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Enantioselective Diamination of Alkenes by Use of a Bisimidoosmium Reagent with the Aid of Chiral Catalysts

Iriux Almodovar,[a][‡] Claas H. Hövelmann,[a] Jan Streuff,[a] Martin Nieger,[b] and Kilian Muñiz*[a]

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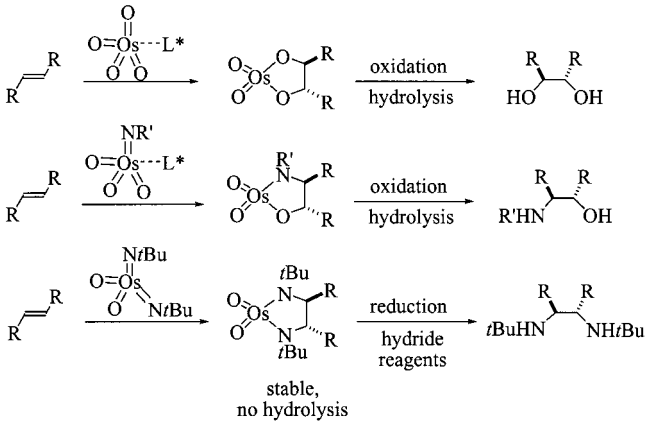
The development of a new method for the diamination of alkenes is reported. It is based on a reaction in the presence of stoichiometric or catalytic amounts of chiral auxiliaries, which permits the direct synthesis of enantiomerically enriched osmaimidazolidines. The combined application of a catalyst-directing oxazolidinone group and a titanium catalyst results in enantioselective alkene diamination with enantiomer ratios of up to 95:5. Absolute configurations of representative osmaimidazolidine products were established unambiguously by solid-state structure analyses.

Introduction

Catalytic enantioselective conversion of olefins into vicinal diols or amino alcohols is usually accomplished with the aid of osmium catalysis. Seminal investigation by Sharpless provided suitable conditions under which osmium tetroxide or related monoimidoosmium compounds catalyse these transformations in the presence of chiral cinchona alkaloid ligands L* (Scheme 1). In general, reoxidants such as NMO (*N*-methylmorpholine *N*-oxide) and $Fe[(CN)_6]^{3-}$ for osmium tetroxide regeneration have made asymmetric dihydroxylation[1] the most versatile means currently available for catalytic enantioselective oxidation of alkenes.[2] Alternatively, nitrenoids bearing acetyl, arylsulfonyl or carbamoyl substituents function both as reoxidant for osmium and as nitrogen source in related asymmetric aminohydroxylation processes[3,4] that provide enantiomerically enriched vicinal amino alcohols from alkenes.

Unfortunately, related diamination reactions do not follow these general paths. In order to generate a stable bisimido derivative, tertiary alkyl substituents at the imido ligand are required,[3] but these afford stable osmaimidazolidines as monomeric oxidation products that do not undergo hydrolytic cleavage.[5,6] Instead, strong hydride reducing agents are required to release the diamine product, making the reaction stoichiometric in osmium.[7,8] In addition, electronic saturation of the electrophilicity at the osmium centre in a bisimido osmium complex does not allow for coordination of chiral ligands, so enantioselectivity cannot be introduced in this way.[9] As a consequence, asymmetric diamination of alkenes based on chiral terpene auxiliaries attached to the substrate was developed (Scheme 2).[10,11]

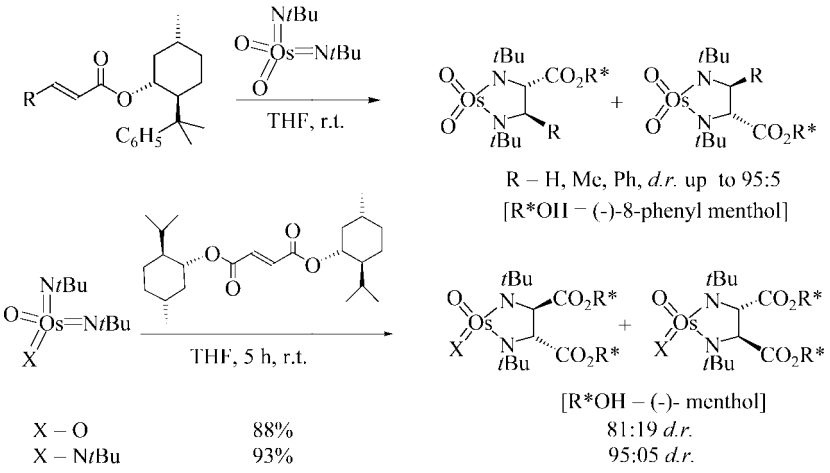


Scheme 1. Alkene oxidation with osmium(VIII) compounds: dihydroxylation, aminohydroxylation and diamination.

These approaches were found to give high general diastereoselectivities and allowed efficient subsequent preparation of enantiomerically pure derivatives.[12] Still, since chiral vicinal diamines constitute a versatile class of compounds in a variety of areas of modern chemistry,[13] a reaction catalytic in stereochemical information would obviously be more desirable.

Enantioselective homogeneous catalysis has come a long way over recent decades, to develop into the most versatile

[a] Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität,
Gerhard-Domagk-Str. 1, 53121 Bonn, Germany
Fax: +49-228-73-5813
E-mail: kilian.muniz@uni-bonn.de
[b] Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität,
Gerhard-Domagk-Str. 1, 53121 Bonn, Germany
E-mail: nieger@joyx.joensuu.fi
[‡] Permanent address: Departamento de Química Orgánica y Fisicoquímica
Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile
Casilla 233, Santiago 1, Chile



Scheme 2. Current state of asymmetric diamination of alkenes: diastereoselective reactions.

tool for the generation of enantiomerically pure compounds.[14] It generally employs the required stereochemical information attached to the chiral catalyst, which may then function through two complementary approaches: it may coordinate to one of the substrates, thereby creating a temporary stereochemical environment for efficient differentiation of two diastereotopic reaction sides during the subsequent functionalisation, or it may alternatively already incorporate the reaction partner either in covalent or coordinative manner and thus may dominate the reaction through efficient differentiation of the substrate's enantiotopic faces.

Results and Discussion

As a consequence of these developments, a complementary scenario for asymmetric alkene diamination – employing stoichiometric amounts of the diamination reagent and substoichiometric amounts of a chiral, non-racemic catalyst – was envisaged. To accomplish efficient enantiodiscrimination between the two enantiotopic faces of the olefin, there are two general ways in which the substrate may contain suitable functional groups for interaction with the catalyst. Here, the catalyst becomes attached either through efficient covalent coordination (Figure 1) or, alternatively, through temporary transformation after functional group reaction. Condensation and hydrolysis function through this approach, for example.

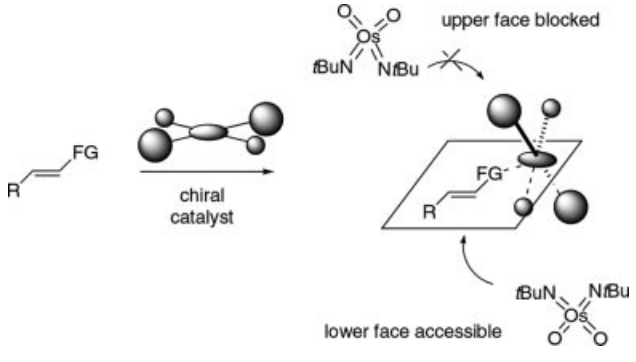
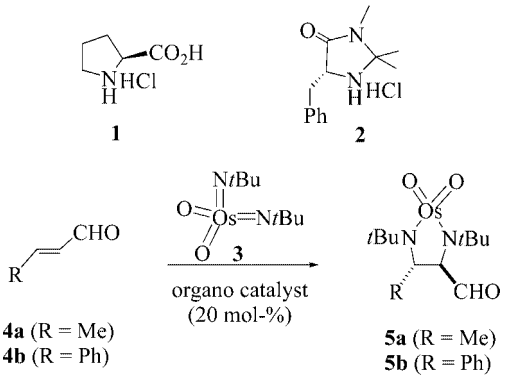


Figure 1. Schematic representation of stereodiscrimination in olefin diamination.

Diamination in the Presence of Organocatalysts

Recent advances in enantioselective catalysis have introduced organocatalysts capable of interacting with carbonyl groups in the substrate through formation of iminium or enamide functionalities.[15] An early application of this concept in enantioselective oxidation was achieved by Jørgensen, who reported an enone epoxidation.[16,17] Initial attempts were therefore carried out with α,β-unsaturated aldehydes as substrates and with the chiral organocatalysts proline (**1**) and **2**[18,19] (Scheme 3, Table 1).



Scheme 3. Diamination in the presence of **1** and **2**.

However, neither of the tested organocatalysts was able to induce an enantioselective reaction course. At a catalyst loading of 20 mol-%, proline had no beneficial influence on the formation of the corresponding diamination product. Chemical yields increased for reactions carried out in the presence of **2**, but no significant inductions were observed. In all cases dichloromethane turned out to be the best solvent (Entry 5). Reactions were finally performed in the presence of stoichiometric amounts of **2**, involving mixing of the α,β-unsaturated aldehyde and the MacMillan salt **2** in dichloromethane or in a methanol/THF mixture. After

Table 1. Diamination of **4a** and **4b** with the bisimido reagent **3** in the presence of organocatalysts **1** (20 mol-%) and **2**.

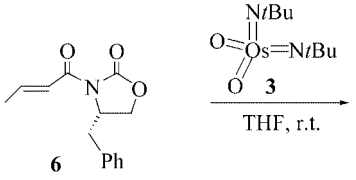
Entry	Substrate	Catalyst	Solvent	Product	Yield [%][a]	Enantiomeric excess [%][b]
1	**4a**	**1**	MeOH/THF	**5a**	75	0
2	**4b**	**1**	MeOH/THF	**5b**	62	3
3	**4a**	**2**	acetone	**5a**	81	2
4	**4a**	**2**	MeOH/THF	**5a**	95	2
5	**4a**	**2**	CH_2Cl_2	**5a**	79	8
6[c]	**4a**	**2**	CH_2Cl_2	**5a**	82	38
7[c]	**4a**	**2**	MeOH/THF	**5a**	76	43
8[c]	**4b**	**2**	MeOH/THF	**5b**	79	27

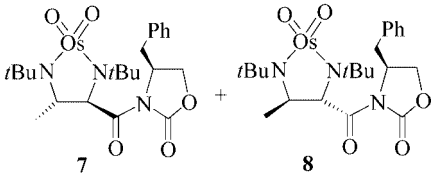
[a] Isolated yield after column chromatography. [b] Determined by chiral HPLC analysis. [c] Stoichiometric reactions.

the reaction mixture had been stirred for 1 h, the diaminating reagent was added in one portion and the reaction mixture was stirred for 8 h and worked up by addition of water. Osmaimidazolidine **5a** obtained in this reaction showed enantiomeric induction, albeit in the low degrees of 38 and 43% *ee*, respectively. Cinnamaldehyde **4b** gave less satisfactory results (Entry 8). These results suggest that the reaction cannot be accelerated sufficiently to proceed by the catalysed pathway in the presence of only a catalytic amount of **2**. Instead, direct reaction between the bisimidoosmium reagent **3** and aldehydes **4a/4b** is significantly faster than the enantioselective process.

Diamination with Transition Metal Catalysis

A second attempt, based on an observation made during the investigation into diastereoselective diamination of olefins, was thus undertaken. Here, the enantiopure (4*S*)-benzyl oxazolidinone **6** (Scheme 4) was investigated as chiral auxiliary, in accordance with the seminal work by Evans.[20,21]





diastereomeric ratio	
no additive:	44:56
$Ti(OiPr)_4$:	21:79
$Cl_2Ti(OiPr)_2$:	08:92

Scheme 4. Diamination of chiral olefin **6**: influence of the addition of titanium activators.

With the crotoyl substrate **6**, the reaction with **3** under standard diamination conditions gave a mixture of the two osmaimidazolidine products **7** and **8**, with only a slight preference for the latter (Scheme 4). More importantly, it gave only a low yield of 45% after the usual 12 hours and required 2 days reaction time in order to go to completion. The two diastereomeric products were purified by chromatography and separated by semipreparative HPLC. The absolute configuration of one of them was unambiguously determined by X-ray analysis (Figure 2). Its (S_{aux},4*R*,5*S*) configuration corresponds to osmaimidazolidine **8** as the major diastereoisomer.

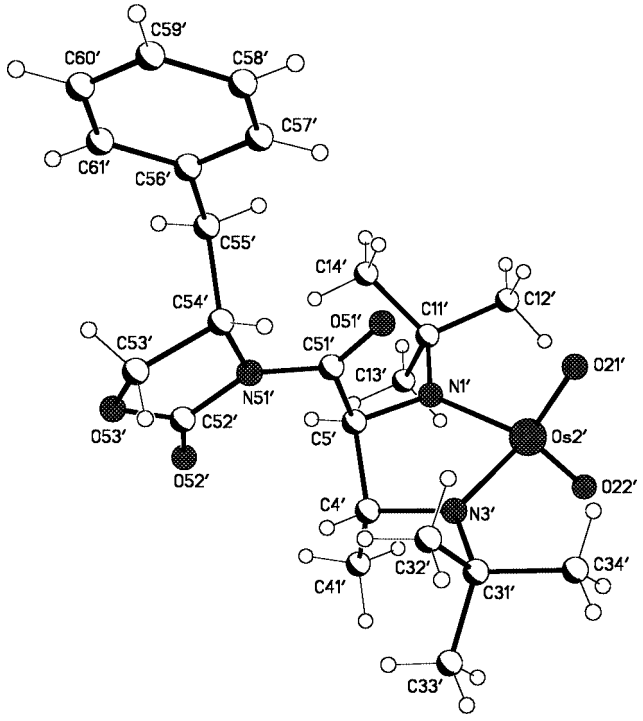
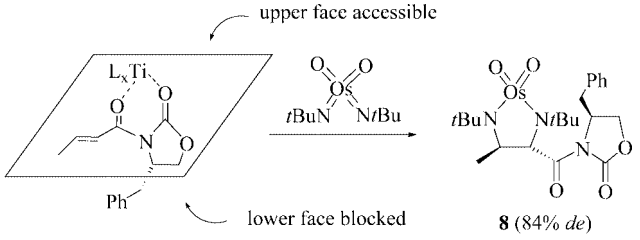


Figure 2. Solid-state structure of (S_{aux},4*R*,5*S*)-**8**. Selected bond lengths [Å] and angles [°]: N(1)–Os(2) 1.915(8), Os(2)–O(22) 1.714(7), Os(2)–O(21) 1.726(6), Os(2)–N(3) 1.844(8), N(3)–Os(2)–N(1) 81.6(3), O(2)–Os(2)–O(1) 118.1(3).

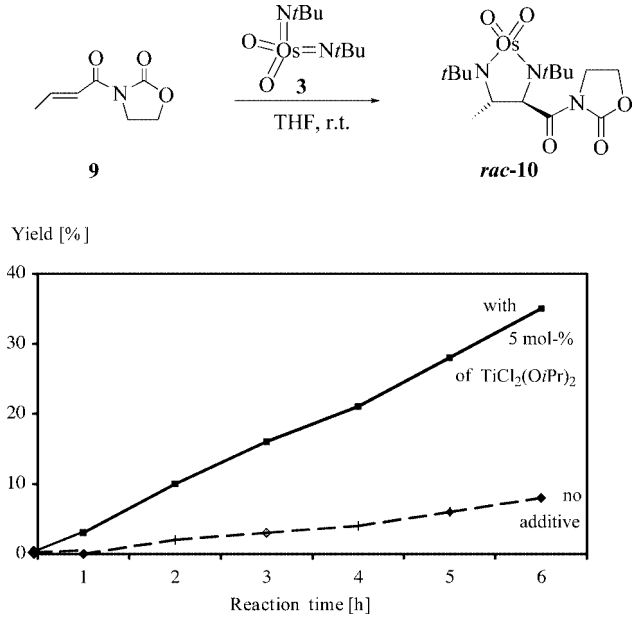
Apparently, the stereodiscrimination during direct diamination of **6** with **3** as reagent is not efficient. This should presumably be due to unrestricted rotation around the amide bond, resulting in two conformers favouring opposite diastereoselectivity with regard to the olefin faces. Hence, coordination of the two carbonyl functionalities to a transition metal should produce a highly organised transition state with one of the two diastereotopic faces of the olefin being efficiently blocked by the chiral auxiliary

(Scheme 5). Indeed, when the reaction was repeated in the presence of titanium complexes, significantly higher diastereomeric ratios were observed. For example, titanium tetraisopropoxide gave a *dr* of 79:21, while the mixed titanium complex $Cl_2Ti(OiPr)_2$ gave a 92:8 *dr* for **8**, which was isolated in 83% yield. Titanium tetrachloride gave an equally high diastereomeric ratio, albeit with significantly lower conversion. This is tentatively attributed to decomposition of the osmium reagent **3** in the presence of the rather acidic $TiCl_4$.



Scheme 5. Enhanced diastereoselectivity through metal complexation in the diamination of **6**.

More important was the observation that the initial diamination of **6** proceeded at an unexpectedly low rate, resulting in the development of the desired enantioselectively catalysed diamination of alkenes.[22] It was found that the achiral substrate **9** underwent diamination only very slowly in the presence of **3**, giving the expected product **10** in less than 7% yield after a total reaction time of 6 h. In contrast, addition of Lewis acidic titanium complexes produced a significant acceleration. In particular, addition of 5 mol-% of dichloro-bis(2-propoxy)titanium(IV) gave an increase in the yield to 37% after 6 h reaction time (Scheme 6).



Scheme 6. Diamination of **9**: influence of titanium additives.

This rate enhancement of diamination through activation of the carbonyl group in **9** suggested that an enantioselective reaction should be achievable through application of transition metal complexes bearing defined stereochemical information. In order to achieve this type of transformation, various chiral metal complexes were screened. Clearly,

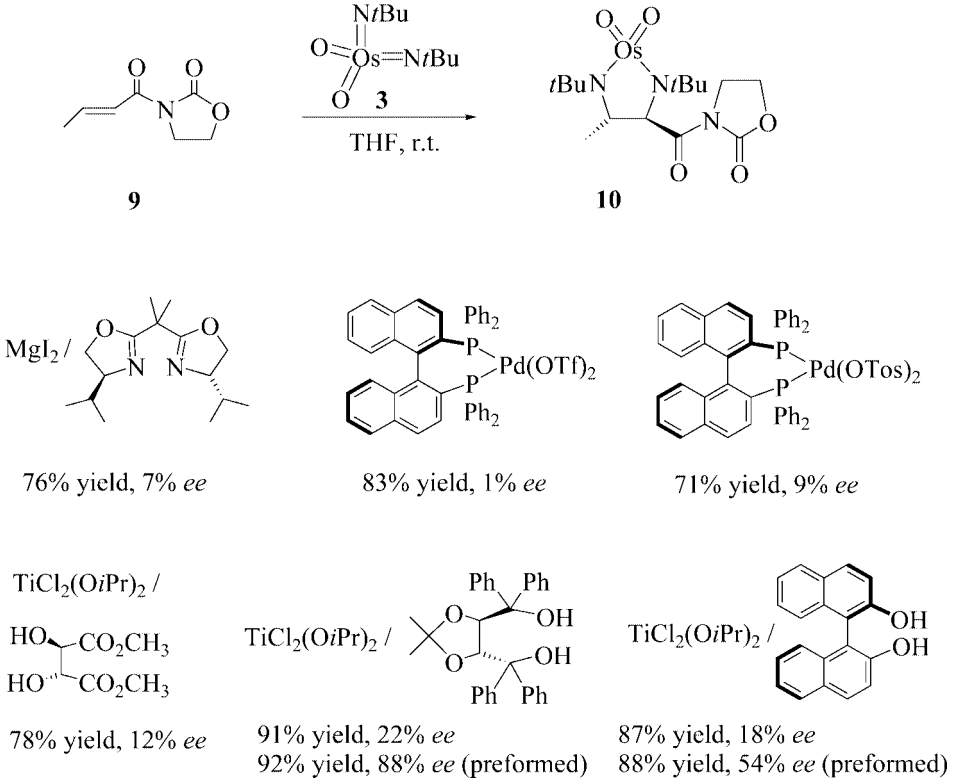
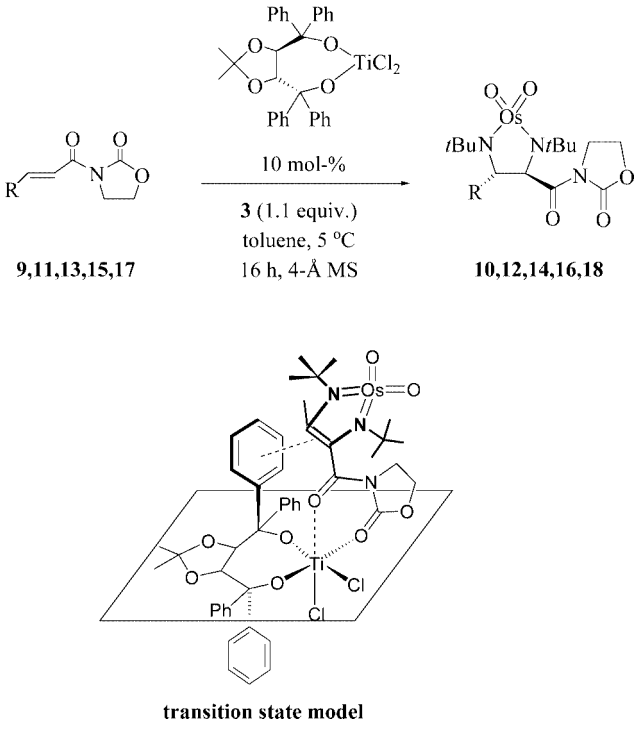


Figure 3. Screening of catalyst combinations for enantioselective diamination of **9**.

oxidation state incompatibility was of major concern, due to the use of the imidoosmium reagent **3** in its highest oxidation state. As a consequence, the successful copper/bisoxazoline motif[23] could not be employed. A review of the literature for previous investigations into the coexistence of related osmium tetroxide and metal ions provided surprisingly few data: it appears that this subject remains limited to the seminal work by Krief on the reversible oxo transfer between osmium and selenium.[24] In the current case it became obvious that usually successful catalysts such as copper and tin readily reacted with **3** and led to partial or complete degradation of the osmium oxidant. Hence, priority was given to metal candidates in their highest oxidation states.

Of the metal/ligand combinations screened, bisoxazolidine-magnesium(II)[25] and BINAP-palladium salts[26] gave only very low enantiomeric excesses (Figure 3). More importantly, only very low rate increases were estimated for these reactions. Titanium(IV) catalysts were thus investigated in detail. While dimethyl tartrate was rather inefficient, BINOL- and TADDOL-derived[27] catalysts formed in situ showed promising behaviour. For these catalysts, higher enantiomeric excesses were obtained when preformed complexes were employed. Under these conditions, TADDOL proved superior to BINOL, especially with regard to reproducibility. The Ti-TADDOL combination was therefore employed as catalyst for subsequent studies on the generality of enantioselective diamination of olefins.

Optimum reaction conditions consisted of mixing of a toluene solution of 10 mol-% of preformed catalyst[28] under argon with the substrate and cooling it to 5 °C. At this point, the reagent **3** was added and the reaction mixture was stirred for 16 h at 5 °C. This procedure ensures enantiomeric induction takes place smoothly for a variety of substrates (Scheme 7, Table 2).



Scheme 7. Enantioselective diamination.

As well as substrate **9**, olefins **11**, **13**, **15** and **17** were all converted into the corresponding osmaimidazolidines with high enantiomeric excesses and in very good overall yields.

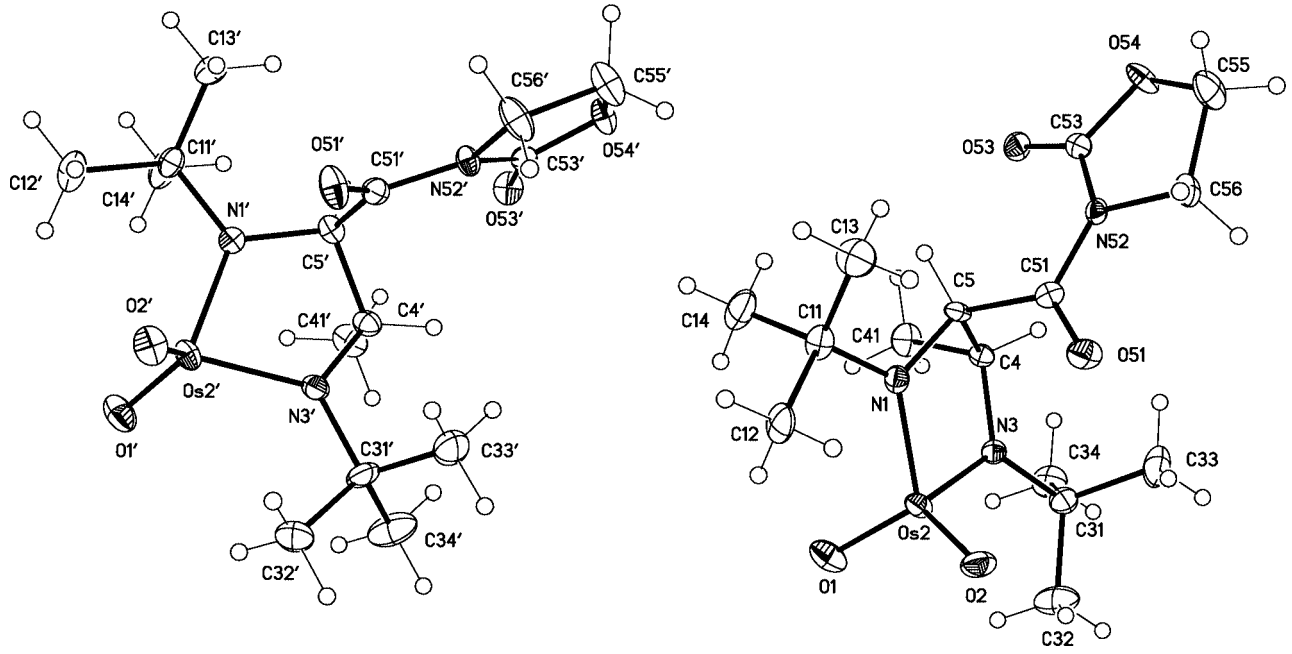


Figure 4. Solid-state structures for diamination product (**+**)-**10**. The two independent molecules from the asymmetric unit are shown. Selected bond lengths [Å] and angles [°]: N(1)–Os(2) 1.886(4), Os(2)–O(2) 1.723(3), Os(2)–O(1) 1.728(3), Os(2)–N(3) 1.885(3), N(3)–Os(2)–N(1) 81.93(14), O(2)–Os(2)–O(1) 120.14(13) [N(1′)-Os(2′) 1.892(3), Os(2′)–O(2′) 1.730(3), Os(2′)–O(1′) 1.715(2), Os(2′)–N(3′) 1.897(4), N(3′)-Os(2′)-N(1) 81.55(14), O(2′)-Os(2′)–O(1′) 119.58(13)].

Table 2. Enantioselective diamination of olefins with (*R*,*R*)-Ti-TADDOLate catalysis.

Entry	Substrate (R)	Product	Yield [%][a]	*ee* [%][b]
1[c]	**9** (CH_3)	(+)-**10**	91	22
2	**9** (CH_3)	(+)-**10**	92	88
3[d]	**9** (CH_3)	(–)-**10**	90	86
4[e]	**9** (CH_3)	(–)-**10**	81	90
5	**11** (H)	(+)-**12**	97	82
6	**13** (*n*-Pr)	(+)-**14**	91	86
7	**15** (C_6H_5)	(+)-**16**	95	78
8	**17** (CO_2CH_3)	(–)-**18**	83	90

[a] Isolated yield after workup and column chromatography. [b] Determined on a Chiralpak AD column (see Experimental Section for details). [c] With catalyst generated in situ. [d] With the enantiomeric (*S*,*S*)-TADDOL ligand. [e] With an equimolar amount of (*S*,*S*)-TADDOL-Ti complex.

An initial diamination of **9** in the presence of 10 mol-% catalyst gave 88% *ee* with (*R*,*R*)-TADDOL as ligand and 86% *ee* with (*S*,*S*)-TADDOL. A reaction stoichiometric in chiral metal complex yielded 90% *ee* (Table 2, Entry 4). This result confirms that the observed induction and the amount of catalyst loading is sufficient to reach a maximum of induction and reaction rate. Obviously, the presence of 10 mol-% of catalyst makes the uncatalysed background reaction the kinetically disfavoured pathway. This holds true for several related substrates, which all undergo diamination with *ee* values in the 78 to 90% range.

The major enantiomer **(+)-10** was crystallised to enantiopurity and subjected to X-ray analysis (Figure 4). Its absolute configuration was unambiguously established from this analysis to be (*R*,*S*) [Flack's parameter $X^{[29]}$ = –0.003(5)]. This stereochemical reaction outcome is the result of diamination of **9** from the *Re*,*Si* face as depicted in Scheme 7.[30] This stereochemical discrimination model was established by Seebach for related Ti-TADDOLate-catalysed reactions and also dominates the current olefin functionalisation process: under the assumption of a concerted [3+2] addition between **9** and **3**,[31] the latter behaves like the corresponding organic 4π-components in related cycloaddition reactions.

Conclusions

We have described an investigation toward the first enantioselective diamination of alkenes that is catalytic in chiral information. These reactions are based on the use of a stereochemically defined titanium catalyst that makes the enantioselective pathway the kinetically preferred one over the achiral background reaction. As such, an important step forward in the development of alkene diamination has been made. Current efforts to make these reactions catalytic both in metal and in stereochemical information are continuing.[34]

Experimental Section

General Remarks: Organocatalyst **2** was purchased from Aldrich. Osmium reagent **3** was synthesised by a literature procedure.[6] The following starting materials are known compounds described previously: **6**, **9**, **11**, **13**, **15**, **17**.[32,33] 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 were 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 on a Perkin–Elmer 341 polarimeter. Concentrations are given in g/100 mL as dichloromethane solutions. NMR spectra were recorded on a Bruker DPX 300 MHz and Bruker DRX 500 MHz spectrometer. 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 on a Nicolet Magna 550 FT-IR spectrometer. MS and HRMS experiments, and elemental analysis were performed on a Kratos MS 50 and an Elementar Analysensystem Vario EL instrument, respectively, in the service centres at the Kekulé Department, Bonn.

General Procedure A for Diamination of Achiral Olefins with Osmium Imido Complex 3: Solid bisimido-osmium complex **3** was added in one portion to a solution of the appropriate olefin (1.2 mmol) in freshly distilled THF 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 was analysed by NMR spectroscopy. The pure product was obtained by column chromatography as indicated for the individual compound.

***trans*-1,3-Bis(*tert*-butyl)-5-formyl-4-methyl-2-osma(VI)imidazolidine 2,2-Dioxide (5a):** This compound was obtained by General Procedure A as described above, from crotonaldehyde (84 mg, 1.2 mmol) and complex **3** (364 mg, 1.0 mmol) in THF (5 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/diethyl ether, 10:1, v/v) gave the title compound as a dark red solid (370 mg, 0.85 mmol, 85%). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.19 (d, J = 6.2 Hz, 3 H), 1.38 (s, 9 H), 1.40 (s, 9 H), 3.81 (d, J = 3.4 Hz, 1 H), 4.7 (q, J = 6.2 Hz, 1 H), 9.18 (d, J = 3.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 23.65, 30.37, 30.50, 67.33, 67.55, 73.49, 86.10, 202.72 ppm. IR (KBr): $\tilde{\nu}$ = 891, 1192, 1367, 1729, 2974, 3417 cm^{-1}. MS (EI, eV): *m*/*z* (%): 436 [M]$^+$ (27), 407 (88), 351 (98), 310 (12), 295 (100), 265 (11), 84 (13), 57 (31). HRMS: calcd. for $C_{12}H_{24}N_2O_3{}^{188}Os$: 432.1346; found 432.1366. HPLC: Chiralcel OG, *n*-hexane/propan-2-ol, 95:5 (v/v), 0.5 mL min^{-1}. Retention times: 34.1 and 35.6 min.

***trans*-1,3-Bis(*tert*-butyl)-5-formyl-4-phenyl-2-osma(VI)imidazolidine 2,2-Dioxide (5b):** This compound was obtained by General Procedure A as described above from cinnamaldehyde (158 mg, 1.2 mmol) and complex **2** (364 mg, 1.0 mmol) in THF (5 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/diethyl ether, 10:1, v/v) gave the title compound as a dark red solid (456 mg, 0.92 mmol, 92%). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.94 (s, 9 H), 1.09 (s, 9 H), 3.86 (d, J = 3.0 Hz, 1 H), 4.89 (s, 1 H), 6.94–7.07 (m, 5 H), 9.26 (d, J = 3.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 30.12, 30.46, 66.89, 67.88, 80.57, 89.20, 126.85, 128.08, 128.86, 144.82, 201.47 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 1731, 1464, 1366, 1184, 897 cm^{-1}. MS (EI, eV): *m*/*z* (%): 469 [M – CHO]$^+$ (51), 413 (72), 357 (64), 146 (43), 57 (100). HRMS: calcd. for $C_{17}H_{26}N_2O_3{}^{188}Os$: 494.1499; found 494.1495. $C_{17}H_{26}N_2O_3Os$ (498,16): C 41.11, H 5.28, N 5.64; found C 41.00, H 5.71, N 5.67. HPLC: Chiralcel OG, *n*-hexane/propan-2-ol, 95:5 (v/v), 0.5 mL min^{-1}. Retention times: 27.0 and 29.8 min.

Diamination of 6: This was carried out as described in General Procedure A with a solution of **3** (183 mg, 0.5 mmol) in freshly distilled THF (5 mL). The resulting red solution was stirred at room temp. for 12 h, during which it turned dark red. The solvent was removed under reduced pressure to leave a red-brown oil, which was analysed by ^{1}H NMR and then purified by column chromatography on silica gel (hexanes/ethyl acetate 3:1 *v*/*v*). After evaporation of the solvents under reduced pressure, the pure mixture of the two diastereomers (137 mg, 0.22 mmol, 45% yield) was separated by semipreparative HPLC (Knauer Eurospher 100CN, *t*BuOCH$_3$/*n*-hexane, 60:40, v/v, 16 mL min^{-1}, 254 nm). Retention times: 10.1 min for **8** and 12.0 min for **7**. Analytical HPLC: Knauer Eurospher 100 CN, 254 nm, *n*-hexane/*t*BuOCH$_3$, 40:60 (v/v), 1.0 mL min^{-1}, retention times 8.0 min [(–)-**8**], 8.7 min [(+)-**7**].

(4*S*,5*R*,5′*S*)-5-[(5′-Benzyl-2′-oxo-1′,3′-oxazolidin-3′-yl)carbonyl]-1,3-bis(*tert*-butyl)-4-methylosma(VI)imidazolidine 2,2-Dioxide (7): ^{1}H NMR (300 MHz, C_6D_6): δ = 1.20 (s, 9 H), 1.30 (s, 9 H), 1.35 (d, *J* = 6.0 Hz, 3 H), 2.08 (dd, *J* = 11.0, 13.0 Hz, 1 H), 3.10–3.18 (m, 2 H), 3.49 (dd, *J* = 3.0, 9.2 Hz, 1 H), 4.04–4.13 (m, 2 H), 5.46 (s, 1 H), 6.79–6.83 (m, 2 H), 6.99–7.04 (m, 3 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 24.52, 30.23, 30.88, 31.90, 38.12, 55.58, 66.35, 66.49, 74.63, 80.14, 127.47, 129.08, 129.47, 135.46, 153.79, 172.32 ppm. IR (KBr): $\tilde{\nu}$ = 891, 1193, 1219, 1236, 1371, 1711, 1774, 2972, 3417, 3477 cm^{-1}. MS (EI, eV): *m*/*z* (%):610 [*M*]$^+$ (100), 596 (12), 497 (32), 440 (41), 407 (74), 351 (100), 295 (71), 84 (17), 57 (54). HRMS: calcd. for $C_{22}H_{33}N_3O_5{}^{188}Os$: 607.1979; found 607.1980.

(4*R*,5*S*,5′*S*)-5-[(5′-Benzyl-2′-oxo-1′,3′-oxazolidin-3′-yl)carbonyl]-1,3-bis(*tert*-butyl)-4-methylosma(VI)imidazolidine 2,2-Dioxide (8): ^{1}H NMR (300 MHz, C_6D_6): δ = 1.22 (s, 9 H), 1.24 (d, *J* = 6.0 Hz, 9 H), 1.29 (s, 9 H), 2.04 (dd, *J* = 10.3, 13.0 Hz, 1 H), 3.09 (dd, *J* = 2.9, 13.0 Hz, 1 H), 3.17 (dd, *J* = 8.6, 0.9 Hz, 1 H), 3.49 (dd, *J* = 2.9, 9.2 Hz, 1 H), 3.98 (q, *J* = 6.0 Hz, 1 H), 4.04–4.13 (m, 1 H), 5.54 (s, 1 H), 6.77–6.81 (m, 2 H), 7.01–7.04 (m, 3 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 24.57, 30.35, 30.75, 31.89, 37.55, 66.24, 66.53, 74.90, 80.37, 127.44, 129.04, 129.55, 135.42, 153.42, 172.51 ppm. IR (KBr): $\tilde{\nu}$ = 893, 1105, 1198, 1234, 1369, 1387, 1711, 1774, 2966, 3417, 3464 cm^{-1}. MS (EI, eV): *m*/*z* (%): 610 [*M*]$^+$ (100), 596 (17), 497 (21), 440 (38), 407 (66), 351 (100), 295 (96), 84 (11), 57 (43). HRMS: calcd. for $C_{22}H_{33}N_3O_5{}^{188}Os$: 607.1979; found 607.1985.

General Procedure B for Enantioselective Diamination: A quantity of the olefin (0.25 mmol) was dissolved in freshly distilled toluene under argon. The preformed Ti catalyst was added as a stock solution in toluene (1 M, 0.025 mL)[27,28] and the resulting solution was stirred at room temperature. Molecular sieves (ca. 1 g) were introduced and the reaction mixture was cooled to 5 °C before addition of the bisimido osmium compound **3** (90 mg, 0.11 mmol). The reaction mixture was stirred for a period of 16 h before being placed directly on top of a small pad of silica. The product was obtained as the last fraction on changing to ethyl acetate as eluent.

[(4*S*/5*R*)]-1,3-Bis(*tert*-butyl)-4-methyl-5-(2′-oxo-1′,3′-oxazolidin-3′-ylcarbonyl)osma(VI)imidazolidine 2,2-Dioxide (10): This compound was obtained as described in General Procedure B above, with alkene **9** (39 mg) . Yield: 120 mg (92%) of a deep purple solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.23 (d, *J* = 6.0 Hz, 3 H), 1.30 (s, 9 H), 1.32 (s, 9 H), 3.80–3.94 (m, 2 H), 3.96–4.07 (m, 2 H), 4.43 (q, *J* = 6.0 Hz, 1 H), 5.32 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.28, 30.17, 30.65, 42.79, 62.73, 67.06, 67.25, 74.56, 79.90, 153.85, 172.28 ppm. IR (KBr): $\tilde{\nu}$ = 899, 1194, 1221, 1369, 1390, 1709, 1772, 2926, 2968 cm^{-1}. MS (EI, eV): *m*/*z* (%): 521 [*M*]$^+$ (14), 506 (24), 407 (91), 351 (100), 295 (71), 84 (22), 57 (37). HRMS: Calcd. for $C_{15}H_{27}N_3O_5{}^{188}Os$: 517.1510; found 517.1514. HPLC: Chiralpak AD, *n*-hexane/propan-2-ol, 90:10 (v/v), 0.7 mL min^{-1}. Retention times: 24.8 and 28.2 min.

[(5*R*)]-1,3-Bis(*tert*-butyl)-5-(2′-oxo-1′,3′-oxazolidin-3′-ylcarbonyl)osma(VI)imidazolidine 2,2-Dioxide (12): This compound was obtained as described in General Procedure B above, with alkene **11** (35 mg). Yield: 123 mg (97%) of a purple solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.32 (s, 9 H), 1.33 (s, 9 H), 3.70 (d, *J* = 13.1 Hz, 1 H), 3.94 (dt, *J* = 4.2, 8.1 Hz, 2 H), 4.09 (dd, *J* = 6.8, 13.1 Hz, 1 H), 4.44 (t, *J* = 8.1 Hz, 2 H), 5.69 (d, *J* = 6.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.47, 30.10, 42.79, 62.73, 67.22, 67.34, 68.57, 73.11, 154.22, 172.98 ppm. IR (KBr): $\tilde{\nu}$ = 904, 1122, 1198, 1228, 1257, 1371, 1398, 1709, 1774, 2972 cm^{-1}. MS (E.I.): 507 [*M*]$^+$, 492 (3), 393 (100), 337 (41), 281 (62), 149 (33), 57 (61). HRMS: Calcd. for $C_{14}H_{25}N_3O_5{}^{188}Os$: 503.1353; found: 503.1353. HPLC: Chiralpak AD, *n*-hexane/propan-2-ol 90:10 (v/v), 0.7 mL min^{-1}. Retention times: 45.6 and 69.4 min.

[(4*S*/5*R*)]-1,3-Bis(*tert*-butyl)-5-(2′-oxo-1′,3′-oxazolidin-3′-yl-carbonyl)-4-propylosma(VI)imidazolidine 2,2-Dioxide (14): This compound was obtained as described in General Procedure B as described above with 45 mg of alkene **13**. Yield: 125 mg (91%) of a deep red solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.82 (t, *J* = 7.0 Hz, 3 H), 1.27–1.88 (m, 4 H), 1.28 (s, 9 H), 1.29 (s, 9 H), 3.75 (d, dd, *J* = 2.0, 9.8 Hz, 1 H), 3.80–3.88 (m, 1 H), 3.91–3.98 (m, 1 H), 4.36–4.41 (m, 2 H), 5.62 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.27, 19.79, 30.27, 30.70, 40.52, 43.02, 62.55, 67.26, 67.36, 76.18, 79.24, 153.45, 172.96 ppm. IR (KBr): $\tilde{\nu}$ = 891, 1115, 1192, 1221, 1250, 1369, 1386, 1701, 1772, 1970 cm^{-1}. MS (E.I.): 549 [*M*],$^+$ 534 (21), 450 (38), 435 (100), 379 (89), 323 (41), 149 (19), 57 (67). HRMS: Calcd. for $C_{17}H_{31}N_3O_5{}^{188}Os$: 545.1823; found 545.1804. HPLC: Chiralpak AD, *n*-hexane/propan-2-ol 90:10 (v/v), 0.7 mL min^{-1}. Retention times: 33.8 and 36.1 min.

[(4*S*/5*R*)]-1,3-Bis(*tert*-butyl)-5-(2′-oxo-1′,3′-oxazolidin-3′-ylcarbonyl)-4-phenylosma(VI)imidazolidine 2,2-Dioxide (16): This compound was obtained as described in General Procedure B above, with alkene **15** (54 mg). Yield: 138 mg (95%) of a deep red-to-purple solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.17 (s, 9 H), 1.24 (s, 9 H), 3.94–4.01 (m, 2 H), 4.44–4.51 (m, 2 H), 4.91 (s, 1 H), 5.74 (s, 1 H), 7.16–7.29 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.12, 30.72, 43.03, 62.66, 67.34, 68.08, 81.50, 81.62, 127.08, 127.86, 128.35, 144.20, 153.48, 172.66 ppm. IR (KBr): $\tilde{\nu}$ = 710, 758, 901, 1043, 1119, 1194, 1223, 1371, 1396, 1709, 1772, 2976 cm^{-1}. MS (E.I.): 583 [*M* + 1]$^+$, 568 (5), 469 (57), 413 (71), 357 (43), 146 (50), 1044 (36), 57 (100). HRMS: Calcd. for $C_{20}H_{29}N_3O_5{}^{188}Os$: 579.1666; found 579.1669. HPLC: Chiralpak AD, *n*-hexane/ethanol, 90:10 (v/v), 1.0 mL min^{-1}. Retention times: 10.6 and 12.3 min.

[(4*R*/5*R*)]-1,3-Bis(*tert*-butyl)-4-methyloxycarbonyl-5-(2′-oxo-1′,3′-oxazolidin-3′-ylcarbonyl)osma(VI)imidazolidine 2,2-Dioxide (18): This compound was obtained as described in General Procedure B above, with alkene **17** (50 mg). Yield: 117 mg (83%) of a deep red solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (s, 9 H), 1.30 (s, 9 H), 3.67 (s, 3 H), 3.86–3.99 (m, 2 H), 4.39 (s, 1 H), 4.45 (t, *J* = 8.1 Hz, 2 H), 5.89 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.91, 30.02, 42.80. 52.63, 62.66, 67.20, 67.33, 77.84, 80.08, 153.48, 171.38, 171.44 ppm. IR (KBr): $\tilde{\nu}$ = 910, 1124, 1196, 1211, 1254, 1373, 1398, 1707, 1770, 2978 cm^{-1}. MS (E.I.): 565 [*M* + 1]$^+$ (33), 437 (41), 393 (100), 337 (22), 281 (13), 149 (30), 57 (78). HRMS: Calcd. for $C_{16}H_{27}N_3O_7{}^{188}Os$: 561.1408; found 561.1414. HPLC: Chiralpak AD, *n*-hexane/ethanol, 90:10 (v/v), 0.5 mL min^{-1}. Retention times: 70.4 and 81.8 min.

X-ray Structure Analyses: Data for crystal structure analysis were measured on a Nonius KappaCCD diffractometer. **8:**

$C_{22}H_{33}N_3O_5Os$: Pink crystals, crystal dimensions $0.15 \times 0.20 \times 0.25$ mm; M = 609.71; triclinic, space group p1 (No. 1), a = 8.9746(2), b = 11.1862(2), c = 13.5883(3) Å, α = 98.598(1)°, β = 104.037(1)°, γ = 108.466(1)°, V = 1216.72(4) Å^3, Z = 2, μ(Mo-K_α) = 5.276 mm^{-1}, T = 123(2) K, F(000) = 604. 17992 reflection up to $2\theta_{max.}$ = 55° were measured on a Nonius KappaCCD diffractometer with Mo-K_α radiation, 10274 of which were independent and used for all calculations. The structure was solved by direct methods and refined to F^2 anisotropically, the H atoms were refined with a riding model. The final quality coefficient $wR_2(F^2)$ for all data was 0.0617, with a conventional R(F) = 0.0294 for 559 parameters and 3 restraints. The absolute configuration was determined by refinement of Flack's x parameter, x = –0.012(6). An empirical absorption correction was applied.

Compound (+)-10: $C_{15}H_{27}N_3O_5Os$, monoclinic, $P2(1)$ (No. 4), a = 10.8391(2), b = 14.8658(2), c = 11.5981(2) Å, β = 99.432(1)°, V = 1843.56(5) Å^3, Z = 4, T = 123 K, μ(Mo-K_α) = 6.945 mm^{-1}, 19723 reflections, 8200 unique reflections ($2\theta_{max}$ = 50°), R_1 = 0.0206 [$I > 2\sigma(I)$], wR_2 = 0.0421 (all data), 433 parameters and 1 restraint. Empirical absorption correction was applied.

CCDC-270625 (for **8**) and -260572 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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