Utility of Osmium(II) in the Catalysis of Asymmetric Diels−Alder Reactions

J. W. Faller*,† and Jonathan Parr*,‡

Departments of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06520, and Loughborough University, Loughborough, Leicestershire LE11 3TU, U.K.

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Half-sandwich complexes of osmium(II) comprising either (*S*)-BINAP or (*S*)-BINPO can be used to prepare formally dipositive 16-electron Lewis acidic species. These in turn can be used to catalyze the Diels−Alder condensation of either methacrolein or ethylacrolein with cyclopentadiene in high ee (>90%). The complex containing the non-C_2-symmetric bisphosphine monoxide was found to be markedly more effective than the C_2-symmetric bisphosphine.

Introduction

Since the first reports of transition-metal-catalyzed stereoselective Diels−Alder reactions there has been a continuous development of new ligands and new complexes which can be used for this reaction,[1] and among these, some ruthenium complexes have proved very promising.[2−4] We have recently reported on the role of chiral bisphosphine monoxide (BPMO) complexes of ruthenium(II) in the catalysis of an asymmetric Diels−Alder condensation reaction[5] and upon diastereoselectivity in chiral osmium complexes of a chelating BPMO ligand.[6] Following the observation that complexes of the type $[(\eta^6\text{-Cy})Os(BPMO)(aldehyde)]^{2+}$ contain σ-bound aldehydes in much the same way as the corresponding ruthenium species, it seemed reasonable to investigate the potential of such osmium(II) compounds as catalysts for this class of reaction.

We report the synthesis of the Lewis acidic compounds $[(\eta^6\text{-Cy})OsCl(L)](SbF_6)$, where L = (*S*)-BINAP (**1**) or its monoxide, (*S*)-BINPO[7] (**2**), and examine the efficacy of the corresponding dipositive 16-electron Lewis acids $[(\eta^6\text{-Cy})Os(L)](SbF_6)_2$ (L = (*S*)-BINAP (**3**), (*S*)-BINPO (**4**)) as catalysts in the condensation of methacrolein and ethylacrolein with cyclopentadiene.

Results and Discussion

The interaction of $[(\eta^6\text{-Cy})OsCl_2]_2$ with (*S*)-BINAP or (*S*)-BINPO in a 1:2 mole ratio in the presence of $NaSbF_6$ gives the yellow monocationic complexes $[(\eta^6\text{-Cy})OsCl(\eta^2\text{-BINAP})]SbF_6$ and $[(\eta^6\text{-Cy})OsCl(\eta^2\text{-BINPO})]SbF_6$ in very good yield (Scheme 1). In the case of complex **2** the chelation leads to the formation of a chiral center at the osmium[8] and, hence, the possibility of diastereomeric products. The spectroscopic data indicate that the chelation proceeds in a selective manner, giving only one of the two possible isomers, shown by an X-ray crystallographic investigation to be R_{Os},S (Figure 1).

Scheme 1[a]

$$^1/_2\,[CyOsCl_2]_2 + BINPO \xrightarrow{(i)} [CyOsCl(\eta^2\text{-BINPO-}P,O)]SbF_6\ (\mathbf{2})$$
$$\downarrow (ii)$$
$$[CyOs(\eta^2\text{-BINPO-}P,O)](SbF_6)_2\ (\mathbf{4})$$

[a] Key: (i) $NaSbF_6$ (−NaCl), CH_2Cl_2, 25 °C; (ii) $AgSbF_6$ (−AgCl), CH_2Cl_2, 25 °C.

This finding is in contrast to our previous observation that $Ph_2PCH(CH_3)P(O)Ph_2$ will chelate initially in both relative configurations at the metal to the $[(\eta^6\text{-Cy})OsCl]$ fragment. The reasons for this are not clear but may lie in the slower rate of chloride abstraction by the $NaSbF_6$ used in this preparation relative to that of the silver salt used in the other preparation. Alternatively, there may be a greater steric difference between the P(III) phenyls and the P(V) phenyls of the BINPO compared to that of $Ph_2PCH(CH_3)P(O)Ph_2$, owing to the difference in chelate ring size.

Treatment of **1** or **2** with $AgSbF_6$ leads to the abstraction of the remaining chloride ligand and the formation of the corresponding dipositive species, **3** or **4**. The successful application of **3** and **4** to catalysis of the Diels−Alder reactions suggests that there is a preference for σ-bonding of aldehyde substrates by these osmium(II) complexes. Furthermore, there should be a structural similarity of the aldehyde complex of **4** to a previously reported BPMO ruthenium analogue.[6] An osmium(II) center would not ordinarily be considered a hard Lewis acid, but it appears, nevertheless, to be sufficiently acidic to activate the dienophile in these reactions.

† Yale University.
‡ Loughborough University.

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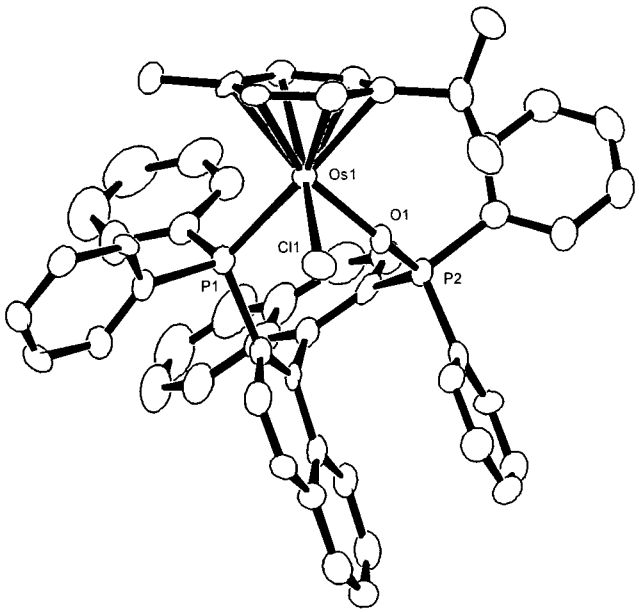


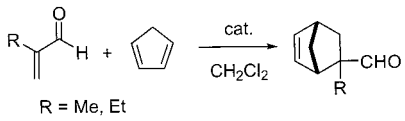
Figure 1. ORTEP view of the cation in (R_{Os})-[CyOsCl(η^2-(*S*)-BINPO-*P*,*O*)]SbF_6 (**2**) with 50% probability ellipsoids.

Some reference to the metrical data from the X-ray structure shown in Figure 1 provides some insight into the diastereomer preference and the enantioselectivity. The (R_{Os})-[CyOsCl(η^2-(*S*)-BINPO-*P*,*O*)]SbF_6 structure found for **2** shows that the preferred diastereomer has the relative configuration of *R**,*S**. Although some modest flexibility might be expected from rotation about the bond connecting the naphthyl groups, they are approximately at right angles with a dihedral angle between them of 81(1)°. The configuration of the binaphthyl portion of the ligand apparently forces a configuration of the Ph_2P fragment which sterically controls the preference for the orientation of chelation. The ligand backbone requires an unusually large Os−O−P angle of 161.5(5)°. Even though there is an eight-membered chelate ring, it produces a quite small bite angle of 82.1(2)°, which is slightly larger than that found in the ruthenium analogue of 81.5(1)°. Although the coordination about the metal can be considered pseudo-tetrahedral for purposes of chirality descriptors, one should note that all of the angles between P, O, and Cl are less than 90°. We suggest that a major feature of the stereocontrol of the Diels−Alder reaction with the BINPO complex is the differential back-bonding provided by the d-orbitals aligned with the Os−P and Os−O bonds. This provides a preferential orientation of the aldehyde which should be superior to that found in the BINAP complex, for which the conformation is determined largely on steric interactions.

Osmium-mediated Diels−Alder reactions are not entirely new. A protocol involving osmium pentaammine complexes in the dearomatization of substituted styrenes to yield activated diene fragments that then undergo Diels−Alder reactions has appeared.[9] This procedure, while efficient, is a stoichiometric reaction in which the osmium complex plays a role altogether different from that reported here.

Inspection of the results from the catalytic reactions in Table 1 reveals greater enantioselectivity arising in reactions mediated by the BPMO complex. This is consistent with the results from similar reactions undertaken with the corresponding ruthenium complexes as catalyst and seems to indicate that electronic asymmetry in a C_1-symmetric ligand can be more effective in inducing selectivity than corresponding C_2-symmetric ligands.[4] The utility of C_2-symmetric ligands has been widely reported in the literature in a variety of reactions,[10] and the C_2 symmetry has often been viewed as a key factor in their effectiveness. The recent success of non-C_2-symmetric ligands in this BINPO case, as well as others,[11] suggests that non-C_2-symmetric ligands, as a class, may well be more effective.

Table 1. Lewis Acid Catalysis of Diels−Alder Condensation of CpH with Methacrolein (R = Me) and Ethylacrolein (R = Et)



R = Me, Et

catalyst	R	*T*, °C	de, %[c]	ee, %[d]
3[a]	Me	−24	92	9
3[a]	Me	−78	96	15
3[b]	Et	−24	89	8
3[b]	Et	−78	91	12
4[a]	Me	−24	98	65
4[a]	Me	−78	99	93
4[b]	Et	−24	94	86
4[b]	Et	−78	94	91

[a] Catalyst loading at 4 mol %, with 0.24 mmol of methacrolein and 2.9 mmol of CpH. [b] Catalyst loading at 4.5 mol %, with 0.22 mmol of ethylacrolein and 2.9 mmol of CpH. [c] Determined from the ^{1}H NMR and refers to the excess of the exo isomer. [d] For R = Me, the *S*-(+) isomer is in excess. For R = Et, it is assumed to be the same.

Experimental Section

General Procedures. All synthetic and spectroscopic operations were carried out as described previously.[5,6]

Preparation of [(η^6-Cy)OsCl(η^2-(*S*)-BINAP)]SbF_6 (1). To a solution of [(η^6-Cy)$OsCl_2$]$_2$ (50 mg, 0.063 mmol) in 5 mL of dichloromethane was added (*S*)-BINAP (79 mg, 0.127 mmol) and $NaSbF_6$ (33 mg, 0.128 mmol). The mixture was stirred for 4 h, the solvent was removed under reduced pressure, and the residue was extracted with 2 mL of methylene chloride. The extract was filtered through Celite and ether added to the filtrate until precipitation was complete. The yellow microcrystalline product was collected, washed with diethyl ether, and dried under vacuum. Yield: 127 mg, 82%. ^{1}H NMR (CD_2Cl_2, 293 K, δ): 8.02−5.92 (32H, m, arom), 6.49 (1H, d, 6.5 Hz, Cy H), 6.34 (1H, d, 6.5 Hz, Cy H), 5.83 (1H, d, 6.5 Hz, Cy H), 5.41 (1H, d, 6.5 Hz, Cy H), 2.95 (1H, sept., 6.5 Hz, C*H*(CH_3)$_2$)), 1.99 (3H, s, Cy−CH_3), 1.36 (3H, d, 6.5 Hz, C*H*$_3$C(H)CH_3), 0.98 (3H, d, 6.5 Hz, C*H*$_3$C(H)CH_3). ^{31}P{^{1}H} NMR (δ): −5.85 (d, 34 Hz), −14.60 (d, 34 Hz). Anal. Calcd for $C_{54}H_{46}F_6P_2$ClOsSb: C, 53.22; H, 3.72. Found: C, 53.50; H, 3.68.

Preparation of [(η^6-Cy)OsCl(η^2-(*S*)-BINPO)]SbF_6 (2). To a solution of [(η^6-Cy)$OsCl_2$]$_2$ (50 mg, 0.063 mmol) in 5 mL of

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(11) Examples of successful asymmetric reactions using complexes of C_1-symmetric ligands are as follows. Phosphinooxazoline: Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336−345. Sagasser, I.; Helmchen, G. *Tetrahedron Lett.* **1998**, *39*, 261−264. Dawson, G. S.; Frost, C. G.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1993**, *34*, 3149. Thiophenooxazolines: Allen, V. J.; Bowen, J. F.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1994**, *5*, 1895. Phosphinoamines: Cahill, J. P.; Bohnen, F. M.; Goddard, R.; Kruger, C.; Guiry, P. J. *Tetrahedron: Asymmetry* **1998**, *9*, 3831. Suzuki, Y.; Ogatu, Y.; Hiroi, K. *Tetrahedron: Asymmetry* **1999**, *10*, 1219.

dichloromethane was added (*S*)-BINPO (80 mg, 0,127 mmol) and $NaSbF_6$ (33 mg, 0.128 mmol). The reaction and workup was as above. Yield: 138 mg, 88%. ^{1}H NMR (CD_2Cl_2, 293 K, δ): 8.16−5.95 (32H, m, arom), 6.49 (1H, d, 5.5 Hz, Cy H), 6.22 (1H, d, 5.5 Hz, Cy H), 5.64 (1H, d, 5.5 Hz, Cy H), 5.22 (1H, d, 5.5 Hz, Cy H), 2.24 (1H, hept, 6.5 Hz, C*H*(CH_3)$_2$)), 1.45 (3H, s, Cy−CH_3), 1.08 (3H, d, 6.5 Hz, C*H*$_3$C(H)CH_3), 0.85 (3H, d, 6.5 Hz, C*H*$_3$C(H)CH_3). ^{31}P{^{1}H} NMR (δ): 50.24 (P(V)), 14.25 (P(III)). Anal. Calcd for $C_{54}H_{46}OF_6P_2ClOsSb$: C, 52.51; H, 3.76. Found: C, 52.29; H, 3.87.

Preparation of [(η^6-Cy)Os(η^2-(*S*)-BINAP)](SbF$_6$)$_2$ (3). To a solution of [(η^6-Cy)OsCl(η^2-(*S*)-BINAP)]SbF_6 (50 mg, 0.041 mmol) in 4 mL of dichloromethane was added $AgSbF_6$ (13 mg, 0.038 mmol) in 4 mL of dichloromethane. After precipitation was complete, the reaction mixture was centrifuged and the supernatant removed by syringe. The solution was used directly for the catalytic reactions without isolation of the dipositive complex. ^{1}H NMR (CD_2Cl_2, 293 K, δ): 8.20−6.08 (32H, m, arom), 6.30 (1H, d, 6.0 Hz, Cy H), 5.92 (1H, d, 6.0 Hz, Cy H), 5.83 (1H, d, 6.0 Hz, Cy H), 5.76 (1H, d, 6.0 Hz, Cy H), 2.97(1H, hept, 7.0 Hz, C*H*(CH_3)$_2$)), 1.99 (3H, s, Cy−CH_3), 1.39 (3H, d, 7.0 Hz, C*H*$_3$C(H)CH_3), 0.99 (3H, d, 7.0 Hz, C*H*$_3$C(H)CH_3). ^{31}P{^{1}H} NMR (δ): −6.05 (d, 40 Hz), −16.55 (d, 40 Hz).

Preparation of [(η^6-Cy)Os(η^2-(*S*)-BINPO)](SbF$_6$)$_2$ (4). The dipositive catalyst **4** was prepared in the same way using the same concentrations and again used directly without isolation. ^{1}H NMR (CD_2Cl_2, 293 K, δ): 8.20−6.02 (32H, m, arom), 6.38 (1H, d, 6.5 Hz, Cy H), 6.25 (1H, d, 6.5 Hz, Cy H), 5.91 (1H, d, 6.5 Hz, Cy H), 5.80 (1H, d, 6.5 Hz, Cy H), 2.92 (1H, hept, 7 Hz, C*H*(CH_3)$_2$)), 1.89 (3H, s, Cy−CH_3), 1.04 (3H, d, 7 Hz, C*H*$_3$C(H)CH_3), 0.84 (3H, d, 7 Hz, C*H*$_3$C(H)CH_3). ^{31}P-{^{1}H} NMR (δ): 80.36 (P(V)), 27.18 (P(III)).

Catalytic Reactions. For both **1** and **2** the catalytic reactions were carried out on the four fractions a−d as follows: (a) addition of methacrolein (0.017 g, 0.24 mmol) and CpH (0.197 g, 2.9 mmol) at −24 °C; (b) as for (a) at −78 °C; (c) addition of ethylacrolein (0.022 g, 0.21 mmol) and CpH (0.197 g, 2.9 mmol) at −24 °C; (d) as for (c) at −78 °C.

Reactions were allowed to reach completion (18−24 h), the dichloromethane was removed under reduced pressure, and the residue was extracted with 2 × 5 mL of pentane to separate the organic product from the inorganic component. The volatiles were removed under reduced pressure and the product aldehyde analyzed by NMR.

2-Methylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde. ^{1}H NMR ($CDCl_3$, 298 K, 500 MHz, δ): 9.69 exo-C*H*O (major); 9.39 endo-C*H*O (minor). The chiral shift reagent Eu(hfc)$_3$ was used to determine the enantioselectivity of the exo diastereomer. It was observed that the signal for the *S* enantiomer was consistently shifted further downfield than the signal for the *R* enantiomer. This was established by comparison of the sign of the optical rotation to the literature values.[12] The enantioselectivity was then determined by line shape analysis of the two signals.

2-Ethylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde. ^{1}H NMR ($CDCl_3$, 298 K, 500 MHz, δ): 9.70 exo-C*H*O (major) 9.40 endo-C*H*O (minor). Use of the chiral europium shift reagent, Eu(hfc)$_3$ failed to distinguish the enantiomers. The enantioselectivity of the exo diastereomer was determined by derivatization with (2*R*,4*R*)-2,4-pentanediol to the corresponding diastereomeric acetals. Integration of the resonances for the C*H*O_2 protons at δ 4.85 and 4.82 was used to determine the enantioselectivity. The signal at δ 4.85 corresponded to the major enantiomer.[4] The configuration of the major enantiomer was not determined but is presumed to be the same as that for the major isomer found for methacrolein, i.e, *S*.

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Table 2. Crystallographic Data for the X-ray Diffraction Study of (R_{Os})-[CyOsCl(η^2-(*S*)-BINPO-*P*,*O*)]SbF$_6$ (2)

formula	$SbOsClP_2F_6OC_{54}H_{46}$
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a, Å	12.3190(4)
b, Å	15.2290(6)
c, Å	12.9244(5)
β, deg	97.539(2)
V, Å^3	2403.7(1)
fw	1234.30
D_{calcd}, g/cm^3	1.583 ($Z = 2$)
abs coeff, cm^{-1}	10.60
cryst size, mm	0.24 × 0.24 × 0.05
diffractometer	Nonius KappaCCD
monochromator	graphite
radiatn	Mo Kα (0.710 73 Å)
max 2θ, deg	55
T, °C	−90
no. of rflns measd	19 092
no. of data used, $F^2 > 3\sigma(F^2)$	4025
no. of params refined	593
p factor	0.02
final residuals *R*, R_w	0.038, 0.035
convergence, largest shift/error	0.00
GOF	1.05
largest $\Delta(\rho)$, e Å^{-3}	1.29

Table 3. Selected Bond Distances (Å) and Angles (deg) for [CyOsCl(η^2-(*S*)-BINPO-*P*,*O*)]SbF$_6$ (2)

Os(1)−Cl(1)	2.396(2)	Os(1)−P(1)	2.386(2)
Os(1)−O(1)	2.138 (5)	P(2)−O(1)	1.496(4)
Cl(1)−Os(1)−P(1)	84.95(6)	Cl(1)−Os(1)−O(1)	84.7(3)
P(1)−Os(1)−O(1)	82.1(2)	Os(1)−O(1)−	161.5(5)

X-ray Crystallography. Single crystals suitable for X-ray analysis were formed by vapor diffusion of diethyl ether into a methanol solution of **2**. Crystallographic data are summarized in Tables 2 and 3. The structure of **2** was determined from data collected with a Nonius KappaCCD at −90 °C. Lorentz and polarization corrections were applied to all data. An empirical absorption correction was applied using SORTAV.[13] Intensities of equivalent reflections, excluding Friedel pairs, were averaged. The structure was solved by direct methods (SIR92[14]) using the teXan crystal structure analysis package, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms were placed at calculated positions before each refinement and were included in the refinement but were not refined. The absolute configuration was determined by reference to the configuration of (*S*)-BINPO.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond lengths and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000896G

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