of 18 h^{-1}, faster than that of acetonitrile. However, due probably to steric grounds, a second phenyl group gives rise to a significant reduction of the reaction rate. Diphenylacetonitrile (run 10) is hydrated with a $TOF_{50\%}$ value of 8 h^{-1}, lower than those obtained for both acetonitrile and benzylnitrile. Other secondary nitriles are also efficiently hydrated at similar rates. Ibuprofenamide, which is widely employed as an advanced intermediate in the preparation of several ibuprofen prodrugs as well as other pharmacologically active compounds,[21] is obtained with a $TOF_{50\%}$ value of 7 h^{-1} from the commercially available 2-(4-isobutylphenyl)propionitrile (run 11), whereas the hydration of isopropylnitrile (run 12) occurs with a $TOF_{50\%}$ value of 4 h^{-1}.

Table 1. Hydration of Nitriles into Amides Catalyzed by Complex [Os(η^6-*p*-cymene)(OH)IPr]OTf[a]

Run	Substrate	t (h)	Yield[b] (%)	$TOF_{50\%}$[c] (h^{-1})
1		4	99 (91)	16
2		3	95	22
3		4	98	14
4		5	98	12
5		24	63	2
6		0,75	99 (91)	186
7		0,5	99 (87)	196
8	CH_3-C≡N	6	97 (96)	15
9		4	96	18
10		9	91	8
11		6	67	7
12		16	97 (83)	4

[a]Reactions performed under an Ar atmosphere at 120 °C using 1 mmol of the corresponding nitrile (0.33 M in 1/1 water/2-propanol). Os/substrate ratio: 0.03. KOH/substrate ratio: 0.1. [b]Yields determined by HPLC and GC. Isolated yields are given in parentheses. [c]Turnover frequencies ((mol of product/mol of Os)/time) were calculated at 50% conversion.

In summary, to the best of our knowledge, efficient hydration by Os-based catalysts applicable to a wide range of nitriles, including nitrogen-containing heteroaromatic species, and the formation of nonsteroidal antiinflammatory drugs is unprecedented.

CONCLUDING REMARKS

This study has revealed that the five-coordinate [Os(η^6-*p*-cymene)(OH)IPr]$^+$ cation reacts with nitriles to afford κ^2-amidate derivatives via six-coordinate hydroxo−nitrile intermediates. The formation of the four-membered heterometalla-

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cycle proceeds in two steps: (i) the intramolecular attack of the OH group at the electrophilic C(sp) atom of the coordinated nitrile and (ii) subsequent hydrogen migration from the oxygen to the nitrogen atom. The κ^2-amidate species are water sensitive. Thus, in the presence of water, they give amides and regenerate the starting five-coordinate hydroxide complex. In agreement with this, the complex $[Os(\eta^6\text{-}p\text{-cymene})(OH)IPr]^+$ has proved to be an efficient catalyst for the selective hydration of aromatic and aliphatic nitriles to amides, including nitrogen-containing heteroaromatic nitriles and the formation of nonsteroidal antiinflammatory drugs such as ibuprofenamide.

In conclusion, we report the most active and versatile osmium catalyst described up to now for the selective hydration of nitriles to amides and the isolation and characterization, by X-ray diffraction analysis, of a key Os(κ^2-amidate) catalytic intermediate.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Organic solvents and reagents were dried by standard procedures and distilled under argon prior to use. The starting material $[(\eta^6\text{-}p\text{-cymene})Os(OH)(IPr)]OTf$ was prepared as previously described in the literature.[6] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker Avance 300 or Bruker Avance 500 instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$). Coupling constants, J, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (in the solid state). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Catalytic experiments were followed either by HPLC (samples were introduced as 5 mM methanol solutions using an Agilent 1200 HPLC operated at a flow rate of 0.5 mL/min in 0.8/0.2 methanol/water) or by GC, depending on the nitrile used. For acetonitrile, an HP5890 II series gas chromatograph with a flame ionization detector was employed, using 100% cross-linked methyl silicone gum column (25 m × 0.32 mm, with 0.17 μm film thickness); the oven temperature was programmed at 100 °C for 6 min. In the case of isopropylnitrile an Agilent 4890D series gas chromatograph with a flame ionization detector was employed, using an HP INNOWAX cross-linked polyethylene glycol column (25 m × 0.2 mm, with 0.4 μm film thickness). The oven temperature was programmed as follows: 3 min, 60 °C; 3 min, 10 °C/min; 7 min, 20 °C/min; 2 min, 230 °C. An HP6890 gas chromatograph with a flame ionization detector was employed for cyanopyridines, using a Supelco Beta-Dex 120 column (30 m × 0.25 mm, with 0.25 μm film thickness). The oven temperature was programmed as follows: 3 min, 160 °C; 3 min, 20 °C/min, 20 min, 220 °C.

The identity of the resulting amides was assessed by comparison of their ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data with those reported in the literature, by comparison of their retention times with those observed for pure samples and by their fragmentation in GC-MS (experiments run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system; samples injected into a 30 m × 0.25 mm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 μm).

Preparation of [Os(η^6-*p*-cymene){κ^2*O*,*N*-NHC(O)Ph}IPr]OTf (2). A solution of $[(\eta^6\text{-}p\text{-cymene})Os(IPr)(OH)]OTf$ (**1**; 0.1 g, 0.1138 mmol) in 0.5 mL of benzonitrile was stirring for 2.5 h at room temperature. After this time, the addition of pentane to the orange solution caused the formation of a brown oil that was washed several times with pentane to give a yellow solid. Yield: 61 mg (55%). Anal. Calcd for $C_{45}H_{56}N_3F_3SO_4Os\cdot CH_2Cl_2$: C, 51.77; H, 5.99; N, 3.99; S, 3.00. Found: C, 52.02; H, 5.51; N, 4.03; S, 2.84. IR (cm^{-1}): ν(NH) 3429 (w); ν(CO) 1711 and 1674 (w); ν_s(N−C═O) 1548 (m); ν(NH) 1454 (m); $\nu_a(SO_3)$ 1267 (s); $\nu_s(CF_3)$ 1224 (m); $\nu_a(CF_3)$ 1150 (s); $\nu_s(SO_3)$ 1031 (s); $\nu_a(SO_3)$ 636 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): 7.59 (t, J_{H-H} = 7.6, 2H, H_p-2,6-^{i}Pr$_2$Ph), 7.50−7.30 (m, 7H, H_m-2,6-^{i}Pr$_2$Ph + H_m-Ph + H_p-Ph), 7.26 (s, 2H, NCH), 7.23 (d, J_{H-H} = 7.2, 2H, H_o-Ph), 6.51 (br, 1H, NH), 5.49 (br, 2H, Ph-*p*-cymene), 5.28 and 5.17 (br, 1H each, Ph-*p*-cymene), 2.96 and 2.55 (br, 2H each, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 2.04 (br, 1H, C*H*(CH$_3$)$_2$-*p*-cymene), 1.82 (s, 3H, C*H*$_3$-*p*-cymene), 1.43 and 1.05 (br, 6H each, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.13 (br, 12H, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 0.97 (d, J_{H-H} = 6.6, 6H, CH(C*H*$_3$)$_2$-*p*-cymene). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): 182.0 (s, OsNH═*C*Ph), 164.0 (s, NCN), 146.2 (s, C_o-2,6-^{i}Pr$_2$Ph), 137.1 (s, C_{ipso}-2,6-^{i}Pr$_2$Ph), 133.2 (s, C_{ipso}-Ph), 132.3 (s, C_p-Ph), 131.1 (s, C_p-2,6-^{i}Pr$_2$Ph), 128.2 (s, C_m-Ph), 126.9 (s, C_m-2,6-^{i}Pr$_2$Ph), 126.5 (s, C_o-Ph), 125.0 (br s, NCH), 101.0 (s, C_{ipso}-*p*-cymene), 84.8 (s, C_{ipso}-*p*-cymene), 78.4, 77.0, 76.2, and 74.9 (all br s, Ph-*p*-cymene), 32.0 (s, *C*H(CH$_3$)$_2$-*p*-cymene), 29.1 (s, CH(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 26.4, 22.6, and 22.5 (all s, CH(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 23.7 and 21.4 (s, CH(*C*H$_3$)$_2$-*p*-cymene), 18.5 (s, *C*H$_3$-*p*-cymene).

Preparation of [Os(η^6-*p*-cymene){κ^2*O*,*N*-NHC(O)Me}IPr]OTf (3). A solution of $[(\eta^6\text{-}p\text{-cymene})Os(IPr)(OH)]OTf$ (**1**; 0.1 g, 0.1138 mmol) in 5 mL of acetonitrile was stirred for 2.5 h at room temperature. After this time, the resulting orange solution was evaporated to dryness and the addition of diethyl ether caused the formation of a pale yellow solid that was washed with diethyl ether (2 × 2 mL). Yield: 75 mg (72%). Anal. Calcd for $C_{40}H_{54}N_3F_3SO_4Os\cdot 0.5CH_2Cl_2$: C, 50.53; H, 5.76; N, 4.37; S, 3.33. Found: 50.81; H, 6.10; N, 4.33; S, 3.05. IR (cm^{-1}): ν(NH) 3327 (m); ν_s(N−C═O) 1577 (m); ν(NH) 1454 (m); $\nu_a(SO_3)$ 1277 (s) and 1254 (s); $\nu_s(CF_3)$ 1223 (m); $\nu_a(CF_3)$ 1151 (s); $\nu_s(SO_3)$ 1029 (s); $\nu_a(SO_3)$ 629 (s). ^1H NMR (500 MHz, CD_2Cl_2, 293 K): 7.55 (t, J_{H-H} = 7.6, 2H, H_p-2,6-^{i}Pr$_2$Ph), 7.40 (d, J_{H-H} = 7.6, 4H, H_m-2,6-^{i}Pr$_2$Ph), 7.24 (s, 2H, NCH), 5.95 (br, 1H, NH), 5.56, 5.41, 5.28, and 5.22 (br s, 4H each, Ph-*p*-cymene), 2.80 (sept, J_{H-H} = 6.5, 1H, C*H*(CH$_3$)$_2$-*p*-cymene), 2.68 (sept, J_{H-H} = 7.0, 4H, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.64 (s, 3H, HN═CC*H*$_3$), 1.49 and 1.13 (d, J_{H-H} = 7.0, 12H each, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.28 (s, 3H, C*H*$_3$-*p*-cymene), 0.91 and 0.62 (d, J_{H-H} = 6.5, 3H each, CH(C*H*$_3$)$_2$-*p*-cymene). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (125.7 MHz, CD_2Cl_2, 293 K): 185.5 (s, OsNH═*C*Me), 167.8 (s, NCN), 147.2 and 146.2 (s, C_o-2,6-^{i}Pr$_2$Ph), 136.2 (s, C_{ipso}-2,6-^{i}Pr$_2$Ph), 131.4 (s, C_p-2,6-^{i}Pr$_2$Ph), 126.6 (br s, NCH), 125.0 and 124.3 (s, C_m-2,6-^{i}Pr$_2$Ph), 91.5 (s, C_{ipso}-*p*-cymene), 86.9 (s, C_{ipso}-*p*-cymene), 79.1, 77.2, 76.0, and 75.1 (all br s, Ph-*p*-cymene), 31.9 (s, *C*H(CH$_3$)$_2$-*p*-cymene), 29.7 and 29.6 (s, *C*H(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 27.7, 27.4, 22.8, and 22.5 (all s, CH(*C*H$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 24.3 (s, N═*C*CH$_3$), 23.4 and 22.9 (s, CH(CH$_3$)$_2$-*p*-cymene), 17.6 (s, *C*H$_3$-*p*-cymene).

Reaction of $[(\eta^6\text{-}p\text{-cymene})Os(IPr)(CH_3CN)_2](BF_4)_2$ with KOH. A solution of $[(\eta^6\text{-}p\text{-cymene})Os(IPr)(CH_3CN)_2](BF_4)_2$ (0.150 g, 0.1545 mmol) in 6 mL of acetonitrile was stirred with 2.3 equiv of KOH (0.020 g, 0.8564 mmol) for 24 h at room temperature. After this time, a sample of the reaction mixture was analyzed by NMR, showing the same spectrum as that of the starting compound.

Reaction of [Os(η^6-*p*-cymene){κ^2*O*,*N*-NHC(O)Ph}IPr]OTf in 1/1 Water/2-Propanol. A solution of [Os(η^6-*p*-cymene){κ^2*O*,*N*-NHC(O)Ph}IPr]OTf (0.0531 g, 0.0541 mmol) in 1 mL of 1/1 water/2-propanol was stirred for 7.5 h at 120 °C. After this time, a sample of the reaction mixture was analyzed by NMR, showing the signals corresponding to $[OsH_3(\eta^6\text{-}p\text{-cymene})IPr]OTf$, benzamide, and acetone. The presence of benzamide was corroborated by GC-MS.

Reaction of [Os(η^6-*p*-cymene){κ^2*O*,*N*-NHC(O)Ph}IPr]OTf with KOH in 1/1 Water/2-Propanol. A solution of [Os(η^6-*p*-cymene)-{κ^2*O*,*N*-NHC(O)Ph}IPr]OTf (0.0531 g, 0.0541 mmol) in 1 mL of 1/1 water/2-propanol was stirred with KOH (0.0005 g, 0.009 mmol) for 4 h at 120 °C. After this time, a sample of the reaction mixture was analyzed by NMR, showing the signals corresponding to $[OsH_3(\eta^6\text{-}p\text{-cymene})IPr]OTf$, benzamide, and acetone. The presence of benzamide was corroborated by GC-MS.

General Procedure for the Catalytic Hydration Reactions. Under an argon atmosphere, the corresponding nitrile (1 mmol), the catalyst (**1**; 26.4 mg, 0.03 mmol), KOH (5.7 mg, 0.1 mmol), *p*-xylene (120 μL, 1 mmol), and 3 mL of a 1/1 water/2-propanol mixture were introduced into a sealed tube. The reaction mixture was stirred at 120 °C for the indicated time (see Table 1). The course of the reaction was

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monitored either by HPLC or by GC, depending on the substrate. Thus, for aromatic substrates, 15 μL samples of the reaction mixture were regularly analyzed by HPLC, quantifying the disappearance of the corresponding nitrile. Once the reaction was finished, the reaction mixture was evaporated to dryness. The resulting residue was dissolved in 500 mL of methanol to afford a 4 mM solution of the corresponding amide. A 15 μL sample of this solution was analyzed by HPLC, quantifying the formation of the amide. For aliphatic nitriles and cyanopyridines, 15 μL samples of the reaction mixture, after extraction with a 1/1 CH_2Cl_2/methanol mixture, were analyzed by GC. After elimination of the solvent under reduced pressure, the crude reaction mixture was purified by column chromatography over silica gel using diethyl ether as the eluent.

Structural Analysis of Complex 2. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into saturated solutions of **2** in CH_2Cl_2. X-ray data were collected on a Bruker Smart APEX diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.710 73 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s, covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[22] The structures were solved by direct methods and conventional Fourier techniques and refined by full-matrix least squares on F^2 with SHELXL97.[23] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or refined using a restricted riding model, except for the amidate hydrogen, which was refined freely.

Crystal data for **2**: $C_{45}H_{56}F_3N_3O_4OsS$, mol wt 982.19, yellow, irregular block (0.20 × 0.08 × 0.04 mm), monoclinic, space group $P2_1/n$, a = 12.0160(7) Å, b = 26.7052(16) Å, c = 13.3195(8) Å, β = 93.0490(10)°, V = 4268.0(4) Å^3, Z = 4, D_{calcd} = 1.529 g cm^{-3}, $F(000)$ = 1992, T = 110(2) K, μ = 3.095 mm^{-1}, 51 865 measured reflections (2θ = 3−58°, ω scans 0.3°), 10 306 unique reflections (R_{int} = 0.0464), minimum/maximum transmission factors 0.625/0.862, final agreement factors R1 = 0.0272 (8312 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.0652, 10 306/0/529 data/restraints/parameters, GOF = 0.974, largest peak and hole 1.115 and −0.626 e/Å^3.

Computational Details. The theoretical calculations were carried out on the model complexes by optimizing the structures at the M06-DFT level with the Gaussian 09 program.[24] The basis sets used were the LANL2DZ basis and pseudopotentials for Os and 6-31G(d,p) for the rest of the atoms. All minima were verified to have no negative frequencies and the transition state to have one negative frequency. All calculations were carried out in vacuo. The connections between the starting reactant and final product have been checked by slightly perturbing the TS geometry toward the minimum geometries and reoptimizing to verify the nature of the reactant and product.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving the complete ref 24, tables giving optimized coordinates for the complexes $\mathbf{C_{Me}}$, $\mathbf{TS_{CA}}$, $\mathbf{A_{Me}}$, and **3t**, and a CIF file giving crystallographic data for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: maester@unizar.es (M.A.E.); jgh@uniovi.es (J.G.).

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Corberán, R.; Mas-Marzá, E.; Peris, E. *Eur. J. Inorg. Chem.* **2009**, 1700. (c) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677. (d) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612.

(2) (a) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 826. (b) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 837. (c) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 772. (d) Cabeza, J. A.; da Silva, I.; del Rio, I.; Sanchez-Vega, M. G. *Dalton Trans.* **2006**, 3960. (e) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 13044. (f) Cooke, C. E.; Jennings, M. C.; Pomeroy, R. K.; Clyburne, J. A. C. *Organometallics* **2007**, *26*, 6059. (g) Cooke, C. E.; Ramnial, T.; Jennings, M. C.; Pomeroy, R. K.; Clyburne, J. A. C. *Dalton Trans.* **2007**, 1755. (h) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2129. (i) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 3082. (j) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2007**, *129*, 10998. (k) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *Organometallics* **2007**, *26*, 5239. (l) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 6556. (m) Cooke, C. E.; Jennings, M. C.; Katz, M. J.; Pomeroy, R. K.; Clyburne, J. A. C. *Organometallics* **2008**, *27*, 5777. (n) Cabeza, J. A.; del Rio, I.; Miguel, D.; Perez-Carreño, E.; Sanchez-Vega, M. G. *Organometallics* **2008**, *27*, 211. (o) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Puerta, M. *Organometallics* **2008**, *27*, 445. (p) Castarlenas, R.; Esteruelas, M. A.; Lalrempuia, R.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 795. (q) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 4680. (r) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *Organometallics* **2008**, *27*, 6236. (s) Cabeza, J. A.; Perez-Carreño, E. *Organometallics* **2008**, *27*, 4697. (t) Aktas, H.; Slootweg, J. C.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Organometallics* **2009**, *28*, 5166. (u) Wong, C.-Y.; Lai, L.-M.; Pat, P.-K.; Chung, L.-H. *Organometallics* **2010**, *29*, 2533. (v) Cabeza, J. A.; del Rio, I.; Fernández-Colinas, J. M.; Perez-Carreño, E.; Sanchez-Vega, M. G.; Vazquez-Garcia, D. *Organometallics* **2010**, *29*, 3828. (w) Buil, M. L.; Castarlenas, R.; Esteruelas, M. A.; Izquierdo, S.; Lalrempuia, R.; Oñate, E. *Organometallics* **2010**, *29*, 876. (x) Bolaño, T.; Buil, M. L.; Esteruelas, M. A.; Izquierdo, S.; Lalrempuia, R.; Oliván, M.; Oñate, E. *Organometallics* **2010**, *29*, 4517. (y) O, W. W. N.; Lough, A. J.; Morris, R. H. *Organometallics* **2011**, *30*, 1236. (z) Eguillor, B.; Esteruelas, M. A.; Garcia-Raboso, J.; Oliván, M.; Oñate, E.; Pastor, I. M.; Peñafiel, I.; Yus, M. *Organometallics* **2011**, *30*, 1658.

(3) (a) Esteruelas, M. A.; Oro, L. A. *Adv. Organomet. Chem.* **2001**, *47*, 1. (b) Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, *24*, 3584. (c) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, *251*, 795. (d) Jia, G. *Coord. Chem. Rev.* **2007**, *251*, 2167.

(4) See for example: (a) Esteruelas, M. A.; Herrero, J.; López, A. M.; Oliván, M. *Organometallics* **2001**, *20*, 3202. (b) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1340. (c) Cobo, N.; Esteruelas, M. A.; Gonzalez, F.; Herrero, J.; López, A. M.; Lucio, P.; Oliván, M. *J. Catal.* **2004**, *223*, 319. (d) Clapham, S. E.; Morris, R. H. *Organometallics* **2005**, *24*, 479. (e) Baratta, W.; Herdtweck, E.; Siega, K.; Tonintti, M.; Rigo, P. *Organometallics* **2005**, *24*, 1660. (f) Donohoe, T. J.; Butterworth, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 4766. (g) Baratta, W.; Ballico, M.; Baldino, S.; Chelucci, G.; Herdtweck, E.; Siega, K.; Magnolia, S.; Rigo, P. *Chem. Eur. J.* **2008**, *14*, 9148. (h) Esteruelas, M. A.; Garcia-Yebra, C.; Oñate, E. *Organometallics* **2008**, *27*, 3029. (i) Baratta, W.; Ballico, M.; Baldino, S.; Chelucci, G.; Herdtweck, E.; Siega, K.; Rigo, P. *Angew. Chem., Int. Ed.* **2008**, *27*, 4362. (j) Baratta, W.; Ballico, M.; Del Zotto, A.; Siega, K.; Magnolia, S.; Rigo, P. *Chem. Eur. J.* **2008**, *14*, 2557. (k) Donohoe, T. J.; Wheelhouse, K. M. P.; Lindsay-Scott, P. J.; Glossop, P. A.; Nash, I. A.; Parker, J. S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2872. (l) Esteruelas, M. A.; Garcia-Yebra, C.;

Oliván, M.; Oñate, E.; Valencia, M. *Organometallics* **2008**, *27*, 4892. (m) Eguillor, B.; Esteruelas, M. A.; Garcia-Raboso, J.; Oliván, M.; Oñate, E. *Organometallics* **2009**, *28*, 3700. (n) Batuecas, M.; Esteruelas, M. A.; Garcia-Yebra, C.; Oñate, E. *Organometallics* **2010**, *29*, 2166. (o) Varela-Fernandez, A.; Garcia-Yebra, C.; Varela, J. A.; Esteruelas, M. A.; Saá, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 4278. (p) Baratta, W.; Barbatto, C.; Magnolia, S.; Siega, K.; Rigo, P. *Chem. Eur. J.* **2010**, *16*, 3201. (q) Baratta, W.; Benedetti, F.; Del Zotto, A.; Fanfoni, L.; Felluga, F.; Magnolia, S.; Putignano, E.; Rigo, P. *Organometallics* **2010**, *29*, 3563. (r) Baratta, W.; Bossi, G.; Putignano, E.; Rigo, P. *Chem. Eur. J.* **2011**, *17*, 3474. (s) Esteruelas, M. A.; Honczeck, N.; Oliván, M.; Oñate, E.; Valencia, M. *Organometallics* **2011**, *30*, 2468. (t) Donohoe, T. J.; Callens, C. K. A.; Flores, A.; Mesch, S.; Poole, D. L.; Raslan, I. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 10957. (u) Bertoli, M.; Chonaleb, A.; Lough, A. L.; Moore, B.; Spasynk, D.; Gusev, D. G. *Organometallics* **2011**, *30*, 3479. (v) Esteruelas, M. A.; Garcia-Obregón, T.; Herrero, J.; Oliván, M. *Organometallics* **2011**, *30*, 6402. (w) Spayunk, D.; Swith, S.; Gusev, D. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 2772.

(5) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343.

(6) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2008**, *27*, 3240.

(7) (a) Zabicky, J. *The Chemistry of Amides*; Wiley-Interscience: New York, 1970. (b) Greenberg, A.; Breneman, C. M.; Liebman, J. F. *The Amide Linkage: Structural Significance in Chemistry, Biochemistry, and Material Science*; Wiley: New York, 2000.

(8) Chin, J. *Acc. Chem. Res.* **1991**, *24*, 145.

(9) Kovacs, J. A. *Chem. Rev.* **2004**, *104*, 825.

(10) (a) Kukushkin, V. Y.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **2005**, *358*, 1. (b) Oshiki, T.; Yamashita, H.; Sawada, K.; Utsunomiya, M.; Takahashi, K.; Takai, K. *Organometallics* **2005**, *24*, 6287. (c) Ahmed, T. J.; Zakharov, L. N.; Tyler, D. R. *Organometallics* **2007**, *26*, 5179. (d) Šmejkal, T.; Breit, B. *Organometallics* **2007**, *26*, 2461. (e) Leung, C. W.; Zheng, W.; Wang, D.; Ng, S. M.; Yeung, C. H.; Zhou, Z.; Lin, Z.; Lau, C. P. *Organometallics* **2007**, *26*, 1924. (f) Zinn, P. J.; Sorrell, T. N.; Powell, D. R.; Day, V. W.; Borovik, A. S. *Inorg. Chem.* **2007**, *46*, 10120. (g) Cadierno, V.; Francos, J.; Gimeno, J. *Chem. Eur. J.* **2008**, *14*, 6601. (h) Yi, C. S.; Zeczycki, T. N.; Lindeman, S. V. *Organometallics* **2008**, *27*, 2030. (i) Leung, C. W.; Zheng, W.; Zhou, Z.; Lin, Z.; Lau, C. P. *Organometallics* **2008**, *27*, 4957. (j) Ahmed, T. J.; Fox, B. R.; Knapp, S. M. M.; Yelle, R. B.; Juliette, J. J.; Tyler, D. R. *Inorg. Chem.* **2009**, *48*, 7828. (k) Crestani, M. G.; Steffen, A.; Kenwright, A. M.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Organometallics* **2009**, *28*, 2904. (l) Ramón, R. S.; Marion, N.; Nolan, S. P. *Chem. Eur. J.* **2009**, *15*, 8695. (m) Martín, M.; Horváth, H.; Sola, E.; Kathó, Á.; Joó, F. *Organometallics* **2009**, *28*, 561. (n) Cavarzan, A.; Scarso, A.; Strukul, G. *Green Chem.* **2010**, *12*, 790. (o) Cadierno, V.; Díez, J.; Francos, J.; Gimeno, J. *Chem. Eur. J.* **2010**, *16*, 9808. (p) García-Álvarez, R.; Díez, J.; Crochet, P.; Cadierno, V. *Organometallics* **2010**, *29*, 3955. (q) García-Álvarez, R.; Díez, J.; Crochet, P.; Cadierno, V. *Organometallics* **2011**, *30*, 5442. (r) García-Álvarez, R.; Francos, J.; Crochet, P.; Cadierno, V. *Tetrahedron Lett.* **2011**, *52*, 4218. (s) Muranaka, M.; Hyodo, I.; Okumura, W.; Oshiki, T. *Catal. Today* **2011**, *164*, 552. (t) Ahmed, T. J.; Knapp, S. M. M.; Tyler, D. R. *Coord. Chem. Rev.* **2011**, *255*, 949. (u) Knapp, S. M. M.; Sherbow, T. J.; Juliette, J. J.; Tyler, D. R. *Organometallics* **2012**, *31*, 2941. (v) Daw, P.; Sinha, A.; Rahaman, S. M. W.; Dinda, S.; Bera, J. K. *Organometallics* **2012**, *31*, 3790. (w) Lee, W.-C.; Frost, B. J. *Green Chem.* **2012**, *14*, 62. (x) Li, Z.; Wang, L.; Zhuo, X. *Adv. Synth. Catal.* **2012**, *354*, 584. (y) García-Álvarez, R.; García-Garrido, S. E.; Díez, J.; Crochet, P.; Cadierno, V. *Eur. J. Inorg. Chem.* **2012**, *26*, 4218.

(11) (a) Cariati, E.; Dragonetti, C.; Manassero, L.; Roberto, D.; Tessore, F.; Lucenti, E. *J. Mol. Catal. A: Chem.* **2003**, *204–205*, 279. (b) Stepanenko, I. N.; Cebrián-Losantos, B.; Arion, V. B.; Krokhin, A. A.; Nazarov, A. A.; Keppler, B. K. *Eur. J. Inorg. Chem.* **2007**, 400. (c) Ashraf, S. M.; Kandioller, W.; Mendoza-Ferri, M.-G.; Nazarov, A. A.; Hartinger, C. G.; Keppler, B. K. *Chem. Biodivers.* **2008**, *5*, 2060.

(12) (a) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723. (b) Breno, K. L.; Pluth, M. D.; Tyler, D. R. *Organometallics* **2003**, *22*, 1203. (c) Tílvez, E.; Menéndez, M. I.; López, R. *Organometallics* **2012**, *31*, 1618.

(13) Yamaguchi, K.; Matsushita, M.; Mizuno, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 1576.

(14) Lee, J.; Kim, M.; Chang, S.; Lee, H.-Y. *Org. Lett.* **2009**, *11*, 5598.

(15) Kaminskaia, N. V.; Kostić, N. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3677.

(16) Ghaffar, T.; Parkins, A. W. *J. Mol. Catal. A: Chem.* **2000**, *160*, 249.

(17) (a) Kim, J. H.; Britten, J.; Chin, J. *J. Am. Chem. Soc.* **1993**, *115*, 3618. (b) Swartz, R. D.; Coggins, M. K.; Kaminsky, W.; Kovacs, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 3954.

(18) Edwards, J. A.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828.

(19) Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado, E.; Ruiz, N. *Organometallics* **1997**, *16*, 5748.

(20) (a) Roy, S. C.; Dutta, P.; Nandy, L. N.; Roy, S. K.; Samuel, P.; Pillai, S. M.; Kaushik, V. K.; Ravindranathan, M. *Appl. Catal. A: Gen.* **2005**, *290*, 175. (b) Crisóstomo, C.; Crestani, M. G.; García, J. J. *Inorg. Chim. Acta* **2010**, *363*, 1092. (c) Hirano, T.; Uehara, K.; Kamata, K.; Mizuno, N. *J. Am. Chem. Soc.* **2012**, *134*, 6425.

(21) See, for example: (a) Rajasekaran, A.; Sivakumur, P.; Jayakar, B. *Indian J. Pharm. Sci.* **1999**, *61*, 158. (b) Bertini, R.; Bizzarri, C.; Sabbatini, V.; Porzio, S.; Caselli, G.; Allegretti, M.; Cesta, M. C.; Gandolfi, C. A.; Mantovanini, M.; Colotta, F. PTC International Patent Application WO2000024710, 2000. (c) Nakatsuka, M.; Nakatani, S.; Okada, S.-I.; Tsuboi, K.; Nishikaku, F. PTC International Patent Application WO2001005774, 2001. (d) Doshi, A.; Samant, S. D.; Deshpande, S. G. *Indian J. Pharm. Sci.* **2002**, *64*, 440. (e) Doshi, A.; Deshpande, S. G. *Indian J. Pharm. Sci.* **2002**, *64*, 445. (f) Bertini, R.; Allegretti, M.; Bizzarri, C.; Moriconi, A.; Locati, M.; Zampella, G.; Cervellera, M. N.; Di Cioccio, V.; Cesta, M. C.; Galliera, E.; Martinez, F. O.; Di Bitondo, R.; Troiani, G.; Sabbatini, V.; ÓAnniballe, G.; Anacardio, R.; Cutrín, J. C.; Cavalieri, B.; Mainiero, F.; Strippoli, R.; Villa, P.; Di Girolamo, M.; Martin, F.; Gentile, M.; Santoni, A.; Corda, D.; Poli, G.; Mantovani, A.; Ghezzi, P.; Colotta, F. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 11791. (g) Allegretti, M.; Cesta, M. C.; Nano, G.; Bertini, R.; Bizarri, C.; Colotta, PCT International Patent Application WO2005028425, 2005. (h) Guo, C. B.; Cai, Z. F.; Guo, Z. R.; Feng, Z. Q.; Chu, F. M.; Cheng, G. F. *Chin. Chem. Lett.* **2006**, *17*, 325. (i) Doshi, A.; Deshpande, S. G. *Indian J. Pharm. Sci.* **2007**, *69*, 824. (j) Marjanović, M.; Zorc, B; Pejnović, L.; Zovko, M.; Kralj, M. *Chem. Biol. Drug Des.* **2007**, *69*, 222.

(22) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. *SADABS: Area-detector absorption correction*; Bruker-AXS, Madison, WI.

(23) *SHELXTL Package v. 6.10*; Bruker-AXS, Madison, WI, 2000 Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(24) Gaussian 09 software: Frisch, M. J. et al. *Gaussian 09, revision A.02*; Gaussian, Inc., Wallingford, CT, 2009.