Synthesis and Crystal Structure of a Chiral C_3-Symmetric Oxygen Tripodal Ligand and Its Applications to Asymmetric Catalysis

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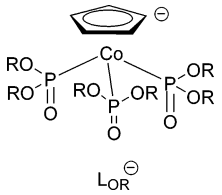
Treatment of Na[P(O)(*S*-BINOL)] (*S*-BINOL = (*S*)-(−)-bi-2-naphthol) with [CpCo(CO)I_2] afforded the chiral C_3-symmetric oxygen tripodal ligand Na[Co{P(O)(*S*-BINOL)}$_3$] (Na(**1**)). Recrystallization of Na(**1**) from acetone/toluene yielded Na(**1**)($C_6H_{12}O_2$)$_2$ ($C_6H_{12}O_2$ = diacetone alcohol), which has been characterized by X-ray diffraction. The solid-state structure of Na(**1**)($C_6H_{12}O_2$)$_2$ features a six-coordinated Na with one η^2 and one η^1 diacetone alcohol ligand. Treatment of Na(**1**) with [(η^6-*p*-cymene)$RuCl_2$]$_2$, [Ru(CO)Cl(CH=CHPh)(PPh_3)$_3$], and [Pr(OTf)$_3$] (OTf = triflate) afforded [(η^6-*p*-cymene)Ru(**1**)][PF_6] (**3**), [Ru(**1**)(CO)(CH=CHPh)(PPh_3)] (**4**), and [Pr(**1**)$_2$(OTf)] (**5**), respectively. Treatment of Na(**1**) with [Cu(MeCN)$_4$][BF_4] in the presence of PhC≡CH and Me_3SiC≡$CSiMe_3$ afforded [Cu(**1**)(η^2-PhC≡CH)] (**6**) and [Cu(**1**)(η^2-Me_3SiC≡$CSiMe_3$)] (**7**), respectively, which have been characterized by X-ray diffraction. In both **6** and **7**, the Cu atom exhibits a distorted 2 + 1 tripod ligand coordination with one Cu−O bond significantly longer than the other two. Na(**1**) has been employed for the Cu-catalyzed enantioselective aziridination of styrene, the Ti-catalyzed azidolysis of cyclohexene oxide, and the allylation of benzaldehyde with allyltrichlorosilane.

Introduction

While C_2-symmetric ligands have been extensively used for metal-mediated enantioselective organic transformations,[1] analogous C_3-symmetric systems have received less attention.[2] Metal catalysts containing ligands possessing C_3 or higher rotational symmetry are expected to permit a higher degree of stereocontrol and reduce the number of possible transition states in, e.g., octahedral complexes compared to those for the C_2-symmetric counterparts and, thus, may find applications in asymmetric catalysis.[2] Chiral C_3-symmetric ligands used for asymmetric catalysis are mostly nitrogen and phosphorus donor systems.[2] Relatively few studies have been made on analogous C_3-symmetric oxygen ligands. One example of C_3-symmetric oxygen ligands are chiral tris(hydroxypropyl)amine ligands that have been used for enantioselective ring opening of epoxides[3] and oxidation of sulfides.[4] We have a long-standing interest in Kläui's oxygen tripodal ligands [CpCo{P(O)(OR)$_2$}$_3$]$^-$ (Cp = η^5-C_5H_5, R = alkyl, aryl) (L_{OR}^-; Chart 1),[6] which have been recognized as oxygen analogues of Cp and hydrotris(pyrazolyl)borate (Tp) ligands.

Chart 1



Like Cp and Tp ligands, π-donating L_{OR}^- ligands exhibit rich organometallic[5−7] and catalytic[8−10] chem-

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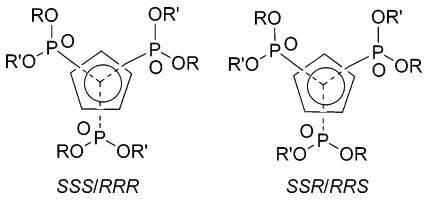
Chart 2. Top View of the Stereoisomers of $L_{(OR)(OR')}^-$



istry. Recently, chiral Tp ligands have been synthesized[11] and used for asymmetric cyclopropanation of olefins.[12,13] This prompted us to develop a chiral version of Kläui's tripodal ligands that form stable complexes with a wide range of metal ions.[6] Previously, Kläui and co-workers reported that if the R and R′ groups differ in size, reaction of $[Cp_2Co]$ with (OR)(OR′)P(O)(H) afforded a mixture of diastereomers of $[CpCo\{P(O)(OR)(OR')\}_3]^-$ ($L_{(OR)(OR')}^-$): namely, the *RRR*/*SSS* and *RRS*/*SSR* isomers (Chart 2),[6,8] which have not yet been separated.

Instead of resolving the stereoisomers of $L_{(OR)(OR')}^-$, we seek to synthesize chiral Kläui tripodal ligands starting from optically active phosphites. We here report on the preparation and crystal structure of a chiral C_3-symmetric oxygen tripodal ligand derived from optically active 1,1′-bi-2-naphthol and its applications to asymmetric catalysis.

Experimental Section

General Considerations. All manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300, 75.5, and 121.5 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H and ^{13}C) and H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, and mass spectra on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K. (*S*)-(−)-1,1′-bi-2-naphthol,[14] (*R*,*R*)-1,2-diphenylethane-1,2-diol,[15] $[CpCo(CO)I_2]$,[16] $[Ru(CO)(Cl)(CH{=}CHPh)(PPh_3)_3]$,[17] $[Cu(MeCN)_4][BF_4]$,[18] and PhI=NTs[19] (Ts = tosyl) were prepared according to literature methods.

Preparation of P(O)(H)(*S*-BINOL) (*S*-BINOL = (*S*)-(−)-1,1′-Bi-2-naphthol).[20] To PCl_3 (0.61 mL, 6.98 mmol) in CH_2Cl_2 (40 mL) was added *t*-BuOH (0.67 mL, 6.98 mmol) dropwise over 1 h at 0 °C, and the mixture was stirred at 0 °C for another 1.5 h. To this resulting solution was added *S*-BINOL (2.0 g, 6.98 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 4.5 h, heated at reflux overnight, and filtered. The volatiles were pumped off to give a white solid, which was washed with hexanes and dried in vacuo. Yield: 2.3 g (99%). ^{1}H NMR ($CDCl_3$): δ 8.05 (d, J = 9 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 7.32−7.63 (m, 8H), 7.31 (d, J = 729 Hz, 1H, P*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 14.94(s). MS (CI): m/z 332 ($M^+ + 1$).

Preparation of Na[CpCo{P(O)(*S*-BINOL)}$_3$] (Na(1)). This compound was prepared according to Kläui's method.[21] A mixture of P(O)(*S*-BINOL)H (2.0 g, 6.01 mmol) and NaH (0.185 g, 4.63 mmol) in THF (40 mL) was stirred at 0 °C for 2 h, and $[CpCoI_2(CO)]$ (0.306 g, 0.754 mmol) in THF (20 mL) was added dropwise over a period of 1 h. The resulting mixture was stirred at room temperature for 4 h and then heated at reflux for 20 h. The yellow mixture was filtered, evaporated to dryness, and extracted with toluene/Et_2O and then acetone/Et_2O. Evaporation of the solvent afforded a yellow solid that was further recrystallized from THF/Et_2O and washed with MeOH (yield: 0.78 g, 91% based on $[CpCo(CO)I_2]$). Recrystallization from THF/acetone gave yellow single crystals that were suitable for X-ray diffraction. ^{1}H NMR (acetone-d_6): δ 8.27 (m, 9H), 8.20 (d, J = 7.8 Hz, 3H), 8.10 (d, J = 8.4 Hz, 3H), 7.95 (d, J = 8.5 Hz, 3H), 7.61 (m, 9H), 7.49 (m, 9H), 4.68 (s, 5H, Cp). ^{31}P{^{1}H} NMR (acetone-d_6): δ 122.53 (br s). MS (FAB): m/z 1141 (M^+). $[\alpha]^{22}_D = -464°$ (CH_2Cl_2, c 0.36). The *R* isomer Na[CpCo{P(O)(*R*-BINOL)}$_3$] was prepared similarly from P(O)(*R*-BINOL)H and $[CpCo(CO)I_2]$, $[\alpha]^{22}_D = 434°$ (CH_2Cl_2, c 1.0).

Preparation of Na[CpCo{P(O)(L)}] (Na(2); LH_2 = (*R*,*R*)-1,2-Diphenylethane-1,2-diol). P(O)(L)H was prepared similarly as for P(O)(BINOL)H from PCl_3, *t*-BuOH, and LH_2. To a solution of P(O)(L)H (2.0 g, 7.69 mmol) in THF (100 mL) at 0 °C was added NaH (60% in mineral oil) (0.23 g, 5.77 mmol), and the mixture was stirred for 30 min. $[CpCo(CO)I_2]$ (0.39 g, 0.958 mmol) was added, and the resulting solution was refluxed for 3 days and evaporated to dryness. The residue was extracted into toluene, and Et_2O and hexanes were added. The yellow solid was collected, washed with MeOH, and Soxhlet extracted into Et_2O. Yield: 192 mg (22%). ^{31}P{^{1}H} NMR (acetone-d_6): δ 124.47 (br s). MS (FAB): m/z 924 (M^+). Despite several attempts, we have not been able to obtain an analytically pure sample of Na(**2**).

Preparation of [Ru(1)(η^6-*p*-cymene)][PF_6] (3). To a solution of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (21.5 mg, 0.035 mmol) and NH_4PF_6 (30 mg, 0.18 mmol) in MeOH/acetone (10 mL) was added Na(**1**) (80 mg, 0.07 mmol) in acetone (5 mL), and the mixture was stirred at room temperature for 10 min. The solvent was removed in vacuo, and the residue washed with water and toluene. Recrystallization from acetone/Et_2O afforded yellow needles. Yield: 63 mg (60%). ^{1}H NMR ($CDCl_3$): δ 7.26−8.58 (m, 36H), 5.33 (m, 1H), 5.15 (m, 2H), 4.98−5.05 (m, 1H), 4.75 (s, 5H), 2.22−2.30 (m, 1H), 1.74 (s, 3H), 0.82 (dd, J = 9.3, 6.9 Hz, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 135.05 (br s), 72.5 (sept). MS (FAB): m/z 1353 ($M^+ - PF_6$). Anal. Calcd for $C_{75}H_{55}CoF_6O_9P_4Ru$: C, 60.10; H, 3.70. Found: C, 60.10; H, 3.80.

Preparation of [Ru(1)(CO)(CH=CHPh)(PPh_3)] (4). To a solution of $[Ru(CO)(CH{=}CHPh)Cl(PPh_3)_3]$ (120 mg, 0.15 mmol) in THF (20 mL) was added Na(**1**) (150 mg, 0.13 mmol), and the mixture was stirred at room temperature for 1 day. The volatiles were removed in vacuo, and the residue was washed with Et_2O. Recrystallization from CH_2Cl_2/Et_2O gave an orange powder. Yield: 22 mg (10%). ^{1}H NMR ($CDCl_3$): δ 6.80−8.47 (m, 56H), 6.37 (d, J = 9 Hz, 1H), 5.58 (d, J = 9 Hz, 1H), 4.48 (s, 5H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 57.9 (d), 123.6 (br s). MS (FAB): m/z 1612 ($M^+ + 1$). IR (KBr, cm^{-1}): 1930 (ν_{CO}).

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Anal. Calcd for $C_{92}H_{63}CoO_{10}P_4Ru\cdot 4H_2O$: C, 65.60; H, 4.21. Found: C, 65.44; H, 4.01.

Preparation of [Pr(1)$_2$(OTf)] (5; OTf = Triflate). To a solution of Na(**1**) (134.7 mg, 0.11 mmol) in acetone/MeOH (5 mL, 1:5) was added [Pr(OTf)$_3$] (34.7 mg, 0.059 mmol) in acetone (2 mL), and the mixture was stirred at room temperature overnight. The solvent was pumped off and the residue extracted into CH_2Cl_2. Recrystallization from acetone/Et_2O gave a yellow microcrystalline solid. Yield: 134 mg (89%). MS (FAB): *m*/*z* 2529 (M^+), 2378 (M^+ − OTf). Anal. Calcd for $C_{131}H_{82}Co_2F_3O_{21}P_6PrS\cdot 6H_2O$: C, 59.73; H, 3.57. Found: C, 59.60; H, 3.65.

Preparation of [Cu(1)(η^2-PhC≡CH)] (6). To a mixture of [Cu(MeCN)$_4$][BF$_4$] (6.1 mg, 0.02 mmol) and Na(**1**) (26 mg, 0.023 mmol) in CH_2Cl_2 (10 mL) was added phenylacetylene (0.1 mL), and the mixture was stirred for 15 min. The solvent was pumped off and the residue recrystallized from CH_2Cl_2/toluene/hexane at 4 °C to afford yellow blocks that were suitable for X-ray crystallography. Yield: 22 mg (85%). ^{1}H NMR ($CDCl_3$): δ 7.86−8.04 (m, 18H), 7.28−7.60 (m, 20H), 6.95 (m, 1H), 6.69 (t, 2H), 4.64 (s, 5H, Cp), 0.85 (s, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 128.6 (br. s). MS (FAB): *m*/*z* 1181 (M^+ − PhC_2H). IR (KBr, cm^{-1}): 1915 ($\nu_{C\equiv C}$). Anal. Calcd for $C_{73}H_{47}O_9P_3CoCu\cdot H_2O$: C, 67.29; H, 3.67. Found: C, 67.29; H, 3.66.

Preparation of [Cu(1)(η^2-Me$_3$SiC≡CSiMe$_3$)] (7). This compound was prepared similarly as for **6**, using bis(trimethylsilyl)acetylene instead of phenylacetylene. Yield: 14 mg (51%). ^{1}H NMR ($CDCl_3$): δ 7.95 (m, 15H), 7.81 (m, 3H), 5.56 (m, 3H), 7.46 (m, 6H), 7.26−7.40 (m, 9H), 4.62 (s, 5H, Cp), −0.16 (s, 18H, Si*Me*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 126.67 (br s). MS (FAB): *m*/*z* 1181 (M^+ − $Me_3SiC\equiv CSiMe_3$).

General Procedure for the Cu-Mediated Aziridination of Styrene. A mixture of styrene (0.9 mL, 7.7 mol), PhI=NTs (143 mg, 0.38 mmol), [Cu(MeCN)$_4$][BF$_4$] (6 mg, 0.019 mmol), and Na(**1**) (26 mg, 0.023 mmol) was stirred in CH_2Cl_2 (2 mL) at 0 °C for 2−4 h. The solvent was removed in vacuo, and the aziridine product was purified by column chromatography (silica gel; eluant Et_2O/hexanes, 3:7) and characterized by NMR spectroscopy. The enantioselectivity was determined by chiral HPLC analysis using a (*S*,*S*) WHELK-O column.

Catalytic Ring Opening of Cyclohexene Oxide with Me$_3$SiN$_3$. A mixture of Na(**1**) (70 mg, 0.06 mmol) and [Ti(O-*i*-Pr)$_2$Cl$_2$] (14.2 mg, 0.06 mmol) in THF (1 mL) was stirred at −20 °C for 15 min, and cyclohexene oxide (0.3 mL, 3 mmol) and Me_3SiN_3 (0.45 mL, 3.3 mmol) were added successively. The resulting solution was stirred at room temperature for 15 h and evaporated to dryness. Column chromatography (silica gel; eluant hexane/Et_2O 9:1) afforded the product 2-azido-1-((trimethylsilyl)oxy)cyclohexane, which was characterized by NMR spectroscopy. Yield: 480 mg (74%). The enantioselectivity of the product was determined to be 23% *R* by chiral GLC analysis using a cyclodextrin-β column.

Catalytic Allylation of Benzaldehyde with Allyltrichlorosilane. To a solution of Na(**1**) (224 mg, 0.2 mmol), freshly distilled benzaldehyde (106 mg, 1 mmol), and *i*-Pr$_2$EtN (1.4 mL) in dry CH_2Cl_2 (2.0 mL) at room temperature was added allyltrichlorosilane (0.17 mL, 1.2 mmol). The resulting mixture was stirred for 2 h and quenched with 1 mL of saturated $NaHCO_3$ solution and 10 mL of water. The solution was extracted into diethyl ether (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether 1:10) to afford the oily product 4-phenyl-1-buten-4-ol, which was identified by NMR spectroscopy. Yield: 80%. MS: *m*/*z* 140 (M^+), 107 (M^+ − 41). The enantioselectivity was determined to be 30% ee (*R*) by HPLC analysis using a Daicel Chiralcel OD column.

X-ray Crystallography. A summary of crystallographic data and experimental details for Na(**1**)($C_6H_{12}O_2$)$_2$·THF·(acetone), **6**·(toluene)·2CH_2Cl_2, and **7**·(toluene)·CH_2Cl_2 are listed in Table 1. Intensity data of all complexes were collected on a Bruker SMART APEX 1000 area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.701 73 Å). The structures were solved by direct methods and refined by full-matrix least-squares analyses on F^2. In Na(**1**)($C_6H_{12}O_2$)$_2$·THF·(acetone), the η^2-diacetone alcohol ligand and the cocrystallized THF molecule were found to be disordered. The carbonyl oxygen and carbon atoms in the η^2-diacetone alcohol were each refined with two positions, namely O(12) and O(12A) and C(73) and C(73A), respectively, with site occupancies of 75 and 25%. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their calculated positions. Calculations were performed using the SHELXTL[22] crystallographic software packages.

Table 1. Crystallographic Data and Experimental Details for Na(1)($C_6H_{12}O_2$)$_2$·C_4H_8O·C_3H_6O, 6·C_7H_8·2CH_2Cl_2, and 7·C_7H_8·CH_2Cl_2

	Na(**1**)($C_6H_{12}O_2$)$_2$·C_4H_8O·C_3H_6O	**6**·C_7H_8·2CH_2Cl_2	**7**·C_7H_8·CH_2Cl_2
formula	$C_{84}H_{79}CoNaO_{15}P_3$	$C_{82}H_{59}Cl_4CoCuO_9P_3$	$C_{81}H_{69}Cl_2CoCuO_9P_3Si_2$
fw	1503.30	1545.47	1528.82
a, Å	12.1884(7)	11.724(6)	12.339(3)
b, Å	21.180(1)	21.40(1)	21.186(5)
c, Å	27.271(2)	27.57(1)	27.436(6)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
V, Å^3	7040.0(7)	6919(6)	7172(3)
Z	4	4	4
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
ρ_{calcd}, g cm^{-3}	1.418	1.484	1.416
T, K	100(2)	100(2)	100(2)
μ, mm^{-1}	0.390	0.833	0.762
F(000)	3144	3168	3160
no. of rflns	35 119	34 464	31 786
no. of indep rflns	12 253	11 942	12 473
R_{int}	0.0461	0.0528	0.0917
R1, wR2 ($I > 2.0\sigma(I)$)	0.0541, 0.1318	0.0507, 0.1076	0.0613, 0.0927
R1, wR2 (all data)	0.0764, 0.1419	0.0687, 0.1131	0.1087, 0.1027
GOF	0.983	1.074	0.964

Results and Discussion

Ligand Synthesis. Treatment of P(O)(H)Cl_2[20] prepared from PCl_3 and *t*-BuOH with *S*-BINOL afforded P(O)(H)(*S*-BINOL). Deprotonation of P(O)(H)(*S*-BINOL) with NaH in THF followed by reaction with [CpCo(CO)I_2] gave the tripodal ligand Na[CpCo{P(O)(*S*-BINOL)$_3$}] (Na(**1**)), isolated as an air-stable yellow solid in 91% yield (Scheme 1).

The FAB mass spectrum shows a signal at *m*/*z* 924 corresponding to mononuclear Na(**1**), consistent with the solid-state structure (vide infra). Na(**1**) is soluble in polar organic solvents such as methanol, acetone, and CH_2Cl_2 but insoluble in Et_2O. The chiral nature of Na(**1**) is indicated by its large measured optical rotation, $[\alpha]^{22}_D$ = −464° (CH_2Cl_2, *c* 0.36). The ^{31}P{^{1}H} NMR spectrum displays a broad singlet at δ 122.5, which is more downfield than that for [Na$_2$(L$_{OPh}$)$_2$] (δ 103.8).[21] The *R* isomer Na[CpCo{P(O)(*R*-BINOL)}$_3$] was prepared similarly from P(O)(*R*-BINOL)H and [CpCo(CO)I_2].

Recrystallization of Na(**1**) from acetone/THF afforded yellow crystals characterized as the bis(diacetone alco-

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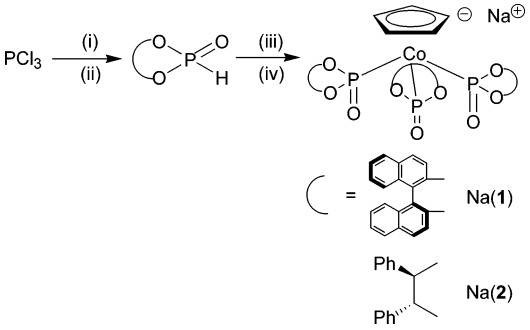
Scheme 1[a]



[a] Reagents and conditions: (i) *t*-BuOH, CH_2Cl_2, 0 °C; (ii) *S*-BINOL or LH_2, reflux; (iii) NaH, THF, 0 °C; (iv) [CpCo(CO)I_2], reflux.

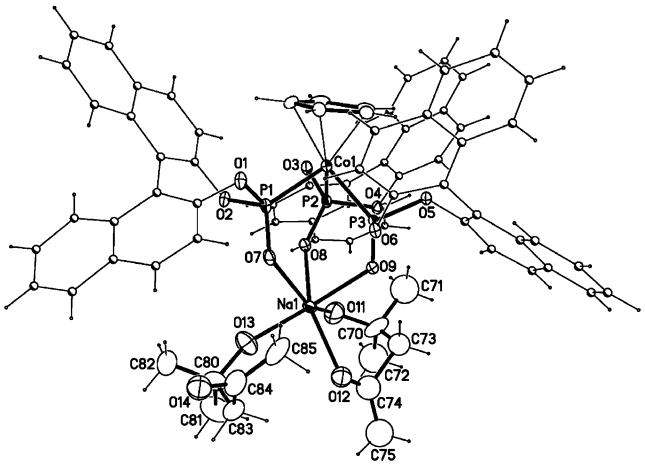


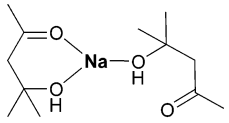
Figure 1. Perspective view of Na(*S*-**1**)$(C_6H_{12}O_2)_2$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Na(1)$(C_6H_{12}O_2)_2$

Na(1)−O(8)	2.305(3)	Na(1)−O(9)	2.289(3)
Na(1)−O(7)	2.375(4)	Na(1)−O(13)	2.328(5)
Na(1)−O(11)	2.872(7)	Na(1)−O(12)	2.319(7)
Na(1)−O(12A)	2.31(2)	P(1)−O(7)	1.473(3)
P(2)−O(8)	1.479(3)	P(3)−O(9)	1.466(3)
O(9)−Na(1)−O(8)	82.2(1)	O(9)−Na(1)−O(12)	102.2(2)
O(9)−Na(1)−O(13)	133.4(2)	O(8)−Na(1)−O(13)	124.5(2)
O(8)−Na(1)−O(12)	128.2(2)	O(13)−Na(1)−O(12)	89.7(2)
O(12)−Na(1)−O(11)	67.8(2)	O(9)−Na(1)−O(7)	81.5(1)
O(8)−Na(1)−O(7)	82.3(1)	O(13)−Na(1)−O(7)	67.5(2)
O(12)−Na(1)−O(7)	149.4(2)	O(7)−Na(1)−O(11)	142.1(2)
O(9)−Na(1)−O(11)	100.0(2)	O(8)−Na(1)−O(11)	60.7(1)
O(13)−Na(1)−O(11)	125.9(2)		

hol) adduct Na(**1**)$(C_6H_{12}O_2)_2$·THF·(acetone) ($C_6H_{12}O_2$ = $MeCOCH_2CMe_2OH$) by X-ray crystallography. Figure 1 shows a perspective view of Na(**1**)$(C_6H_{12}O_2)_2$; selected bond lengths and angles are listed in Table 2. In contrast with $[Na_3(L_{OMe})_3(\mu_3\text{-}H_2O)_2]$[6a] and $[Na_2(L_{OPh})_2]$,[21] which bind to Na in a μ-κ_3:κ_1 fashion, Na(**1**)$(C_6H_{12}O_2)_2$ is monomeric, containing a nonbridging κ_3 tripodal ligand and η^1- and η^2-diacetone alcohol ligands (Chart 3). The η^1-diacetone alcohol ligand binds to Na via the hydroxyl oxygen. Although metal compounds with η^2-$C_6H_{12}O_2$ ligands are well-known (e.g. $[Li(C_6H_{12}O_2)_2][Li(TMPP)]$, where H_2TMPP = *meso*-tris(3,4,5-methoxyphenyl)porphyrin),[23] to our knowledge, Na(**1**)$(C_6H_{12}O_2)_2$ is the first structurally characterized Na compound

Chart 3. Structure of Na(1)$(C_6H_{12}O_2)_2$



Na = Na(**1**)

containing an η^1-$C_6H_{10}O_2$ ligand. The diacetone alcohol ligands were apparently derived from the aldol reaction of the acetone solvent with residual NaH in the crude product,[23] because Na(**1**) alone did not induce an aldol reaction. The carbonyl oxygen and carbon atoms in the η^2-$C_6H_{10}O_2$ ligand are disordered, and the two sites were refined with an occupancy ratio of 3:1. The Na−O(η^1-$C_6H_{10}O_2$) distance (2.868(7) Å) is considerably longer than the Na−O(η^2-$C_6H_{10}O_2$) distances (average 2.323(7) Å), which is comparable to those in $[Na(MeOH)_6]^+$ (2.367 Å),[24] indicating that the η^1-$C_6H_{10}O_2$ ligand is only weakly coordinating. The average P−O (1.473 Å) and Na−O(P) (2.323 Å) distances are similar to those in $[Na_2(L_{OPh})_2]$ (1.474 and 2.284 Å, respectively).[21]

An attempt has been made to prepare a chiral tripodal ligand starting from chiral (*R*,*R*)-1,2-diphenylethane-1,2-diol (LH_2). Treatment of P(O)(H)(L) with NaH followed by reaction with [CpCo(CO)I_2] afforded Na[CpCo{P(O)(L)}$_3$] (Na(**2**)), characterized by mass spectrometry (*m*/*z* 924) and $^{31}P\{^1H\}$ NMR spectroscopy (δ 124). Unfortunately, despite several attempts, we did not obtain an analytically pure sample of Na(**2**).

Metal Complexes. Like NaL_{OR} (see Chart 1),[6] Na(**1**) forms stable complexes with main-group, lanthanide, and transition-metal ions. For example, treatment of Na(**1**) with [(η^6-*p*-cymene)$RuCl_2]_2$ in the presence of NH_4PF_6 afforded the mixed-sandwich compound [Ru(η^6-*p*-cymene)(1)][PF_6] (**3**). Reaction of Na(**1**) with [Ru(CO)Cl(CH=CHPh)$(PPh_3)_3$] afforded [Ru(**1**)(CO)(CH=CHPh)(PPh_3)] (**4**). The ^{31}P resonance for the PPh_3 ligand in **4** appeared as a doublet at δ 57.9, possibly due to coupling with a phosphorus nucleus in the tripodal ligand. The IR C−O stretching frequency for **4** is 1930 cm^{-1}, which is about 12 cm^{-1} higher than that for the ethoxy analogue [Ru(L_{OEt})(CO)(CH=CHPh)(PPh_3)],[5a] indicating that **1**$^-$ is a weaker donor than L_{OEt}^-.

Treatment of Na(**1**) with [Pr$(OTf)_3$] gave the bis-tripod compound [Pr(**1**)$_2$(OTf)] (**5**). It seems likely that the triflate in **5** is a coordinating ligand instead of a counteranion, given the preference of Pr(III) for higher coordination numbers and the observation of the molecular ion (*m*/*z* 2529) in the FAB mass spectrum. It may be noted that seven- and eight-coordinated lanthanide complexes containing L_{OR}^- (e.g. $[Y(L_{OMe})_2(MeCO_2)]$[25]) are well documented.

Copper complexes with tripodal ligands are of special interest, due to the finding that Cu(I) chiral Tp complexes are capable of catalyzing enantioselective cyclopropanation of olefins.[12] To this end, Cu(**1**) complexes were synthesized and their catalytic activity examined. Treatment of Na(**1**) with [Cu$(MeCN)_4$][BF_4] afforded an orange solution that presumably contains [Cu(**1**)-

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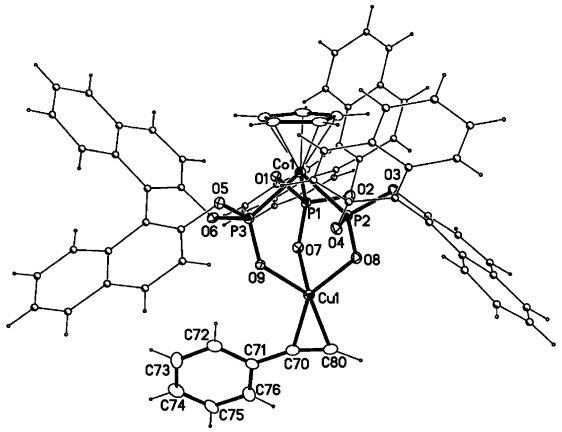

Figure 2. Perspective view of [Cu(**1**)(η^2-PhC≡CH)] (**6**).

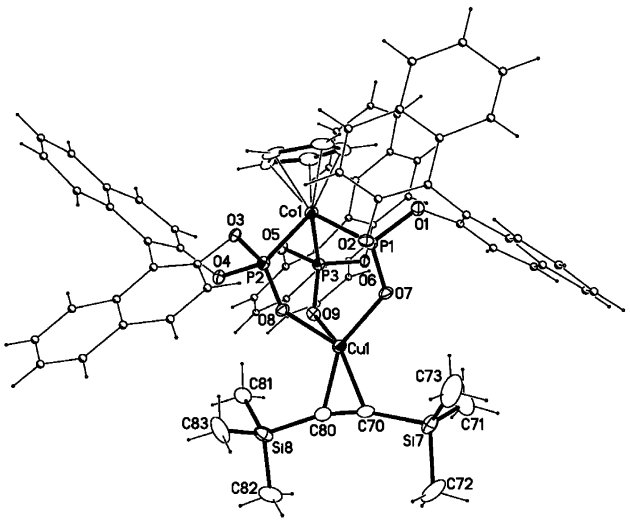

Figure 3. Perspective view of [Cu(**1**)(η^2-$Me_3SiC{\equiv}CSiMe_3$)] (**7**).

(MeCN)]. As reported by Kläui and co-workers,[26] [Cu(**1**)(MeCN)] reacted with olefins and acetylenes to give Cu(I) η^2-olefin and η^2-acetylene complexes, respectively. However, we were not able to isolate analytically pure samples of Cu(I) η^2-olefin complexes, presumably due to rapid dissociation/exchange of the labile olefin ligands during recrystallization.[26] In contrast, the analogous η^2-acetylene compounds are stable in solution and could be isolated as crystalline solids. Thus, treatment of [Cu(MeCN)$_4$][BF_4] with Na(**1**) in the presence of PhC≡CH and $Me_3SiC{\equiv}CSiMe_3$ afforded [Cu(**1**)(η^2-PhC≡CH)] (**6**) and [Cu(**1**)(η^2-$Me_3SiC{\equiv}CSiMe_3$)] (**7**), respectively. The IR C≡C stretching frequency for **6** was determined to be 1915 cm^{-1}, which is ca. 150 cm^{-1} lower than that for free phenylacetylene (2065 cm^{-1}), indicating that the Cu-to-acetylene back-bonding is not very strong.[27]

Both **6** and **7** have been characterized by X-ray diffraction. The molecular structures of **6** and **7** are shown in Figures 2 and 3, respectively. The corresponding selected bond lengths and angles are listed in Tables 3 and 4. Like [Cu(L_{OMe})(bq)] (bq = *p*-benzoquinone),[26b] both **6** and **7** exhibit a "2 + 1" distorted tripod ligand

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6

Cu(1)−C(80)	1.934(5)	Cu(1)−C(70)	1.961(5)
Cu(1)−O(8)	1.995(3)	Cu(1)−O(9)	2.046(3)
Cu(1)−O(7)	2.234(3)	P(1)−O(7)	1.481(3)
P(2)−O(8)	1.489(3)	P(3)−O(9)	1.483(3)
C(70)−C(80)	1.208(7)		
C(80)−Cu(1)−C(70)	36.1(2)	C(80)−Cu(1)−O(8)	111.0(2)
C(70)−Cu(1)−O(8)	146.9(2)	C(80)−Cu(1)−O(9)	143.7(2)
C(70)−Cu(1)−O(9)	112.6(2)	O(8)−Cu(1)−O(9)	96.0(1)
C(80)−Cu(1)−O(7)	117.7(2)	C(70)−Cu(1)−O(7)	109.1(2)
O(8)−Cu(1)−O(7)	88.3(1)	O(9)−Cu(1)−O(7)	85.8(1)
C(80)−C(70)−C(71)	160.2(5)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 7

Cu(1)−C(80)	1.976(6)	Cu(1)−C(70)	1.994(6)
Cu(1)−O(7)	2.008(4)	Cu(1)−O(8)	2.129(3)
Cu(1)−O(9)	2.161(4)	P(1)−O(7)	1.488(4)
P(2)−O(8)	1.495(3)	P(3)−O(9)	1.489(4)
C(70)−C(80)	1.250(7)		
C(80)−Cu(1)−C(70)	36.7(2)	C(80)−Cu(1)−O(7)	151.7(2)
C(70)−Cu(1)−O(7)	115.0(2)	C(80)−Cu(1)−O(8)	107.0(2)
C(70)−Cu(1)−O(8)	129.9(2)	O(7)−Cu(1)−O(8)	93.7(1)
C(80)−Cu(1)−O(9)	108.6(2)	C(70)−Cu(1)−O(9)	123.0(2)
O(7)−Cu(1)−O(9)	91.4(1)	O(8)−Cu(1)−O(9)	86.1(1)
Si(7)−C(70)−Cu(1)	123.5(3)	C(70)−C(80)−Si(8)	165.5(5)

coordination, with one Cu−O bond significantly longer than the other two. The distortion has been attributed to the tendency of a coordination number of 3 in Cu(I)−olefin compounds.[26] For **6**, the Cu−O(7) bond (2.234(3) Å) is ca. 0.2 Å longer than the other two Cu−O bonds (1.995(3) and 2.046(3) Å). The difference between the long (2.161(4) Å) and the short (2.008(4) and 2.129(3) Å) Cu−O bonds for **7** is, however, smaller, probably due to the steric effects of the trimethylsilyl group. The Cu−C distances in **6** and **7** (average 1.948 and 1.985 Å, respectively) are comparable to that in [Cu(hfac)(η^2-PhC≡CPh)] (hfac = 1,1,1,5,5,5-hexafluoropentanedionate; 1.958 Å)[27] and are shorter than that in [Cu(L_{OMe})(bq)] (2.015 Å).[26b] The short C≡C distances (1.208(7) and 1.250(7) Å) and large $C_\alpha-C_\beta-C(Si)$ angles (160.2(5) and 165.5(5)°, respectively) for **6** and **7**, which are comparable to that in [Cu(hfac)(η^2-$Me_3SiC{\equiv}CSiMe_3$)] (average 164°), indicate that the Cu-to-acetylene back-bonding is weak.[28]

Asymmetric Catalysis with Na(1). The potential of Na(**1**) for asymmetric catalysis has been evaluated. For example, Cu(**1**) complexes were found to be active catalysts for aziridination of olefins with PhI=NTs (Ts = tosyl) (Table 5). The Cu catalyst was most conveniently prepared in situ from [Cu(MeCN)$_4$][BF_4] and Na(**1**). Thus, treatment of styrene with PhI=NTs in the presence of 5 mol % of the Cu catalyst in CH_2Cl_2 at 0 °C afforded styrene aziridine in 67% yield and 41% ee (*R*). A similar yield and ee were obtained when the acetylene compound **6** was used as catalyst. It appears that the enantioselectivity of aziridination was enhanced by electron-withdrawing substituents of styrene. For example, the ee for 4-chlorostyrene aziridine is 61%, while that for 4-methylsytrene aziridine is 27%. The aziridination of 2-chlorostyrene was very slow, presumably due to steric effects. CH_2Cl_2 appears to be the best solvent for the catalytic aziridination. A poor yield and

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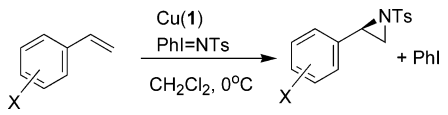
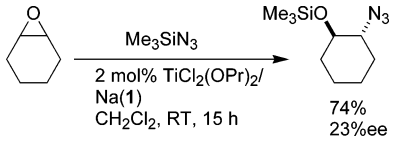
Table 5. Cu-Catalyzed Asymmetric Aziridination of Substituted Styrenes[a]



entry	X	solvent	time (h)	yield[b] (%)	ee (%),[c] config[d]
1	H	CH_2Cl_2	3	85	41, *R*
2[e]	H	CH_2Cl_2	3	88	43, *S*
3	4-F	CH_2Cl_2	3	82	32, *R*
4	4-Cl	CH_2Cl_2	3	82	61, *R*
5	4-Br	CH_2Cl_2	3	67	41, *R*
6	4-Me	CH_2Cl_2	3	77	34, *R*
7	3-Cl	CH_2Cl_2	3	87	27, *R*
8	2-Cl	CH_2Cl_2	3	trace	nd[f]
9	4-Cl	toluene	4	95	50, *R*
10	4-Cl	MeCN	3	35	25, *R*

[a] Experimental conditions: styrene (7.7 mmol), PhI=NTs (0.38 mmol), $[Cu(MeCN)_4][BF_4]$ (0.019 mmol), and Na(**1**) (0.023 mmol) were stirred in CH_2Cl_2 (2 mL) at 0 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Determined by optical rotation. [e] The enantiomeric complex Na(*R*-**1**) was used as the ligand. [f] Not determined.

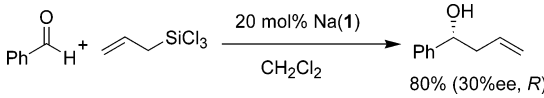
Scheme 2



selectivity were obtained when coordinating MeCN was used as the solvent. A Cu nitrene species has been postulated as the reactive intermediate in Cu-catalyzed aziridination.[29] An attempt to isolate the Cu nitrene intermediate by reacting **6** with a stoichiometric amount of PhI=NTs at low temperature was unsuccessful. Treatment of more soluble $[L_{OEt}Cu(MeCN)]$ with PhI=NTs in CH_2Cl_2 yielded a red species that exhibited an absorption peak at 750 nm in the optical spectrum. However, recrystallization of this red species from CH_2Cl_2/hexane led to isolation of the known Cu(II) bis-tripod compound $[Cu(L_{OEt})_2]$.[30]

Apart from aziridination of olefins, catalytic ring opening of epoxides with Na(**1**) (Chart 3) has been investigated. For example, Na(**1**) in conjunction with $[Ti(O\text{-}i\text{-}Pr)_2Cl_2]$ was found to be an active catalyst for ring opening of epoxides. In the presence of 2 mol % of $[Ti(O\text{-}i\text{-}Pr)_2Cl_2]$/Na(**1**), cyclohexene oxide was ring-opened by Me_3SiN_3 to give 2-azido-1-((trimethylsilyl)-oxy)cyclohexane in 74% yield and 23% ee (1*R*,2*R*) (Scheme 2). The Pr(III) bis-tripod compound **5** was not capable of catalyzing ring opening of epoxides, probably due to steric effects.

Scheme 3



The use of chelating P=O ligands as chiral Lewis base catalysts for allylation of aldehydes with allyltrichlorosilane has attracted much attention recently.[31] In this connection, the activity of Na(**1**) toward the allylation of benzaldehyde was examined. Treatment of benzaldehyde with allyltrichlorosilane in the presence of 20 mol % of Na(**1**) afforded the homoallyl alcohol 4-phenyl-1-buten-4-ol in 80% yield and 30% ee (Scheme 3).

The generally accepted mechanism for Lewis base catalyzed allylation of aldehydes involves binding and activation of the silyl group by the P=O chelate and subsequent allylation.[30] It is not clear whether $\mathbf{1}^-$ binds to Si in a bidentate or tridentate fashion. It may be noted that half-sandwich complexes of the type $[L_{OEt}\text{-}SnCl_3]$[6a] have been isolated and structurally characterized. Although the enantioselectivity of the allylation reaction is modest, Na(**1**) represents a new type of tridentate P=O Lewis base ligand for the catalytic allylation reaction.

Conclusion

In summary, we have synthesized the first chiral C_3-symmetric anionic tris(phosphinite) ligand, Na(**1**), derived from optically active bi-2-naphthol. The solid-state structure and absolute configuration of this tripodal ligand have been unambiguously established by X-ray crystallography. Na(**1**) proved to be a versatile ligand that is compatible with both hard and soft metal ions. The crystal structures of two Cu(**1**) η^2-acetylene complexes that exhibit a 2 + 1 distorted ligand coordination have been determined. The utility of Na(**1**) in asymmetric organic reactions, namely the Cu-catalyzed aziridination of styrene, the Ti-catalyzed ring opening of cyclohexene oxide, and the allylation of benzaldehyde, has been demonstrated. Efforts are being made to improve the stereocontrol of this chiral oxygen tripodal ligand by tuning the steric and/or electronic factors of the BINOL groups.

Acknowledgment. Financial support from the Hong Kong Research Grants Council (HKUST6066/98P and 606623) and the Hong Kong University Grants Committee (Area of Excellence Scheme, AoE/P-10/01-1) is gratefully acknowledged. We thank the reviewers for pointing out the errors in the manuscript.

Supporting Information Available: X-ray crystallographic data for Na(*S*-**1**)$(C_6H_{12}O_2)_2$, **6**, and **7** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034320D

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