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Synthesis, structure determination and chemoselective catalytic studies of amino acids complexes of osmium(II)

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The two new half sandwich amino acids complexes of osmium, i.e. [Os(η6-*p*-cymene)(κ1-*N*-(rac)-phenylglycine methylester)Cl_2] (A) and [Os(η6-*p*-cymene)(κ1-*N*,*N*′-(*S*)-phenylalanineamido)Cl] (B) have been synthesized and employed for chemoselective reduction of ketones (nine α,β-unsaturated ketones and three saturated ketones). The complexes were characterized by spectroscopic as well as analytical methods; their solid structures were confirmed by single-crystal X-ray analysis. Both of the osmium complexes catalyze the reduction of α,β-unsaturated ketones to saturated ketones via isomerization of the initially produced allylic alcohols. The reducible substrates were studied to obtain information on the steric and electronic factors which may affect the interaction of the substrate with the metal center and, thus, control the selectivity of the hydrogen-transfer reductions. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: osmium; X-ray studies; N ligands; amino acids; half sandwich complexes

Introduction

Transition metals such as Rh, Pd, Pt and Ru have been extensively used as heterogeneous catalysts[1,2] for various transformations of molecules. A great number of transition metal complexes have been prepared and used as homogeneous catalysts,[3,4] because they are considered as an intermediate of metal-catalyzed reactions.

In general, not much is known about the chemistry, especially the chemoselective catalytic activity, of osmium arene complexes compared with those of iron and ruthenium, as evidenced by literature. Ruthenium and platinum complexes containing chelating *N*,*N*-heterocyclic ligands, for example phenanthroline (phen), bipyridine (bipy) and phenylazo-pyridine (azpy), have been extensively studied, and some have been reported to show anticancer activity as well.[5–7]

The extensive use of amino acids and their derivatives as ligands is a well-defined topic in organometallic chemistry.[8] Metal complexes involving amino acid-type ligands have applications mainly in bio-inorganic chemistry, for example in the synthesis of peptides[9] or bio-inorganic models.[10]

Out of various reducible substrates of much importance, α,β-unsaturated ketones are those containing both a carbonyl group as well as C=C bond. The ability to reduce only one group (especially the former) while leaving the other one unaffected is a difficult job in organic synthesis, predominantly for the formation of pharmaceutical and agrochemical products. The transfer hydrogenation of α,β-unsaturated ketones in the presence of alcohols is efficiently catalyzed by a limited number of transition-metal complexes with Zr, Hf, Ru, Os and Ir.[11] An even smaller number of metal complexes with Zr, Hf or Ir, are known to carry out the chemoselective catalytic reduction of the C=O group, which is difficult to reduce as compared with the double bond.[12]

In the present study, we illustrate the synthesis, characterization, spectroscopic and X-ray structure analysis as well as chemoselective catalytic hydrogen transfer ability of two new half-sandwich osmium(II) complexes obtained using (*R*)-phenylglycine methyl ester (**L1**) and (*S*)-phenylalanineamide (**L2**) as ligands. Studies of the anticancer activity and further catalytic behavior of the reported complexes is underway in our laboratories.

Experimental

General methods

All of the reactions were performed under an atmosphere of dry nitrogen, using standard Schlenk techniques. Solvents were dried prior to use and stored over molecular sieves and under nitrogen. ^{1}H NMR spectra were obtained at 300 K on a Bruker 300 FT spectrometer, using $SiMe_4$ as internal standard. Infrared spectra were recorded with a Nicolet 5700 FT-IR spectrophotometer in the range 4000–400 cm^{-1}. Elemental analysis (C, H, N) was performed using a Flash model EA 1112 analyzer. The catalytic reactions were monitored using GLC on a Perkin-Elmer Sigma 3B gas chromatograph using either a Supelcowax 10 wide-bore capillary column (30 m × 0.75 mm i.d.) or a CP-Si14 CB widebore capillary column (25 m × 0.53 mm i.d.). Alternatively, the reaction products were identified by GC-MS using a Hewlett-Packard 5971

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A mass detector coupled with a 589 011 gas chromatograph on an SP255 capillary column (25 m × 3 mm). The hydrochloride forms of enantiomerically pure (*R*)-phenylglycine methylester (L1•HCl) and *S*-phenylalanine amide (HL2•HCl) were purchased from Aldrich, while $[Os(p\text{-cymene})Cl_2]_2$ was synthesized following a previously reported method.[13] Acetophenone (Aldrich) and cyclohexanone (Fluka) were utilized as received.

Preparation of the Os(II) Complexes

[Os(η6-*p*-cymene) (κ1-*N*-L1)Cl_2] (A)

Aliquots of 198 mg (0.9 mmol) of L1•HCl and 100 mg (0.9 mmol) of *t*-BuOK were dissolved in 30 ml of ethanol at room temperature; *n*-pentane was added and KCl was filtered off. A chloroform solution (15 ml) of $[Os(p\text{-cymene})Cl_2]_2$ (475 mg, 0.5 mmol) was then added and the resulting dark brown solution was put in an ultrasonic bath at room temperature for 1 h. A brown solid precipitated. This was filtered off, washed with diethyl ether and dried in vacuum. A further crop of solid was recovered from the refrigerated mother liquor. Brown crystals for X-ray analysis were obtained following their re-crystallization in ethanol. Yield: 298 mg (79%). M.p.: 188–200 °C. Anal. calcd for $C_{19}H_{23}Cl_2\text{-}NO_2Os$: C, 40.71; H, 4.50; N, 2.50%. Found: C, 40.47; H, 4.59; N, 2.66%. ^{1}H NMR ($CDCl_3$): d 1.29 (d, 3H, *p*-cymene, $^3J_{HH}$ = 7 Hz), 1.35 (d, 3H, *p*-cymene, $^3J_{HH}$ = 7 Hz), 2.18 [s, ^{1}H, H(Ph)NH_2], 2.27(s, 3H, *p*-cymene), 3.10 (m, ^{1}H, NH), 2.91 (m, ^{1}H, *p*-cymene), 3.75 (s, 3H, (O)OCH_3), 5.26(d, ^{1}H, *p*-cymene, $^3J_{HH}$ = 6 Hz), 5.31 (d, ^{1}H, *p*-cymene, $^3J_{HH}$ = 6 Hz), 5.45 (m, 2H, *p*-cymene), 7.40 (m, 5H, Ph), 7.69 (m, ^{1}H, NH). IR: 3274–3221–3149 m(NH_2), 1739m(C═O ester), 1258 m(C═O ester).

[Os(η6-*p*-cymene)(κ2-*N*,*N*′-L2)Cl]•1/2H_2O (B)

Aliquots of 130 mg (0.6 mmol) of HL2•HCl and 67 mg (0.6 mmol) of *t*-BuOK were dissolved in 30 ml of ethanol. A chloroform solution (15 ml) of $[Os(p\text{-cymene})\text{-}Cl_2]_2$ (252 mg, 0.3 mmol) was then added and the resulting brownish solution was agitated in an ultrasonicator at room temperature for 1 h. The solvents were then removed in vacuum and the residue was treated with chloroform, filtering the KCl off. The remaining light brown solution was refrigerated at 5 °C, obtaining brown prismatic crystals. After filtration, a further yield of solid (orange powder) was obtained by treating the mother liquor with diethyl ether. Yield: 262 mg (75%). M.p.: 241–245 °C. Anal. calcd for $C_{19}H_{25}ClN_2OOs.1/2H_2O$: C, 42.89; H, 4.93; N, 5.26%. Found: C, 42.65; H, 4.74; N, 5.41% ^{1}H NMR (CD_3OD): major diastereomer d 1.25 (d, 3H, *p*-cymene, $^3J_{HH}$ = 7 Hz), 1.34 (d, 3H, *p*-cymene, $^3J_{HH}$ = 7 Hz), 2.08 (sbr, ^{1}H, NH), 2.11 (s, 3H, *p*-cymene), 2.44 (m, 2H, CH_2), 2.73 (m, ^{1}H, *p*-cymene), 3.10 [dd, ^{1}H, CH(Bz)NH_2, $^2J_{HH}$ = 4.3 Hz], 5.54 (d, ^{1}H, pcymene, $^3J_{HH}$ = 6 Hz), 5.63 (d, ^{1}H, *p*-cymene, $^3J_{HH}$ = 5.8 Hz), 6.14 (d, ^{1}H, *p*-cymene, $^3J_{HH}$ = 5.8 Hz), 6.48(d, 1H, *p*-cymene, $^3J_{HH}$ = 6 Hz), 7.32–7.09 (m, 7H, Ph + NH_2); minor diastereomer d 1.16 (d, 3H, *p*-cymene, $^3J_{HH}$ = 6.9 Hz), 5.20 (dbr, 2H, *p*-cymene, $^3J_{HH}$ = 5.7 Hz), 5.41 (dbr, 2H, *p*-cymene, $^3J_{HH}$ = 4.7 Hz). IR: 3288–3120 (NH), 1580(C═O amide).

X-Ray Structures

Single crystals of **A** and **B** were mounted on glass fibers and X-ray diffraction data were collected on a Bruker-Siemens Smart AXS 1000 equipped with CCD detector, using graphite monochromated Mo Kα radiation (k = 0.71073 Å). Data collection details are: crystal to detector distance = 5.0 cm, 2424 frames collected (complete sphere mode), time per frame = 30 s, oscillation $\Delta\Omega$ = 0.300°. Crystal decay was negligible in both cases. Data reduction was performed up to d = 0.70 and 0.90 Å for **A** and **B**, respectively, by the SAINT package[14] and data were corrected for absorption effects by the SADABS[15] procedure (T_{max} = 1.000, T_{min} = 0.788 for 1 and T_{max} = 1.000, T_{min} = 0.848 for **B**). The phase problem was solved by direct methods[16] and refined by full-matrix least-squares on all F2,[17] implemented in the WINGX package.[18] Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were introduced in calculated positions, except for amine and amide hydrogens, which were located from Fourier maps and refined isotropically. A partially occupied (50%) water molecule completes the asymmetric unit contents for **B**. Absolute structure for **B** was assessed by Flack's parameter = −0.11;[10] final maps were featureless. Use of the Cambridge Crystallographic Database[19] facilities was made for structure discussion. Data collection and refinement results are summarized in Table 1. For hydrogen transfer reactions 0.05 mmol of **B** was dissolved in 5 ml of *i*-PrOH and the solution was thermostatted at the desired temperature (room temperature or 70 °C). An *i*-PrOH solution (5 ml) of the ketone (50 mmol) was added and after an hour an *i*-PrOH solution (5 ml) of *t*-BuOK (0.1 mmol, 11 mg) was added. After an additional hour of reaction a small portion of the reactant solution was withdrawn, quenched with water, extracted with diethyl ether, eluted through a short silica column with diethyl ether and finally analyzed by GC.

Results and Discussion

$[Os(p\text{-cymene})Cl_2]_2$ in an ethanol–chloroform mixture was made to react with L1•HCl at room temperature forming complex **A** (Scheme 1). The reaction was carried out under extremely dry conditions to avoid the hydrolysis of the methyl-ester group of the ligand. **A** was isolated and obtained as a powder with brownish color, and was found to have a pseudo-tetrahedral geometry, where osmium was surrounded by two chloride ligands, the amine group of L1 and an η6-coordinated *p*-cymene molecule. The complexes were stable in the solid state as well as in open air solution form.

The ester group remains out of the coordination sphere, which was evidenced by the strong IR stretching band at 1739 cm^{-1}, equivalent to that of L1•HCl. The stretching signals of the amine group are in the range of 3267 to 3148 cm^{-1}. In the ^{1}H NMR spectrum, the splitting of the NH_2 signals (two multiplets at 3.06 and 7.05 ppm, respectively) was obvious, as a result of interaction of the nitrogen donor with the metal center; moreover, all other signals also show the expected chemical shifts.

To establish the structure of the complex, very fine single crystals of **A** were grown in ethanol. The crystal structure of **A** (Fig. 1) shows that the coordination geometry of the $[OsNCl_2(\eta6\text{-}C6)]$ moiety, summarized in Table 2, may be described as tetrahedral by considering the center (Cy) of the η6-*p*-cymene aromatic ring being the fourth ligand. The Os–C distances relative to the *p*-cymene coordination range from 2.167 (**B**) to 2.200 (**A**) Å, where Os–Cy = 1.659(A) Å. On the whole, the shape of the **A** may hence be called a piano stool-like geometry.

The experimental conditions for HL2 reaction with $[Os(p\text{-cymene})Cl_2]_2$ are the same, for the formation of complex **B**

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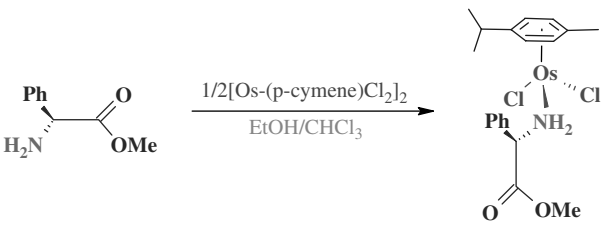
Table 1. Crystal data and structure elucidation for **A** and **B**

Identification code	**A**	**B**
Empirical formula	$C_{19}H_{25}Cl_2NO_2Os$	$[C_{19}H_{25}C_lN_2OOs]2 \cdot 1/2H_2O$
Formula weight	560.00	1054.00
Wavelength (´Å)	0.71069	0.71069
Crystal system	Triclinic	Tetragonal
Space group	PI	I41
Unit cell dimensions		
a (Å)	9.7090(9)	23.551(2)
b (Å)	9.7698(9)	
c (Å)	10.765(1)	14.721(1)
α (deg)	97.615(2)	
β (deg)	97.412(2)	
γ (deg)	105.011(2)	
Volume ($Å^3$)	965.92(15)	8190(1)
Z	2	8
D_{calc} (mg m^{-3})	1.6154	1.425
Absorption coefficient (mm^{-1})	1.0995	0.907
F (000)	480	3595
θ range for data collection (deg)	1.93–3033	1.51–24.01
Reflections collected ($I > 2$ sigma)	13 591	36 800
Data/restraints/parameters	5256/0/240	5920/9/440
Goodness-of-fit on F^2	1.3036	1.171
Final *R* indices [$I > 2\sigma$ (*I*)]	$R_1 = 0.0210$, $wR_2 = 0.0531$	$R_1 = 0.0361$, $wR_2 = 0.9981$
R indices (all data)	$R_1 = 0.0240$, $wR_2 = 0.0551$	$R_1 = 0.0539$, $wR_2 = 0.1202$
Largest d*F* maximum/minimum (e $Å^{-3}$)	0.485/−0.459	0.912/−0.310



Scheme 1. Synthesis of the Half-Sandwich Osmium(II) Complex A.

(Scheme 2) as for **A**. The complex **B**, too, is stable in the solid state as well as in open air solutions. The ligand exhibits a bidentate behavior, bonding to the metal through the amine and amide nitrogen atoms. The complexation occurs with exclusion of an HCl molecule, resulting in the mono-deprotonation of the amide nitrogen, and then L1 acts as an anionic *N,N′* bidentate ligand. The ^{1}H NMR evidenced the presence of two diastereomers; at room temperature they were in a 3 : 1 ratio. Thus, in the presence of an enantiomerically pure ligand, the two diastereomers $R_{Os}S_C$ and $S_{Os}S_C$ appear in the present case having an S_C configuration. The IR spectrum shows that the stretching of the NH bonds originates an unresolved band in the region 3280–3120 cm^{-1}, while a strong stretching band of the amide C═O group occurs at 1575 cm^{-1}.

The X-ray diffraction analysis of a single crystal of **B** obtained at 5 °C from a chloroform solution showed the presence of both diastereomers. The X-ray analysis of **B** indicates that L2 has retained its configuration at the stereogenic carbon atom, contrary to ligand L1. The presence of two diasteromers in the same crystal has already been observed for ruthenium, a congener of osmium in Ru(η6-arene)(LL′)Cl type complexes, as reported in the literature.[20] The majority deal with the type of complexes

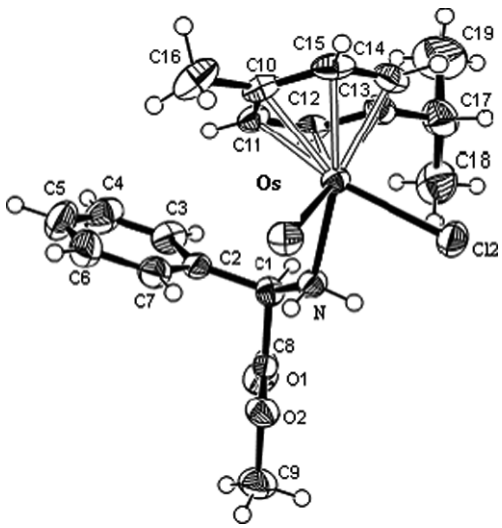


Figure 1. Thermal ellipsoids drawn at the 40% probability level. Perspective view and labeling scheme of **A**.

of general formula [M(η6-*p*-cymene)(salicylaldiminate-ligand)Cl], and only in one case is the ligand *N,N′*.[20] Table 2 shows the most similar geometric features of the two molecules, co-crystallized in the acentric polar space group *I*41 (Figure 2).

Chemoselective hydrogen-transfer reduction of ketones catalyzed by A

The compounds selected in present work for hydrogen-transfer reduction assisted by the complexes **A** and **B** were (i) ketones

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Table 2. Coordination bond lengths (Å) and angles (deg) for **A** and **B**

Sample no.	Bonds	Bond lengths	Bonded atoms	Angles
A				
1	Os–N	2.162(1)	N–Os–Cl2	82.19(4)
2	Os–(C10–C15)	2.153(1)–2.200(1)	N–Os–Cl1	82.07(4)
3	Os–Cy	1.61	Cl2–Os –Cl1	87.11(1)
4	Os–Cl2	2.4136(4)	Cy–Os–N	133
5	Os–Cl1	2.4203(4)	Cy–Os–Cl1	125
	–	–	Cy–Os–Cl2	128
B				
1	Os1–N1	2.055(9)/2.123(8)	Os2–N3	2.050(9) Os1–N2
2	(C10–C15)	2.15(1)–2.19(1)	Os2–(C29–C34)	2.13(1)–2.24(1)
3	Os1–Cl1	2.432(3)	Os2–Cl2	2.435(3)
4	Os1–Cy1	1.62	Os2–Cy2	1.67
5	N1–Os1–N2	76.5(3)	N3–Os2–N4	76.5(3)
6	N1–Os1–Cl1	86.3(3)	N3–Os2–Cl2	87.5(3)
7	N2–Os1–Cl1	82.5(2)	N4–Os2–Cl2	82.3(3)
8	Cy1–Os1–N1	130	Cy2–Os2–N3	131
9	Cy1–Os1–N2	131	Cy2–Os 2–N4	132
10	Cy1–Os1–Cl1	127	Cy2–Os2–Cl2	128

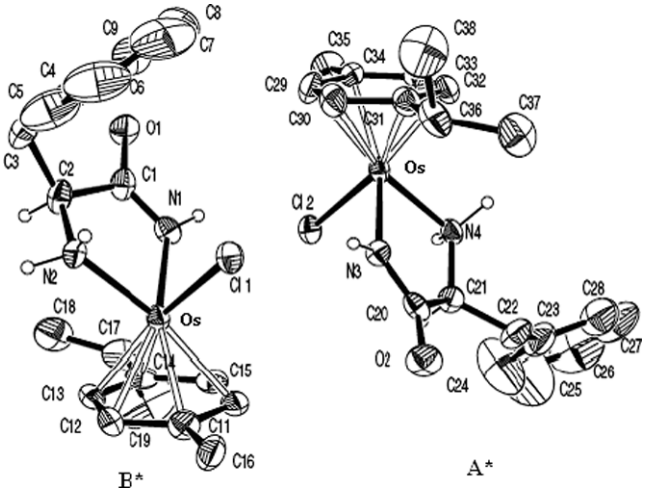
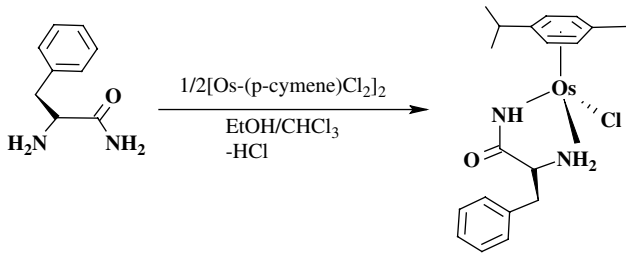


Figure 2. Thermal ellipsoids at the 30% probability level, hydrogens omitted with the exception of those bonded to N and to chiral C atoms. Perspective view and labeling of the two diastereomers $S_{Os}S_C$ (molecule A*) and $R_{Os}S_C$ (molecule B*) co-crystallized in **B**.



Scheme 2. Synthesis of the Half-Sandwich Osmium(II) Complex B.

(nine α,β-unsaturated ketones, viz. entries 4–12 and 3 saturated ketones; entries 1–3) and (ii) aldehydes (entries 13–15). The reactions were carried out by employing propan-2-ol and cyclopentanol, being hydrogen donors as well as solvents. The reactions were slightly faster in the presence of the former, probably due to the lower inhibiting effect of acetone in comparison to cyclopentanol that can quickly be evaporated at higher temperature conditions (80 °C). Both the complexes A and B are very stable and a number of catalytic cycles can be achieved by recharging the system with substrate and hydrogen donors.

Acyclic α,β-unsaturated ketones were reduced with excellent catalytic activity to give corresponding saturated ketones which were further reduced to saturated alcohols (entries 1, 8, 9, 11 and 12 in Table 3). As regards cyclic α,β-unsaturated ketones, the product yield obtained by the reduction of smaller cyclic substrates with minimum steric hindrance around the reducible groups (entries 2 and 4 in Table 3) was much higher than for larger size and steric hindrance. Cyclohexenone gives a mixture of reduction products with C=C and C=O but, upon the hindrance of C=C bond (entries 5, 6 and10 in Table 3), the unsaturated alcohol was preferably formed. Saturated ketones were the major products in the case of five-membered rings (entries 4 and 10).

As far as the reduction of aldehydes is concerned, interestingly, it was performed successfully (entries 13–15, Table 3) by **A**, which is, to the best of our knowledge, quite a rare behavior by Os-arene half sandwich complexes.

Chemoselective hydrogen-transfer reduction of ketones catalyzed by B

The hydrogen-transfer reduction of benzylideneacetone was catalyzed by **B** with high catalytic activity and fair chemoselectivity, the major product being the corresponding unsaturated alcohol; other products found were the saturated ketone and the saturated alcohol (Table 4). The maximum chemoselectivity (~90%) was obtained at the temperature range of 25–40 °C. At higher temperature conditions, the reactions were very fast, and the unsaturated alcohol formed was rapidly reduced to a saturated alcohol. When no substituent was present on the olefin group,

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Table 3. Hydrogen-transfer reduction catalyzed by **A**

Entry	Substrate	Time (h)	Conversion (%)	Percentage saturated ketone/aldehyde	Percentage saturated corresponding alcohol	Percentage unsaturated corresponding alcohol
1	Acetophenone	7	25	9	16	0
2	Cyclohexanone	6	88	0	88	0
3	3-Pentanone	6	35	0	35	0
4	Cyclopentenone	2	95	60	35	0
5	Carvone	9	20	0	20	0
6	3-Methyl-2-cyclohexen-1-one	5	30	0	0	30
7	Cyclohexenone	2	90	0	22	68
8	Chalcone	5	60	45	15	0
9	Benzyldeneacetone	4	100	80	0	20
10	3-Methyl-2-cyclopenten-1-one	5	11	11	0	0
11	4-Hexen-3-one	5	90	70	0	20
12	4-Penten-3-one	7	90	88	2	0
13	Cinnamaldehyde	1	65	15	50	0
14	Benzaldehyde	4	100	20	80	0
15	2-Pentenal	5	55	0	55	0

Table 4. Hydrogen-Transfer Reduction Catalyzed by **B**

Entry	Substrate	Time (h)	Conversion (%)	Percentage saturated ketone/aldehyde	Percentage saturated corresponding alcohol	Percentage unsaturated corresponding alcohol
1	Acetophenone	5	91	0	91	0
2	Cyclohexanone	4	100	0	100	0
3	3-Pentanone	6	87	0	87	0
4	Cyclopentenone	1	90	30	60	0
5	Carvone	6	12	0	0	12
6	3-Methyl-2-cyclohexen-1-one	7	25	0	10	15
7	Cyclohexenone	2	95	12	5	78
8	Chalcone	6	90	22	68	0
9	Benzyldeneacetone	2	96	10	16	70
10	3-Methyl-2-cyclopenten-1-one	7	23	23	0	0
11	4-Hexen-3-one	8	77	77	0	0
12	4-Penten-3-one	7	93	88	5	0
13	Cinnamaldehyde	2	55	5	50	0
14	Benzaldehyde	3	85	0	85	0
15	2-Pentenal	5	25	0	25	0

cyclic enones were reduced at the C=C bond and subsequently to the saturated alcohol. Preferential reduction to the unsaturated alcohol takes place in the case of hindered C=C bonds (entries 6 and 7). **B** also exhibits a fine catalytic activity in the reduction of saturated ketones to the corresponding alcohols (entries 1–3). Substrates bearing a C=C bond conjugated to an electron-withdrawing group were reduced, with a lower catalytic activity as compared with ketone reduction. The overall reduction of unsaturated ketones to unsaturated alcohols was found to be dominant in the case of cyclic ketones as compared with acyclic ones, for both **A** and **B** (Tables 3 and 4). Although, the reduction of aldehydes such as benzaldehyde and cinnamaldehyde by complex **B** (entries 13–15, table 3) was quite healthy, it was comparatively less efficient than that carried out by **A** (entries 13–15, Table 3). Moreover, the reaction time observed in the case of aldehydes was generally shorter than that of ketones, both for **A** and **B**. The two unsubstituted and unsaturated cyclic ketones, i.e. cyclopentenone and cyclohexenone (entries 4 and 7 in Tables 2 and 3) exhibited the highest rates of reduction reaction catalyzed by **A** and **B**. A complete reduction of cyclohexanone (entry 3, Table 4) to the corresponding saturated alcohol by **B** was observed.

We have also tried to study in some detail the effect of the experimental conditions on the catalytic activity of **B** in the reduction of benzylideneacetone. The two hydrogen donors used, propan-2-01 and cyclopentanol, both showed some limitations. Propan-2-01 was dehydrogenated during the reaction to give acetone which, like acyclic ketones, reacts with **B** in a disproportionation reaction, causing slow, irreversible deactivation of the cata1yst. This type of deactivation is insignificant when the substrate reduction is fast, but in the case where **B** is less active, deactivation of the catalyst can be competitive with substrate reduction and, hence, an incomplete conversion was achieved. However, interestingly,

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cyclopentanone, obtained by oxidation of cyclopentanol, did not poison the catalyst; on the other hand, the ketone which forms was not volatile (as was acetone) and may compete with the substrate for coordination to osmium in the course of the catalysis cycle.

This osmium catalyst (**B**), like **A**, is very stable; a number of successive reactions can be performed using the same catalyst with no substantial decay of activity. To the best of our knowledge, no other osmium complex has been reported so far to selectively catalyze the hydrogen-transfer reduction of α,β-unsaturated ketones to allylic alcohols to such an extent.

Conclusions

We synthesized, characterized and tested two new half-sandwich Os(II) complexes containing amino acid derivatives as catalysts for chemoselective reduction of selected α,β-unsaturated ketones. Co-crystallization of the two diastereomers $R_{Os}S_C$ and $S_{Os}S_C$ was found within complex **B**, having (*S*)-phenylalanineamide as a ligand which occurred through an inverted piano-stool-like dimer pattern. The steric and electronic position in the coordination sphere of the catalysts **A** and **B** appears as suitably designed to favor the reduction of the carbonyl group of α,β-unsaturated ketones bearing bulky substituents at the C=C double bond. The reduction of the C=C bond was observed when either an α,β-unsaturated ketone was not sterically hindered or the C=O carbon atom bore a bulky substituent. These complexes were found to be good catalysts for the selective reduction of unsaturated organic substrates. This opens up a quite promising and largely new area of research.

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