Electronic Effects in Olefin Oxidation by Imidoosmium(VIII) Compounds

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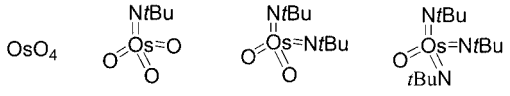
Dedicated to Prof. Dr. Edgar Niecke on the occasion of his 65th birthday

Keywords: Osmium / Oxidations / Imido compounds / Diamination / Heterocycles

Imido osmium(VIII) complexes are versatile oxidants for C–C double bond functionalisation. Despite their structural similarity with OsO_4 their reactivity cannot always be compared with this seminal reagent. Detailed investigations including kinetic competition experiments are presented that uncover the electronic and steric preferences of osmium imido complexes. The different behaviour of OsO_4 and its imido derivatives towards tertiary amines and diamines is clarified. Hammett correlation studies reveal that the reactivity spectrum of the respective oxidants ranges from a strongly electrophilic behaviour in the case of OsO_4 to a rather nucleophilic character as encountered for $OsO(NtBu)_3$.

Introduction

Selective oxidative 1,2-functionalisation by means of defined osmium complexes is the basis of the epoch-making catalytic asymmetric Sharpless dihydroxylation[1−4] and aminohydroxylation[5,6] reactions.[7] These reactions employ the tertiary quinuclidine amino group of *Cinchona* alkaloids for chiral modification of the osmium reagent[1] and for enhancement of the overall reaction rate.[8] The active oxidative species in these reactions is either osmium tetroxide OsO_4 (**1**) or a monoimido trioxoosmium compound which is generally obtained from in situ formation of an osmium(VI) compound and a suitable nitrene precursor. These reagents have not yet been characterised and preformed imido complexes with a tertiary alkyl substituent at nitrogen such as **2** remain the only stable derivatives known to date.[9] Moreover, no detailed comparative studies on the reactivities of osmium oxidants **1**−**4** (Figure 1) have been undertaken. Owing to the vast interest in dihydroxylations, osmium tetroxide and its chemistry have received much attention and its oxidative behaviour toward all kinds of olefin substrate classes is believed to be well understood.[1,10] In the 1970s, Sharpless reported the general reactivity pattern for isolated imido osmium(VIII) complexes and presented selected examples of oxidative conversion of olefin classes employing these reagents.[11−13] We have recently been interested in the chemistry of the related bis- and tris-(imido)osmium complexes **3** and **4**.[14−16] During the course of this investigation, several results were encountered that could not be explained by simply employing the parent osmium tetroxide as a model oxidant. At the same time, there remain certain open features such as chemo- and regioselectivity in aminohydroxylation protocols[5,6,9] that require a deeper understanding of the imido osmium complexes involved. Certainly, a precise knowledge of the electronic properties of complexes such as **2**−**4** is needed and will be indispensable for the development of new reactivity in this area.



1 **2** **3** **4**

Figure 1. Osmium oxidants **1**−**4**

We have thus embarked on a detailed study of the electronic effects involved in olefin oxidation with complexes **2**−**4** and here offer a concise discussion of the differences in electronic features between the common imido osmium complexes **1**−**4** and their consequences for oxidative olefin functionalisation.

Results and Discussion

Electronic Effects of the Substrates

The general preference of **3** and **4** for electron-deficient olefins as substrates was known from previous investigations.[13−16] In addition, a competition experiment for oxidation of dimethyl fumarate had revealed a higher reaction rate for these reagents than for the related compounds **1** and **2**.[15] In fact, the relative reactivities in the

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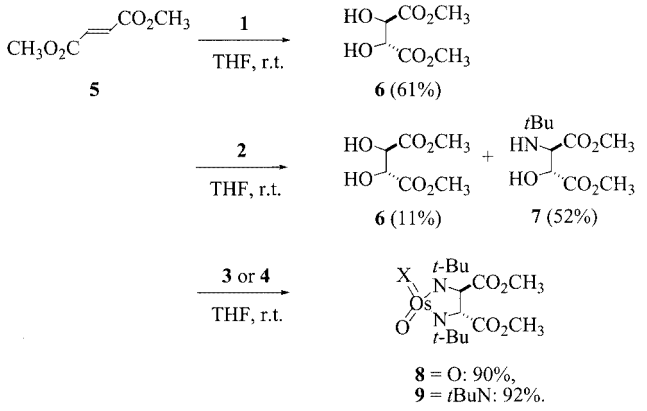
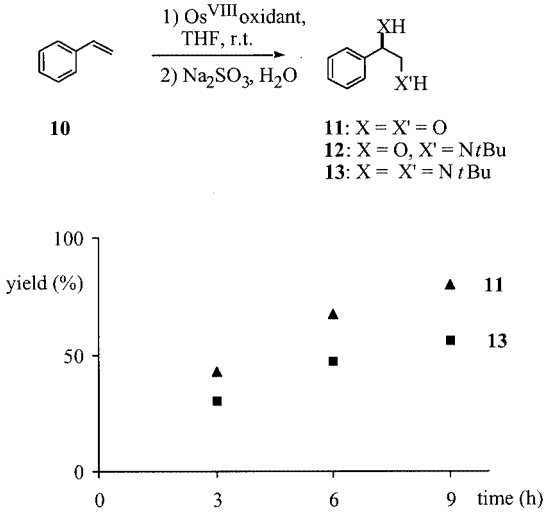
oxidation of dimethylfumarate were found to follow the order: $k(\mathbf{4}) > k(\mathbf{3}) >> k(\mathbf{2}) = k(\mathbf{1})$. It is particularly significant that the sterically very congested tris(imido) species **4** reacts faster than the bis(imido) reagent **3**. This indicates that electronic, not steric, properties are important in the oxidation of electron-deficient olefins with imido complexes (Scheme 1). As a second important observation, compound **2** leads to diol and amino alcohol formation while **3** and **4** display complete chemoselectivity and undergo exclusively diamination reactions.



Scheme 1. Oxidation of dimethyl fumarate[15]

However, the stated reactivity order was found to be reversed when oxidation of styrene was investigated. In this case, osmium tetroxide **1** gave a high yield of 89% after 12 h at room temperature while the imido compounds reacted more slowly (Scheme 2, Table 1). This is exemplified best by comparison of the respective product formation from oxidations of styrene with **1** and **4** (Scheme 2, below).



Scheme 2. Oxidation of styrene with oxidants **1**−**4** and comparison between **1** and **4** in styrene oxidation

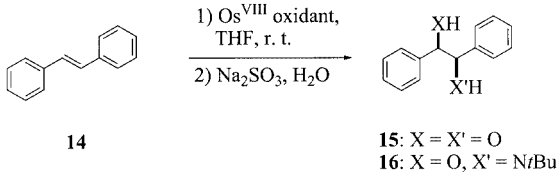
These observations suggest a relative change of reactivity in going from **5** to **10**. Apparently, the observed trend from

Table 1. Styrene oxidation by osmium oxidants **1**−**4**

Entry	Oxidant	Time [h]	Product(s)	Yield [%][a]	Chemoselectivity
1	**1**	12	**11**	85	–
2[b]	**2**	20	**11**, **12**	59	> 95:5 (**12**:**11**)
3[c]	**3**	20	**12**, **13**	76	91:9 (**13**:**12**)
4[d]	**4**	20	**12**, **13**	94	> 98[e] (**13**:**12**)

[a] Combined yield of products after reductive workup. [b] Literature value: 63% yield, 99:1 chemoselectivity (ref.[11]). [c] Literature value: 83% yield, 88:12 chemoselectivity (in CCl_4, ref.[11,12]). [d] Literature value: 92% yield, 97:3 chemoselectivity (in CCl_4, ref.[11,12]). [e] Detection of a single set of signals in the respective 300-MHz ^{1}H NMR spectrum.

electron-withdrawing substrates such as dimethyl fumarate, which showed complete chemoselectivity with **3** but rather low chemoselectivity with **2**, is altered for reaction with neutral olefins (Scheme 2, Table 1). Oxidation with **2** leads almost exclusively to amino alcohol formation while **3** gives an approximately 10:1 ratio for diamine/amino alcohol. A second set of experiments with (*E*)-stilbene as substrate was rather difficult to interpret. Dihydroxylation with **1** gave the usual high yield that is known for this particular substrate from both stoichiometric and catalytic reactions.[1,2] In contrast, oxidation with **2** yielded a nearly equimolar mixture of diol and amino alcohol and both reagents **3** and **4** gave amino alcohol formation only (Scheme 3, Table 2).



Scheme 3. Oxidation of (*E*)-stilbene

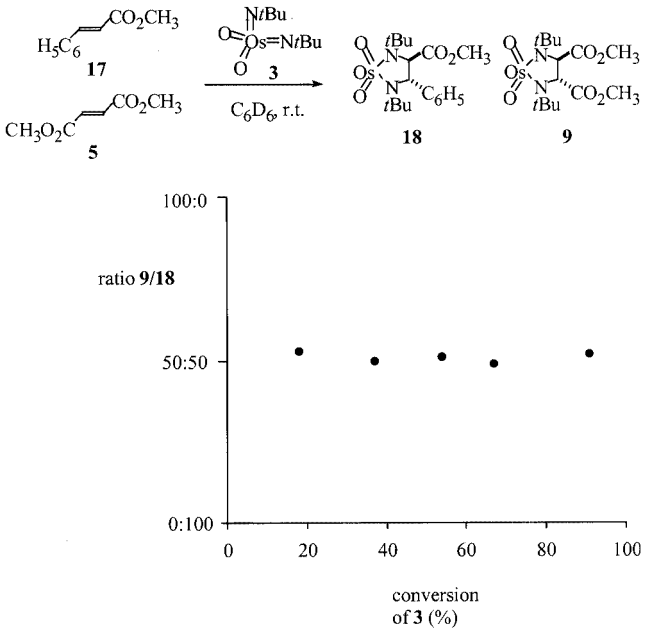
Table 2. Stilbene oxidation by osmium oxidants **1**−**4**

Entry	Oxidant	Temp. (°C)	Time [h]	Product	Yield [%]	Chemoselectivity
1	**1**	room temp.	12	**15**	89 [a]	–
2	**2**	room temp.	20	**15**, **16**	56[b]	> 55:45 (**15**:**16**)
3	**3**	70	36	**16**	41[c]	> 98[d] (**16**)
4	**4**	70	36	**16**	23[e]	> 98[d] (**16**)

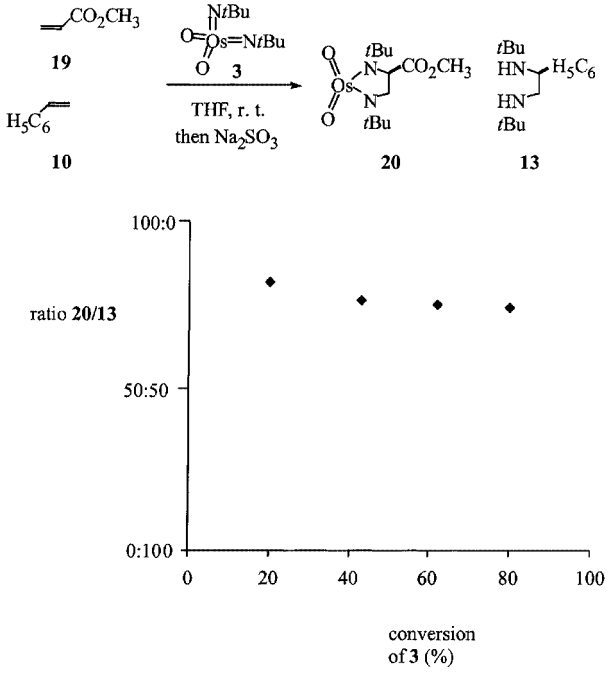
[a] Together with ca. 12% benzaldehyde (6% yield); 100% overall conversion. [b] Combined yield of products; 41% recovered starting material. [c] Together with ca. 18% benzaldehyde (9% yield); 55% conversion. [d] Detection of a single 1,2-difunctionalization product in the respective 300-MHz ^{1}H NMR spectrum. [e] Together with ca. 28% benzaldehyde (14% yield); 40% conversion.

The apparent differences in comparison to the respective oxidations of styrene are not due to electronic reasons but arise from the additional steric hindrance between the olefin and the bulky *tert*-butyl-substituted imido reagents. It should be noted that the absence of diamine formation in the reactions with **3** and **4** is without precedent.

An investigation of the relative reactivities of **3** towards electron-deficient olefins showed nearly equal reactivity for diamination of methyl cinnamate and dimethyl fumarate (Scheme 4).[15] Apparently, there is negligible electronic influence from the second electron-withdrawing group. Importantly, this similarity in reactivity is no longer observed for competition experiments involving monosubstituted olefins such as styrene and methyl acrylate. Here, the electron-demanding olefin undergoes a faster reaction (Scheme 5).

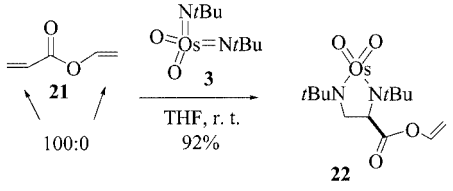


Scheme 4. Competition experiment for diamination with **3**: electron-demanding olefins



Scheme 5. Competition experiment for diamination with **3**: electron-demanding vs. neutral olefin

This result again underlines the importance of electron-demanding substituents in ensuring high reactivity in olefin diamination. These general trends in reactivity of **3** and **4** toward electronically different C=C bonds is best illustrated by the reaction of **3** with vinyl acrylate which represents a substrate with two electronically different C=C bonds (Scheme 6).



Scheme 6. Chemoselective C−C-double bond diamination

In this competition experiment, complete chemoselectivity regarding the reagent (exclusive diamination, no dihydroxylation or aminohydroxylation) and the substrate (exclusive oxidation of the acrylate C−C double bond over the vinylic one) takes place and **22** is formed selectively as the only product out of eight possible ones!

In general, electron-demanding C=C bonds undergo faster diamination than neutral or electron-rich ones. With regards to acceptor-substitution, one electron-withdrawing group is apparently sufficient for the reaction to reach maximum rate. These conclusions hold true for all substrates investigated so far. A single exception has been observed for ferrocenyl acrylates, which will be discussed elsewhere.[17]

Ligand Coordination

Coordination of mono-amine ligands such as DABCO or quinuclidine to OsO_4 or its monoimido derivatives usually increases the reactivity and enhances the chemoselectivity in case of aminohydroxylation with **2** and related alkylimido complexes.[8] The same holds true for the naturally occurring *Cinchona* alkaloids dihydroquinine and dihydroquinidine which create a chiral environment around osmium and thereby guarantee that an asymmetric induction takes place. This principle of reversible ligand coordination and beneficial rate enhancement for the desired chiral oxidant was established as *Ligand Accelerated Catalysis* (or *Ligand Accelerated Synthesis* in the case of stoichiometric reaction conditions).[8]

In indicative sets of experiments no difference in rate was observed for diamination of dimethyl fumarate or methyl cinnamate in the absence or presence of potential ligands such as quinuclidines, DABCO or pyridine. As a result, it was impossible to induce asymmetry in the diamination reactions of various olefins with reagents **3** and **4**.

Careful ^{1}H NMR studies for different ratios of **3** and the standard first-generation PCB ligand of DHQD (**23**)[1] did not suggest any complexation at all.[18] Selected NMR spectra for such investigations are reproduced in Figure 2. This observation is in notable contrast to a related titration study of monoimido complex **2** with **23**, which indicated coordination between the respective quinuclidine unit and **2**.[19]

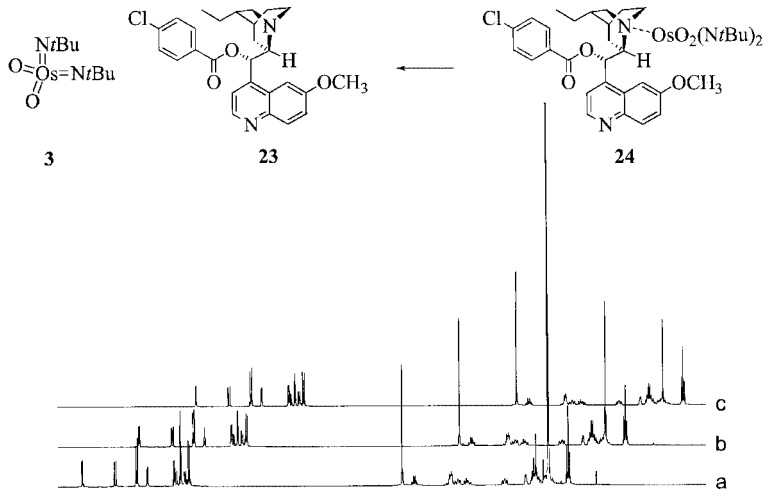
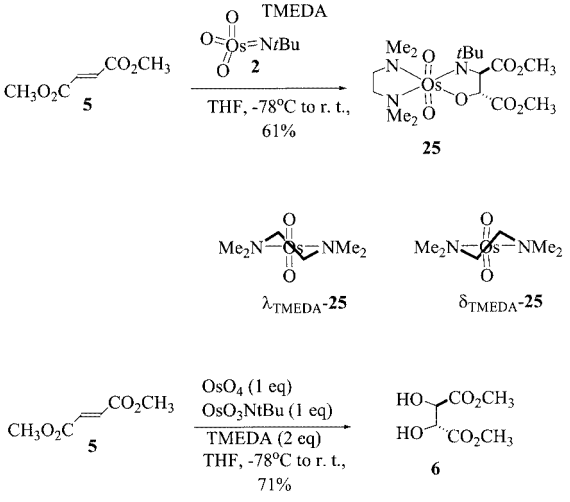


Figure 2. ^{1}H NMR spectra for titration of **3** with *Cinchona* alkaloid **23** [for ratios of **23/3**, 1:1 (**a**), 5:1 (**b**) and 20:1 (**c**)]

Moreover, several reports of spectral investigation of *Cinchona* alkaloid complexes of **1** have become available.[20] For **3** and **4**, the apparent inability to complex external nitrogen ligands stems from the presence of two basic imido groups which saturate the Os centre through alternating electron donation from the nitrogen lone pairs. Such electronic saturation removes all electrophilicity at the Os^{VIII} centre and thereby prevents it from coordinating with external nitrogen donors.

Conceptually different approaches in the area of stoichiometric asymmetric dihydroxylation reactions have employed vicinal diamines. These compounds form stable chelate adducts with osmium tetroxide to furnish extremely reactive dihydroxylating reagents. For example, Corey has reported a chelate complex from **1** and *N*,*N*′-bis(mesitylidene) diphenylethylenediamine that displays high reactivity even at a temperature as low as −70 °C.[21] Moreover, the diamine adducts of the resulting osmate esters are known to have enhanced resistance to hydrolysis.[22] Finally, Donohoe recently succeeded both in the use of TMEDA/**1** combinations for directed dihydroxylation reactions[23,24] and in the isolation of an azaglycolate product from intramolecular aminohydroxylation by TMEDA complexation.[25]

It was anticipated that complexation of **2** with TMEDA would greatly enhance the reactivity and thereby the amount of aminohydroxylation over dihydroxylation. Indeed, reaction of **2** with dimethyl fumarate (**5**) in the presence of TMEDA gave the expected complex **25** (Scheme 7). Since the primarily formed *N*-(*tert*-butyl)azaglycolate has been shown to be rather unstable,[11,12] isolation of **25** proves the beneficial influence of the chelating diamine in stabilising the azaglyolate osmium intermediate as already observed by Donohoe. Product **25** was isolated as an inseparable mixture of two isomers. In accordance with the NMR spectroscopic data, the existence of these two diastereoisomers is assumed to be due to a λ/δ-conformation of the TMEDA ligand in **25** (Scheme 7).



Scheme 7

A competition experiment between OsO_4/TMEDA and OsO_3N*t*Bu/TMEDA yielded, after reductive workup, dimethyl tartrate **6** as the only product. This is a surprising reaction outcome taking into account the preferred reactivity of free **2** over free **1** as established previously.[15] Careful NMR studies revealed that there is no apparent interaction between the monoimido reagent **2** and TMEDA. Over the whole temperature range of −80 to +20 °C only the signals of the respective free, uncomplexed compounds appeared. This indicates an explanation for the reaction outcome from Scheme 7. Apparently, formation of the observed TMEDA chelate **25** takes place during the process of warming to room temperature, and complexation of TMEDA to Os occurs only *after* initial formation of the azaglycol osmate(VI) ester has already taken place.

Since OsO_4 does readily interact with TMEDA even at low temperatures in the region of −80 °C, the OsO_4/TMEDA combination produces the kinetically preferred oxidant leading to formation of **6** only (Scheme 7, below).

Hammett Correlations

We further quantified the observations on electronic influence and have investigated the respective Hammett correlations for diaminations with imido reagents **3** and **4**. 4-Phenyl-substituted cinnamates were chosen as substrates for this investigation.

For osmium tetroxide (**1**) a nonlinear plot was observed. Such a behaviour was also observed by Sharpless for related Os-catalysed reactions in the presence of a chiral tertiary amine ligand.[26] If the data for the *p*-NO_2/*p*-H pair is omitted, a linear regression gives a *p*-value of −0.55 (Figure 3) which is in good agreement with the expected electrophilic character of the 16e-oxidant **1**. A comparable result had been determined by Henbest for dihydroxylation of styrenes.[27]

Initial attempts to undertake the same investigation with the monoimido complex **2** were hampered by the low chemoselectivity of this reagent and the problematic identification of some of the reaction products. However, it had already been noted by Sharpless that **2** represents a slightly softer oxidant than **1** and thus should be regarded as an electrophilic reagent with less pronounced character than **1**.[11,12] This can be explained by the electron lone pair at the imido nitrogen atom which upon coordination to the metal centre diminishes the electrophilicity. Such an assumption is strengthened by X-ray analyses which show a linear imido ligand with a formal 4e count.[28]

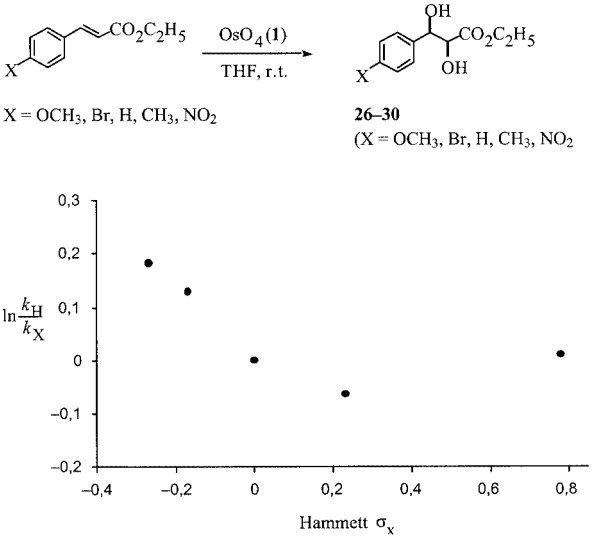


Figure 3. Hammet plot for dihydroxylation of 4-substituted cinnamates by OsO_4

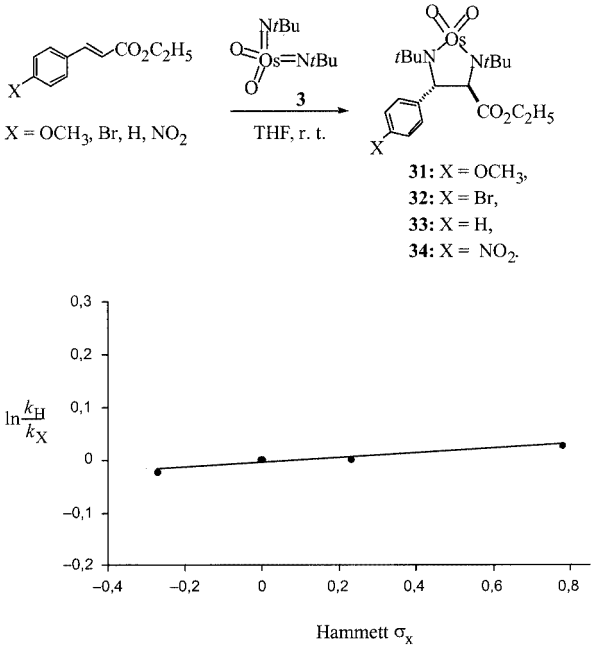
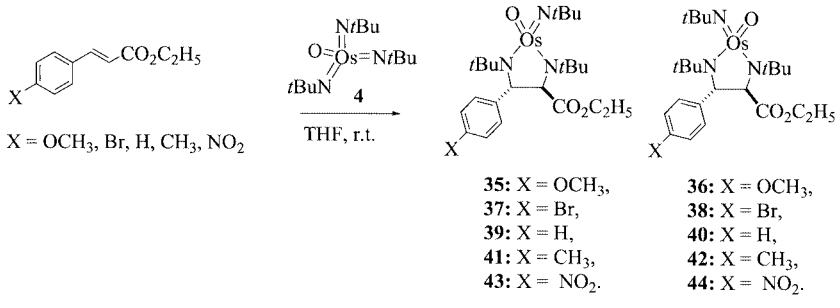


Figure 4. Hammet plot for diamination of 4-substituted cinnamates by bis(imido) reagent **3**

Complex **3** displays a different reactivity pattern, and nearly no electronic influence was observed in the respective oxidations of cinnamates (Figure 4). This observation matches the previous finding that a single electron-withdrawing group is sufficient to reach the optimum rate (Scheme 4). The final Hammett correlation gives a ρ-value of +0.05 which renders **3** a neutral or slightly nucleophilic oxidant.

Reaction of **4** with unsymmetrically substituted olefins forms osmaimidazolidines with a stereogenic metal centre. Thus, a mixture of two diastereomers is obtained.[29] Ap-



Scheme 8. Diamination of 4-substituted cinnamates with tris(imido) reagent **4**

parently, the diastereomeric ratios are nearly independent of the 4′-substitution (Scheme 8, Table 3). As in the case of the related diamination reactions employing reagent **3**, all new compounds were first synthesised in independent reactions and fully characterised. The diastereomeric ratios of each diamination reaction could thus be assured independently.

Table 3. Diamination of 4-substituted cinnamates with tris(imido) reagent **4**

Entry	Substrate (X)	Products	Yield [a]	Diastereomeric ratio[b]
1	OCH_3	**35**, **36**	82	59:41
2	Br	**37**, **38**	88	61:39
3	H	**39**, **40**	93	58:42
4	CH_3	**41**, **42**	89	63:37
5	NO_2	**43**, **44**	96	68:32

[a] Combined yield after purification by column chromatography. [b] Determined from the crude ^{1}H NMR spectrum.

For the competition experiments of the Hammett correlation, product ratios and thus the values for the relative reaction rates were calculated back to the sum of both diastereomers in question and the final Hammett correlation gave a ρ-value of +0.28 (Figure 5). This result characterises **4** as a pronounced nucleophilic oxidant.

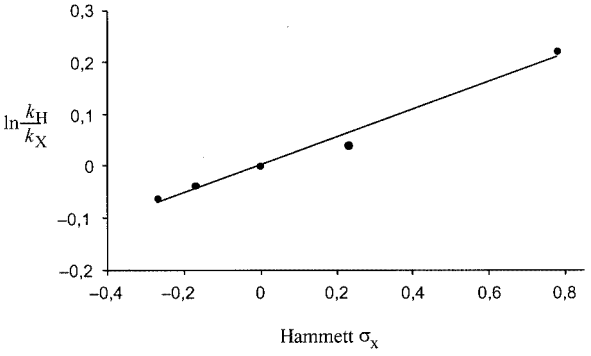


Figure 5. Hammett correlation for diamination of cinnamates with **4**

As a consequence of all these studies, osmium tetroxide (**1**) and the imido derivatives **2**−**4** cannot be compared directly regarding their performance in C=C bond oxidation. While performance of **1** is known to be most efficient in the oxidation of terminal and (*Z*)-configured neutral or electron-rich olefins,[1] imido compounds such as **2** with their reduced electrophilicity give best results with terminal or (*E*)-substituted neutral olefins.[9] In contrast, the bis(imido) complex **3** has a strong preference for (*E*)-configured electron-poor olefins, while tris(imido) complex **4** with its strong steric hindrance reacts only with terminal or (*E*)-substituted olefins[9,13] and is characterised by its nucleophilicity.

Conclusion

We have described a detailed investigation of the electronic nature of imido Os complexes and the resulting consequences for C−C double bond functionalisation. As a result of the obtained data, it is evident that osmium tetroxide **1** cannot be directly compared with its imido complexes **2**, **3** and **4** in respect of reactivity in olefin oxidation. While **1** must be characterised as an electrophilic reagent, this property is diminished by the introduction of subsequent imido groups which results in a dramatically altered reactivity. Thus, bis(imido) complex **3** is a nearly electroneutral oxidant, while the tris(imido) derivative **4** is a nucleophilic oxidant in the oxidation of electron-demanding olefins. Ongoing work is therefore centred on the investigation of the mechanistic pathways involved in olefin oxidation with bis- and tris(imido) osmium(VIII) complexes.

Experimental Section

General Remarks: Osmium(VIII) oxide was purchased from Strem. *tert*-Butylamine, *N*-(trimethylsilyl)-*tert*-butylamine, methyl cinnamate, methyl acrylate and $(DHQD)_2PHAL$ were purchased from Fluka. Dimethyl fumarate, stilbene, styrene and vinyl acrylate were purchased from Aldrich. The following reaction products represent known compounds described previously: **7**−**9**, **11**−**13**, **15**, **18**, **20**, **26**−**30**.[11−13,15,30−33]

THF, *n*-hexane and toluene were distilled from sodium/benzophenone ketyl radical under argon and saturated with argon. Dichloromethane and triethylamine were distilled from CaH_2 under argon. All other solvents were reagent grade and used as received. Column chromatography was performed with silica gel (Merck, type 60, 0.063−0.2 mm and Macherey−Nagel, type 60, 0.015−0.025 mm). Optical rotations were measured with a Perkin−Elmer 341 polarimeter. Concentrations are given in g/100 mL as dichloromethane solutions. NMR spectra were recorded with Bruker DPX 300 MHz and Bruker DRX 500 MHz spectrometers. All chemical shifts in NMR experiments are reported as ppm downfield from TMS. The following calibrations were used: $CDCl_3$: δ = 7.26 and 77.00 ppm, C_6D_6: δ = 7.16 and 128.00 ppm. IR spectra were recorded with a Nicolet Magna 550 FT-IR spectrometer. MS and HRMS experiments, and elemental analyses were performed with a Kratos MS 50 and an Elementar Analysensystem Vario EL, respectively, within the service centres at the Kekulé Department, Bonn.

2-*tert*-Butylamino-1,2-diphenylethanol (16): This was obtained from the reaction between (*E*)-stilbene (360 mg, 2.0 mmol) and complex **3** (382 mg, 1 mmol) in freshly distilled THF (10 mL). After stirring at 70 °C for 36 h, the dark reaction mixture was treated with an aqueous thiosulfate solution and submitted to acid/base extraction with dichloromethane as organic solvent. The organic layers were dried with $MgSO_4$ and the solvents evaporated under reduced pressure to leave the title compound (111 mg, 0.41 mmol, 41%) as a colourless to light-yellow oil which solidified upon standing. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 9 H), 3.73 (d, *J* = 9.5 Hz, 1 H), 4.58 (d, *J* = 9.5 Hz, 1 H), 7.04−7.46 (m, 10 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 30.62, 65.77, 68.37, 87.22, 126.52, 126.89, 127.61, 128.51, 128.67, 134.85, 146.56 ppm. IR (KBr): $\tilde{\nu}$ = 3011, 2967, 2833, 2111, 1365, 1103, 1074, 993, 894 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 270 (55) $[M]^+$, 213 (22), 199 (86), 138 (28), 77 (100).

$C_{19}H_{23}NO$: calcd. C 80.26, H 8.61, N 5.20; found C 80.53, H 8.56, N 5.43.

General Procedure for Diamination of Achiral Olefins with Osmium Imido Complexes 3 and 4: The solid bis(imido) osmium complex **2** was added to a solution of the appropriate olefin (1.2 mmol) in freshly distilled THF in one portion and the resulting solution was stirred at room temperature overnight (approx. 12 h). The solvent was evaporated under reduced pressure and the remaining crude oily residue analysed by NMR spectroscopy. The pure product was obtained by column chromatography as indicated for the individual compound.

Vinyl 1,3-Bis(*tert*-butyl)-2,2-dioxo-2-osma(VI)imidazolidine-4-carboxylate (22): This was obtained from the reaction between vinyl acrylate (65 μL, 0.62 mmol) and the bis(imido) compound **3** (181 mg, 0.5 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:3, v/v) gave the title compound as a purple solid (213 mg, 0.46 mmol, 92%). M.p. 78 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.85 (s, 9 H), 0.95 (s, 9 H), 3.04 (m, *J* = 1.0, 12.6 Hz, 1 H), 3.14 (dd, *J* = 6.6, 12.6 Hz, 1 H), 3.81 (dd, *J* = 1.0, 6.6 Hz,, 1 H), 4.00 (dd, *J* = 1.7, 6.2 Hz, 1 H), 4.71 (dd, *J* = 1.7, 13.9 Hz, 1 H), 6.94 (dd, *J* = 6.2, 13.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 29.31, 29.81, 66.68, 66.76, 68.71, 74.86, 98.82, 140.78, 170.52 ppm. IR (KBr): ṽ = 3033, 3011, 2996, 2304, 2285, 1759, 1697, 1351, 1185, 1109, 871, 860 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 464 (20) $[M]^+$, 449 (22), 393 (100), 337 (43), 281 (59), 57 (76). HRMS: calcd. for $C_{13}H_{24}N_2O_4{}^{188}Os$: 460.1295; found 460.1294.

Osmium(VI) Azaglycolate 25: A solution of the monoimido complex **2** (155 mg, 0.5 mmol) in dichloromethane under argon was cooled to −78 °C and treated with a solution of TMEDA (90 μL, 0.58 mmol) in dichloromethane (1 mL). Solid dimethyl fumarate (144 mg, 1.0 mmol) was added in one portion and the resulting mixture stirred overnight while warming to room temperature. The solvent was removed under reduced pressure and the remaining dark-red solid purified by column chromatography (dichloromethane/methanol, 8:1, v/v) to give the title compound in the form of two isomers as a dark-red solid (174 mg, 0.31 mmol, 61%). M.p. 94 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.98 (s, 9 H), 1.42 (s, 9 H), 3.05 (s, 6 H), 3.17 (s, 6 H), 3.33 (s, 6 H), 3.58 (s, 1 H), 3.62 (s, 1 H), 3.64 (s, 1 H), 4.25 (s, 1 H), 5.66 (s, 2 H), 5.72 (s, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 26.57, 30.00, 30.69, 51.80, 52.15, 52.81, 56.05, 75.02, 81.27, 91.05, 97.22, 168.33, 170.12, 172.0, 173.86 ppm. IR (KBr): ṽ = 3074, 2966, 1784, 1779, 1651, 1544, 1412, 1107, 1044, 982, 781 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 572 (100) $[M]^+$, 453 (23), 399 (18), 339 (25), 116 (43). HRMS: calcd. for $C_{16}H_{33}N_3O_7{}^{188}Os$: 566.9147; found 566.9152.

Diaminations of Ethyl Cinnamates with Bis(imido) Reagent 3: Diaminations of ethyl cinnamates were carried out following the general procedure for diamination reactions outlined above.

Ethyl *trans*-1,3-Bis(*tert*-butyl)-5-(4′-methoxyphenyl)-2,2-dioxo-2-osma(VI)imidazolidine-4-carboxylate (31): This was obtained from the reaction between ethyl 4′-methoxy-cinnamate (124 mg, 0.6 mmol) and the bis(imido) compound **3** (181 mg, 0.5 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:3, v/v) gave the title compound as a purple solid (257 mg, 0.45 mmol, 90%). M.p. 112 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.06 (t, *J* = 7.2 Hz, 3 H), 1.13 (s, 9 H), 1.22 (s, 9 H), 3.26 (s, 3 H), 3.95 (q, *J* = 7.2 Hz, 2 H), 4.37 (s, 1 H), 5.04 (s, 1 H), 6.70 (d, *J* = 8.8 Hz, 2 H), 7.24 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.31, 29.93, 30.72, 54.74, 61.35, 66.86, 67.61, 82.03, 85.37, 114.31, 127.90, 138.11, 159.74, 172.94 ppm. MS (EI, eV): *m*/*z* (%) = 572 (8) $[M]^+$, 557 (8), 499 (89), 443 (100), 387 (269, 359 (10), 134 (16). HRMS: calcd. for $C_{20}H_{32}N_2O_5{}^{188}Os$: 568.2270; found 568.2268.

Ethyl *trans*-5-(4′-Bromophenyl)-1,3-bis(*tert*-butyl)-2,2-dioxo-2-osma(VI)imidazolidine-4-carboxylate (32): This was obtained from the reaction between ethyl 4′-bromocinnamate (153 mg, 0.6 mmol) and the bis(imido) compound **3** (181 mg, 0.5 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:3, v/v) gave the title compound as a purple solid (262 mg, 0.44 mmol, 87%). M.p. 122 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.03 (t, *J* = 7.2 Hz, 3 H), 1.05 (s, 9 H), 1.12 (s, 9 H), 3.94 (q, *J* = 7.2 Hz, 2 H), 4.21 (s, 1 H), 4.85 (s, 1 H), 7.01 (d, *J* = 9.2 Hz, 2 H), 7.17 (d, *J* = 9.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 12.72, 28.45, 29.27, 60.13, 65.38, 66.15, 80.24, 83.75, 120.74, 127.13, 130.69, 143.72, 171.24 ppm. IR (KBr): ṽ = 3423, 2970, 1727, 1728, 1489, 1367, 1230, 1192, 1011, 888, 895 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 619 (7) $[M]^+$, 604 (41), 547 (100), 491 (76), 435 (42), 57 (51). $C_{19}H_{29}BrN_2O_4Os$: calcd. C 36.83, H 4.72, N 4.52; found C 36.44, H 4.39, N 4.81.

Ethyl *trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-5-phenyl-2-osma(VI)imidazolidine-4-carboxylate (33): This was obtained from the reaction between ethyl cinnamate (106 mg, 0.6 mmol) and the bis(imido) compound **3** (181 mg, 0.5 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:3, v/v) gave the title compound as a purple solid (255 mg, 0.47 mmol, 94%). M.p. 98 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.05 (t, *J* = 7.2 Hz, 3 H), 1.09 (s, 9 H), 1.19 (s, 9 H), 3.96 (q, *J* = 7.2 Hz, 2 H), 4.35 (s, 1 H), 5.03 (s, 1 H), 7.03−7.11 (m, 3 H), 7.30−7.36 (m, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.09, 29.85, 30.67, 61.37, 66.78, 67.59, 82.45, 85.40, 126.76, 128.02, 128.86, 146.21, 172.85 ppm. IR (KBr): ṽ = 3419, 2972, 1720, 1473, 1367, 1236, 1186, 1032, 908, 904, 771 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 542 (17) $[M]^+$, 527 (15), 469 (199), 413 (83), 357 (41), 295 (54). HRMS: calcd. for $C_{19}H_{30}N_2O_4{}^{188}Os$: 538.1765; found 538.1767.

Ethyl *trans*-1,3-Bis(*tert*-butyl)-5-(4′-nitrophenyl)-2,2-dioxo-2-osma(VI)imidazolidine-4-carboxylate (34): This was obtained from the reaction between ethyl 4′-nitro-cinnamate (133 mg, 0.6 mmol) and the bis(imido) compound **3** (181 mg, 0.5 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:3, v/v) gave the title compound as a purple solid (249 mg, 0.42 mmol, 85%). M.p. 131 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.02 (s, 9 H), 1.04 (t, *J* = 7.0 Hz, 3 H), 1.08 (s, 9 H), 3.93 (q, *J* = 7.0 Hz, 2 H), 4.12 (s, 1 H), 4.82 (s, 1 H), 7.06 (d, *J* = 9.0 Hz, 2 H), 7.75 (d, *J* = 9.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.04, 29.74, 30.57, 61.70, 66.69, 67.74, 81.28, 84.92, 123.93, 127.32, 147.84, 152.43, 172.27 ppm. IR (KBr): ṽ = 3450, 2975, 2972, 1731, 1525, 1369, 1351, 1190, 901 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 587 (11) $[M]^+$, 572 (12), 514 (100), 458 857), 402 (43), 57 (13). HRMS: calcd. for $C_{19}H_{29}N_3O_6{}^{188}Os$: 583.1615; found 583.1617.

Details of Competitive Diamination Reactions with 3 (Hammett Correlation): Competition experiments were conducted with 2.5 mmol each of the respective 4′-substituted cinnamate and ethyl cinnamate and 0.25 mmol of bis(imido) reagent **3**. Ferrocene was employed as internal standard and THF as solvent (5 mL). After a period of about five hours, the solvent was removed under reduced pressure and the crude reaction mixture was taken up in [D_6]benzene and immediately analysed by ^{1}H NMR spectroscopy. Conversion and relative product formation were calculated from the NMR spectroscopic data and the kinetic expression was calculated using Equation (1).

$$\ln\frac{k_X}{k_H} = \ln\frac{\left[1-\frac{c(\text{Olefin}_X)}{c_0(\text{Olefin}_X)}\right]}{\left[1-\frac{c(\text{Olefin}_H)}{c_0(\text{Olefin}_H)}\right]} \quad (1)$$

The final Hammett correlation as depicted in Figure 4 was obtained employing standard *sr* values.[34]

Diaminations of Ethyl Cinnamates with Tris(imido) Reagent 4: Diaminations of ethyl cinnamates were carried out following the general procedure for diamination reactions outlined above.

Diamination of Ethyl 4′-Methoxycinnamate: This reaction was carried out according to the general procedure with ethyl 4′-methoxycinnamate (72 mg, 0.3 mmol) and the tris(imido) compound **4** (105 mg, 0.25 mmol). Purification by column chromatography (ethyl acetate/hexanes, 1:3, v/v) gave two fractions that contained the pure diastereomers (82% combined yield, 59:41 diastereomeric ratio).

Ethyl [(2*R*,4*R*,5*S*)/(2*S*,4*S*,5*R*)]-*trans*-1,3-Bis(*tert*-butyl)-2-*tert*-butylimido-5-(4′-methyloxophenyl)-2-oxo-2-osma(VI)imidazolidine-4-carboxylate (35): M.p. 89 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.00 (t, *J* = 7.1 Hz, 3 H), 1.22 (s, 9 H), 1.37 (s, 9 H), 1.60 (s, 9 H), 3.30 (s, 3 H), 3.93 (q, *J* = 7.1 Hz, 2 H), 4.43 (s, 1 H), 5.02 (s, 1 H), 6.79−7.60 (m, 5 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.11, 30.15, 32.09, 33.61, 61.29, 62.07, 65.17, 77.06, 77.94, 81.25, 84.82, 125.98, 128.43, 137.28, 142.31, 172.37 ppm. IR (KBr): ṽ = 2958, 2854, 1629, 1456, 1385, 1113, 894, 798 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 625 (2) $[M]^+$, 567 (3), 316 (39), 149 (62), 135 (100), 57 (97). HRMS: calcd. for $C_{24}H_{41}N_3O_4{}^{188}Os$: 623.2656; found 623.2650.

Ethyl [(2*R*,4*S*,5*R*)/(2*S*,4*R*,5*S*)]-*trans*-1,3-Bis(*tert*-butyl)-2-*tert*-butylimido-5-(4′-methyloxophenyl)-2-oxo-2-osma(VI)imidazolidine-4-carboxylate (36): M.p. 93 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.63 (t, *J* = 7.0 Hz, 3 H), 1.25 (s, 9 H), 1.35 (s, 9 H), 1.45 (s, 9 H), 3.31 (s, 3 H), 4.12 (q, *J* = 7.0 Hz, 2 H), 4.45 (d, *J* = 0.6 Hz, 1 H), 5.14 (s, 1 H), 6.75−7.42 (m, 5 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 15.73, 30.89, 31.06, 33.34, 60.99, 62.72, 64.09, 76.91, 78.02, 80.60, 84.34, 126.35, 128.54, 137.52, 142.11, 170.99 ppm. IR (KBr): ṽ = 3071, 1961, 1936, 1743, 1654, 1473, 1389, 1109, 874, 802 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 625 (1) $[M]^+$, 567 (3), 316 (23), 149 (57), 135 (88), 57 (100). HRMS: calcd. for $C_{24}H_{41}N_3O_4{}^{188}Os$: 623.2656; found 623.2652.

Diamination of Ethyl 4′-Bromocinnamate: This was carried out with ethyl 4′-bromocinnamate (77 mg, 0.3 mmol) and the tris(imido) compound **4** (105 mg, 0.25 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:3, v/v) gave two fractions that contained the pure diastereomers (88% combined yield, 61:39 diastereomeric ratio).

Ethyl [(2*R*,4*R*,5*S*)/(2*S*,4*S*,5*R*)]-*trans*-5-(4′-Bromophenyl)-1,3-bis(*tert*-butyl)-2-*tert*-butylimido-2-oxo-2-osma(VI)imidazolidine-4-carboxylate (37): M.p. 64 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.97 (t, *J* = 7.1 Hz, 3 H), 1.14 (s, 9 H), 1.27 (s, 9 H), 1.57 (s, 9 H), 3.89 (q, *J* = 7.1 Hz, 1 H), 3.90 (q, *J* = 7.1 Hz, 1 H), 4.28 (s, 1 H), 4.83 (s, 1 H), 7.29 (d, *J* = 7.9 Hz, 2 H), 7.30 (d, *J* = 7.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.29, 30.47, 31.37, 32.88, 60.75, 63.83, 65.05, 69.67, 80.89, 86.44, 121.43, 129.08, 127.79, 131.70, 146.99, 173.38 ppm. IR (KBr): ṽ = 2968, 2937, 2899, 1751, 1489, 1463, 1360, 1234, 1193, 1174, 1109, 1011, 868 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 675 (13) $[M]^+$, 602 (100), 546 (22), 490 (21), 224 (12), 57 (24). HRMS: calcd. for $C_{23}H_{38}BrN_3O_3{}^{188}Os$: 671.1655; found 671.1652.

Ethyl [(2*R*,4*S*,5*R*)/(2*S*,4*R*,5*S*)]-*trans*-5-(4′-Bromophenyl)-1,3-bis(*tert*-butyl)-2-*tert*-butylimido-2-oxo-2-osma(VI)imidazolidine-4-carboxylate (38): M.p. 68 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.12 (t, *J* = 7.1 Hz, 3 H), 1.17 (s, 9 H), 1.24 (s, 9 H), 1.36 (s, 9 H), 4.07 (q, *J* = 7.1 Hz, 2 H), 4.27 (d, *J* = 0.6 Hz, 1 H), 4.95 (s, 1 H), 6.86 (d, *J* = 8.3 Hz, 2 H), 7.25 (d, *J* = 8.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.27, 30.35, 31.70, 32.35, 61.03, 64.35, 64.50, 69.86, 83.50, 86.01, 121.47, 128.88, 131.14, 145.79, 174.44 ppm. IR (KBr): ṽ = 2970, 2931, 2870, 1747, 1718, 1635, 1234, 1191, 1105, 1011, 891 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 675 (11) $[M]^+$, 602 (100), 546 (23), 490 (29), 182 (18), 57 (18). HRMS: calcd. for $C_{23}H_{38}BrN_3O_3{}^{188}Os$: 671.1655; found 671.1655.

Diamination of Ethyl Cinnamate: This was carried out with ethyl cinnamate (53 mg, 0.3 mmol) and the tris(imido) compound **4** (105 mg, 0.25 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:5, v/v) gave two fractions that contained the pure diastereomers (93% combined yield, 58:42 diastereomeric ratio).

Ethyl [(2*R*,4*R*,5*S*)/(2*S*,4*S*,5*R*)]-*trans*-1,3-Bis(*tert*-butyl)-2-*tert*-butylimido-2-oxo-5-phenyl-2-osma(VI)imidazolidine-4-carboxylate (39): M.p. 88 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.99 (t, *J* = 7.2 Hz, 3 H), 1.01 (s, 9 H), 1.33 (s, 9 H), 1.59 (s, 9 H), 3.93 (q, *J* = 7.2 Hz, 2 H), 4.43 (d, *J* = 0.4 Hz, 1 H), 5.02 (s, 1 H), 7.02−7.22 (m, 3 H), 7.62−7.69 (m, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.31, 30.52, 31.41, 32.96, 60.65, 63.92, 65.15, 69.50, 81.69, 86.78, 127.26, 127.47, 127.85, 128.56, 148.08, 173.67 ppm. IR (KBr): ṽ = 2968, 2931, 1751, 1462, 1363, 1232, 1194, 1161, 1105, 877 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 597 (10) $[M + 1]^+$, 469 (38), 413 (52), 357 (29), 146 (22), 57 (100). HRMS: calcd. for $C_{23}H_{39}N_3O_3{}^{188}Os$: 593.2551; found 593.2555.

Ethyl [(2*R*,4*S*,5*R*)/(2*S*,4*R*,5*S*)]-*trans*-1,3-Bis(*tert*-butyl)-2-*tert*-butylimido-2-oxo-5-phenyl-2-osma(VI)imidazolidine-4-carboxylate (40): M.p. 95 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.15 (t, *J* = 7.1 Hz, 3 H), 1.21 (s, 9 H), 1.31 (s, 9 H), 1.45 (s, 9 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 4.41 (d, *J* = 0.7 Hz, 1 H), 5.13 (s, 1 H), 7.05−7.33 (m, 5 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.30, 30.42, 31.74, 32.41, 60.93, 64.45, 64.61, 69.66, 84.32, 86.25, 126.76, 127.10, 128.86, 146.74, 174.66 ppm. IR (KBr): ṽ = 3389, 2954, 2922, 1761, 1458, 1352, 1209, 1201, 1187, 1158, 1101, 1030, 876 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 597 (1) $[M + 1]^+$, 524 (2) 469 (12), 413 (17), 355 (9), 146 (29), 57 (100). HRMS: calcd. for $C_{23}H_{39}N_3O_3{}^{188}Os$: 593.2551; found 593.2549.

Diamination of Ethyl 4′-Methylcinnamate: This was carried out with ethyl 4′-methylcinnamate (67 mg, 0.3 mmol) and the tris(imido) compound **4** (105 mg, 0.25 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:4, v/v) gave two fractions that contained the pure diastereomers (89% combined yield, 58:42 diastereomeric ratio).

Ethyl [(2*R*,4*R*,5*S*)/(2*S*,4*S*,5*R*)]-*trans*-1,3-Bis(*tert*-butyl)-2-*tert*-butylimido-5-(4′-methylphenyl)-2-oxo-2-osma(VI)imidazolidine-4-carboxylate (41): M.p. 101 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.98 (t, *J* = 7.0 Hz, 3 H), 1.21 (s, 9 H), 1.35 (s, 9 H), 1.59 (s, 9 H), 3.91 (q, *J* = 7.0 Hz, 2 H), 4.45 (d, *J* = 0.4 Hz, 1 H), 5.04 (s, 1 H), 7.04 (d, *J* = 7.9 Hz, 2 H), 7.10−7.18 (m, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.32, 21.02, 30.54, 31.46, 33.00, 60.63, 63.94,

65.19, 69.46, 81.58, 86.82, 127.25, 129.29, 136.83, 145.20, 173.75 ppm. IR (KBr): $\tilde{\nu}$ = 2968, 2924, 2864, 1747, 1647, 1464, 1363, 1236, 1185, 1107, 1028, 872 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 611 (20) $[M + 1]^+$, 596 (11), 538 (100), 482 (20), 426 (17), 160 (22), 57 (24). HRMS: calcd. for $C_{24}H_{41}N_3O_3{}^{188}Os$: 607.2707; found 607.2714.

Ethyl [(2*R*,4*S*,5*R*)/(2*S*,4*R*,5*S*)]-*trans*-1,3-Bis(*tert*-butyl)-2-*tert*-butylimido-5-(4′-methylphenyl)-2-oxo-2-osma(VI)imidazolidine-4-carboxylate (42): M.p. 94 °C (dec.). ^1H NMR (300 MHz, C_6D_6): δ = 1.15 (t, *J* = 7.0 Hz, 3 H), 1.24 (s, 9 H), 1.33 (s, 9 H), 1.47 (s, 9 H), 4.09 (q, *J* = 7.0 Hz, 2 H), 4.44 (d, *J* = 0.4 Hz, 1 H), 5.14 (s, 1 H), 7.03−7.11 (m, 2 H), 7.22−7.28 (m, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.44, 25.06, 30.47, 31.79, 32.46, 61.09, 64.22, 64.94, 69.46, 75.53, 82.28, 84.69, 126.83, 129.47, 133.73, 145.65, 174.01 ppm. IR (KBr): $\tilde{\nu}$ = 2654, 2931, 1756, 1471, 1226, 1100, 1033, 873 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 611 $[M + 1]^+$(18), 596 (10), 538 (100), 482 (23), 426 (16), 160 (21), 57 (20). HRMS: calcd. for $C_{24}H_{41}N_3O_3{}^{188}Os$: 607.2707; found 607.2702.

Diamination of Ethyl 4-Nitrocinnamate: This was carried out with ethyl 4′-nitrocinnamate (67 mg, 0.3 mmol) and tris(imido) compound **4** (105 mg, 0.25 mmol) according to the general procedure. Purification by column chromatography (ethyl acetate/hexanes, 1:4, v/v) gave two fractions that contained the pure diastereomers (96% combined yield, 68:32 diastereomeric ratio).

Ethyl [(2*R*,4*R*,5*S*)/(2*S*,4*S*,5*R*)]-*trans*-1,3-Bis(*tert*-butyl)-2-*tert*-butylimido-5-(4′-nitrophenyl)-2-oxo-2-osma(VI)imidazolidine-4-carboxylate (42): M.p. 86 °C (dec.). ^1H NMR (300 MHz, C_6D_6): δ = 0.98 (t, *J* = 7.2 Hz, 3 H), 1.22 (s, 9 H), 1.43 (s, 9 H), 1.56 (s, 9 H), 3.92 (q, *J* = 7.2 Hz, 2 H), 4.18 (d, *J* = 0.5 Hz, 1 H), 4.81 (s, 1 H), 7.87 (d, *J* = 7.5 Hz, 2 H), 7.88 (d, *J* = 7.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.27, 30.43, 31.31, 32.78, 60.97, 63.73, 64.98, 69.94, 80.73, 86.26, 123.68, 127.48, 127.79, 128.11, 154.67, 173.04 ppm. IR (KBr): $\tilde{\nu}$ = 2968, 2866, 1753, 1525, 1344, 1230, 1191, 1109, 872, 858 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 642 (20) $[M + 1]^+$, 627 (18), 569 (100), 513 (22), 457 (27), 191 (20), 57 (16). HRMS: calcd. for $C_{23}H_{38}N_4O_5{}^{188}Os$: 638.2401; found 638.2400.

Ethyl [(2*R*,4*S*,5*R*)/(2*S*,4*R*,5*S*)]-*trans*-1,3-Bis(*tert*-butyl)-2-*tert*-butylimido-5-(4′-nitrophenyl)-2-oxo-2-osma(VI)imidazolidine-4-carboxylate (43): M.p. 78 °C (dec.). ^1H NMR (300 MHz, C_6D_6): δ = 1.13 (t, *J* = 6.7 Hz, 3 H), 1.14 (s, 9 H), 1.20 (s, 9 H), 1.33 (s, 9 H), 4.09 (q, *J* = 7.2 Hz, 2 H), 4.18 (s, 1 H), 4.92 (s, 1 H), 6.95 (d, *J* = 8.6 Hz, 2 H), 7.88 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 14.24, 30.28, 31.64, 32.27, 53.25, 61.25, 64.25, 64.40, 83.27, 85.92, 123.12, 127.90, 128.02, 128.10, 153.56, 174.15 ppm. IR (KBr): $\tilde{\nu}$ = 3437, 2972, 2929, 1743, 1524, 1344, 1191, 1081, 881 cm^{-1}. MS (EI, eV): *m*/*z* (%) = 642 (11) $[M + 1]^+$, 569 (100), 513 (20), 457 (21), 191 (18), 57 (33). HRMS: calcd. for $C_{23}H_{38}N_4O_5{}^{188}Os$: 638.2401; found 638.2407.

Details of Competitive Diamination Reactions with 4 (Hammett Correlation): Competition experiments were conducted with 2.5 mmol each of the respective 4′-substituted cinnamate and ethyl cinnamate and 0.25 mmol of tris(imido) reagent **4**. Ferrocene was employed as internal standard and THF as solvent (5 mL). After a period of about five hours, the solvent was removed under reduced pressure and the crude reaction mixture was taken up in $[D_6]$benzene and immediately analysed by ^1H NMR spectroscopy. Conversion and relative product formation were calculated from the NMR spectroscopic data using the respective *dr* values as determined from the individual diaminations detailed above and the kinetic expression was calculated using the following Equation (1).

The final Hammett correlation as depicted in Figure 5 was obtained employing standard σ_x values.[34]

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