one halide from dihaloalkanes.[2] However, to the best of our knowledge, this is the first example involving the selective replacement of a single halide by a metal anion from an aliphatic alkanedioyl dihalide.[6]

We investigated these reactions under various conditions in order to gain more insight into the mechanism. When a fivefold excess of **1** is used, **3** is formed in lower yields (5–7%). No bimetallic alkanedioyl complexes were observed. Attempts to isolate intermediate **4** by a slow addition of **1** into a THF solution containing excess alkanedioyl dichloride (up to 5 equiv) at −78 °C were unsuccessful. However, we were able to prepare **4b** by a two-step reaction sequence. Treatment of **3b** with aqueous HCl in THF afforded the corresponding carboxylic acid (**5b**),[7] which was then converted into acyl chloride **4b**[7] by treating with 1.2 equiv of oxalyl chloride at 35 °C for 20 min in CH_2Cl_2 (Scheme II). Complex **4b** may be trapped by H_2O and CH_3OH to form **5b** and $(\eta^5\text{-}C_5H_5)(CO)_3WC(O)(CH_2)_3C(O)OCH_3$ (**6b**),[7] respectively. It cannot be isolated, however, since upon solvent removal, it converts completely into **3b**. The removal of HCl in vacuo presumably drives the reaction toward **3b**. There are several examples of spontaneous cyclization of ω-bromoacyl derivatives into 2-oxacyclopentylidenes.[3] Since acyl chlorides are more reactive than alkyl bromides, our reaction may go through a similar cyclization sequence. This is followed by the deprotonation of the acidic proton α to the carbene carbon by a chloride ion to produce the observed products.[8,9]

Although a base is not required for the transformation from **4** to **3**, we believe the metal anion is important in assisting the cyclization reaction. A solution of **4b** prepared in situ decomposes slowly into $(\eta^5\text{-}C_5H_5)(CO)_3WCl$ with a half-life of approximately 2 h. With the addition of M^- ($M = (\eta^5\text{-}C_5H_5)Fe(CO)_2$, $(\eta^5\text{-}C_5H_5)Mo(CO)_3$, $(\eta^5\text{-}C_5H_5)W(CO)_3$), **3b** and the corresponding M–H are formed within a few minutes. Especially noteworthy is the reaction between **4b** and Fp^-. Our result indicates that the formation of lactone (elimination) is preferred over the acylation of the second acyl chloride (substitution) even with the powerful nucleophile Fp^-. This suggests that the known reaction between Fp^- and alkanedioyl dichlorides may go through a different route rather than the simple disubstitution mechanism. This possibility is currently under investigation.

Acknowledgment. We thank the Research Corp. and the donors of Petroleum Research Fund, administered by the American Chemical Society, for their financial support. Funds for the purchase of the IBM AF 200-MHz FT NMR spectrometer were provided by the National Science Foundation (RUI Grant Number CHE-8513187) and the Fletcher Jones Foundation.

(6) One example of a tetracarbonylferrate(II) replacing one chloride from phthaloyl dichloride was reported: Mitsudo, T. A.; Watanabe, Y.; Tanaka, M.; Yamamoto, K.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 305.

(7) Compound **4b**: IR ($CDCl_3$, cm^{-1}) 2021 (s), 1921 (vs), 1780 (m), 1626 (m); ^1H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.59 (s, 5 H, Cp), 3.00 (t, 2 H, J = 6.8 Hz, $WC(O)CH_2$), 2.89 (t, 2 H, J = 7.3 Hz, $CH_2C(O)Cl$), 1.78 (m, 2 H, $CH_2CH_2CH_2$). Compound **5b**: IR (KBr, cm^{-1}) 2950–3110 (br, m), 2008 (s), 1903 (vs), 1718 (s), 1625 (s); ^1H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.57 (s, 5 H, Cp), 3.01 (t, 2 H, J = 6.9 Hz, $WC(O)CH_2$), 2.28 (t, 2 H, J = 7.4 Hz, $CH_2C(O)OH$), 1.72 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$, 23 °C) δ 244.9 (W–C(O)), 226.0, 220.0 (W–CO), 178.6 (C(O)OH), 95.3 (Cp), 65.5, 32.8, 20.2 (CH_2). Anal. Calcd for $C_{13}H_{12}O_6W$: C, 34.85; H, 2.70. Found: C, 35.19; H, 2.65. Compound **6b**: IR ($CHCl_3$, cm^{-1}) 2018 (s), 1925 (vs), 1731 (m), 1626 (m); ^1H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.56 (s, 5 H, Cp), 3.63 (s, 3 H, OCH_3), 2.97 (t, 2 H, J = 7.0 Hz, $WC(O)CH_2$), 2.22 (t, 2 H, J = 7.4 Hz, $CH_2C(O)OCH_3$), 1.69 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$, 23 °C) δ 244.3 (W–C(O)), 226.1, 220.0 (W–CO), 173.6 ($C(O)OCH_3$), 95.2 (Cp), 65.6 (C_xH_2), 51.3 (OCH_3), 33.0, 20.4 (CH_2). This compound is identical with a sample prepared from $Na(\eta^5\text{-}C_5H_5)W(CO)_3$ and methyl 4-(chloroformyl)butyrate.

(8) The acidity of these protons are well-documented: Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

(9) This cyclic carbene could also be an intermediate in the reaction between **4** and **1**, although we have no evidence for its formation. The reaction between a cationic molybdenum oxacyclopentylidene and $(\eta^5\text{-}C_5H_5)W(CO)_3^-$ was reported to form a bimetallic compound in good yield.[3c]

Chiral and C_2-Symmetrical Bis(oxazolinylpyridine)rhodium(III) Complexes: Effective Catalysts for Asymmetric Hydrosilylation of Ketones

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Summary: Chiral bis(oxazolinylpyridine)rhodium(III) trichloride complexes **2a–c** were synthesized by the reaction of rhodium(III) trichloride with bis(oxazolinylpyridine) (pybox: *py*ridine, *b*is(*ox*azolinyl)) derivatives **1a–c**, which are newly designed as chiral ligands and prepared from pyridine-2,6-dicarboxylic acid and (*S*)-valinol, (*S*)-*sec*-leucinol, and (*S*)-*tert*-leucinol, respectively. We have examined the asymmetric hydrosilylation of ketones with the rhodium complexes **2a–c** and diphenylsilane to find extremely high enantioselectivity in the formation of secondary alcohols having the *S* configuration.

Chiral catalysts in the reduction of ketones have been currently required to attain extremely high level of enantioselectivity.[1] However in the hydrosilylation of ketones any chiral phosphines could not achieve higher optical yields,[2] while it is noteworthy that some nitrogen-containing organic ligands reported by Brunner's group can attain excellent results, more than 90% ee.[3] In terms of molecular and enantioface recognition, we have been interested in designing chiral organic molecules as ligands for transition-metal catalysts. We report here new chiral and C_2-symmetrical terdentate pyridine ligands and their rhodium(III) complexes, which exhibit high enantioselectivity in the hydrosilylation of several ketones.

Our design of the pyridine ligands **1a–c**, *bis*(*ox*azolinyl*py*ridines) (pybox), is distinctive in that the two chiral oxazoline rings having the two bulky alkyl groups make a chiral and C_2-symmetrical concave. In the rhodium complexes **2a–c**, the two alkyl groups are placed as closely

(1) (a) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856. (b) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *Ibid.* **1988**, *110*, 629. (c) Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C.-P.; Singh, V. K. *Ibid.* **1987**, *109*, 7925.

(2) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. For review, see: Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 103.

(3) (a) Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1984**, *3*, 1354. (b) Brunner, H.; Kürzinger, A. *J. Organomet. Chem.* **1988**, *346*, 413.

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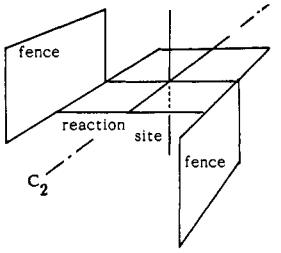
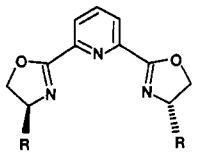
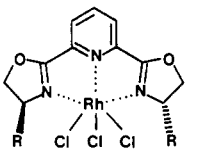
as possible to the reaction site as "chiral fences".





1a (R=i-Pr), b (R=s-Bu), c (R=t-Bu)



2a (R=i-Pr), b (R=s-Bu), c (R=t-Bu)

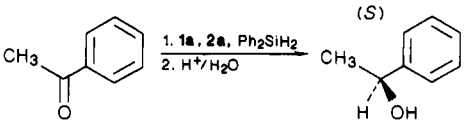
Starting from pyridine-2,6-dicarboxylic acid with (*S*)-valinol, (*S*)-*sec*-leucinol, and (*S*)-*tert*-leucinol,[4] we can prepare 2,6-bis[4′-(*S*)-*R*-oxazolin-2-yl]pyridines (**1a–c**) in four steps (R = *i*-Pr, **1a**, ip-pybox; R = *sec*-Bu, **1b**, sb-pybox; R = *t*-Bu, **1c**, tb-pybox).[5] Treatment of **1a–c** with $RhCl_3(H_2O)_3$ in ethanol at 80 °C for 3 h gave (*R*-pybox)-$RhCl_3$ (**2a–c**), respectively: **2a**, 70%; **2b**, 69%; **2c**, 72%.[6]

Complex **2a** was characterized by a single-crystal X-ray structure study. The rhodium coordination geometry is slightly distorted octahedral; the N(2)–Rh–N(3) angle is 158.7° (Figure 1).[7] The orientation of the both oxazoline rings to the rhodium center makes a reasonable chiral environment with the two isopropyl groups spreading over the reaction site.

We have examined the rhodium complexes **2a–c** as catalysts for asymmetric induction in the hydrosilylation of acetophenone. Complexes **2a–c** showed no catalytic activity for hydrosilylation below 30 °C. However, addition of some silver ions or Lewis acids could make the complexes active to react smoothly, followed by hydrolysis giving (*S*)-1-phenylethanol. Complex **2a** (1 mol %) and diphenylsilane (1.6 equiv) with silver trifluoromethanesulfonate (AgOTf, 1.1 mol %) and $AgBF_4$ (2 mol %) gave high enantioselectivity, 89% ee and 94% ee, respectively (Table I).

Under the same condition **2b** and diphenylsilane with $AgBF_4$ (2 mol %) gave 91% ee for the reduction of acetophenone, while the combination of **2c** and $AgBF_4$ afforded low optical yield. In assistance with AgOTf, **2c** gave 83% ee for acetophenone.

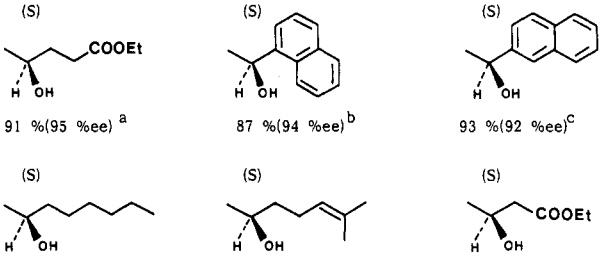
Table I. Hydrosilylation of Acetophenone with (ip-pybox)$RhCl_3$ (2a) and Diphenylsilane[a]



additive (mol %)	1a (ip-pybox), mol%	conditn temp, °C; time, h	yield, %	opt yield, %
no	1.7	room temp	no reaction	
BF_3·Et_2O[b] (1.5)	3.5	0; 14[c]	90	82
$EtAlCl_2$[b] (1.5)	3.5	0; 18[c]	89	67
AgOTf (1.3)	0	0; 26[d]	61	56
AgOTf (1.1)	3.0	0; 17[d]	84	83
AgOTf (1.1)	7.0	−20; 27[c]	96	89
$AgBF_4$ (2.0)	4.0	0; 2	91	94
$AgBF_4$ (1.0)	4.0	−5; 4.5	90	93

[a] PhCOMe (8.0 mmol), Ph_2SiH_2 (12.8 mmol), **2a** (0.08 mmol), additive (0.08–0.16 mmol), without solvent. After hydrolysis with methanol (5 mL) and hydrochloric acid (1 N, 14 mL) at 0 °C, the yields were determined by GPLC (PEG 20M). The conversions were 100%, but small amounts of acetophenone (ca. 5%) derived from the corresponding silyl enol ether were detected. The optical yields were determined on the basis of ^1H NMR study of the MTPA ester and were in accordance with their optical rotation: Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543. Nagai, U.; Shishido, T.; Chiba, R.; Mitsuhashi, H. *Tetrahedron* **1965**, *21*, 1701. [b] At first **2a** was treated in CH_2Cl_2 with the acids at room temperature for 1 h. Then **1a**, the ketone, and the silane were added at 0 °C. [c] CH_2Cl_2 (1.0 mL). [d] THF (6.0 mL).

Several ketones were subjected to hydrosilylation with **2a** (1 mol %) under the following conditions as a standard: ketone (8.0 mmol), $AgBF_4$ (2 mol %), **1a** (6 mol %), Ph_2SiH_2 (12.8 mmol), THF (1.0 mL), at −5 to −10 °C. The reactions gave high enantioselection to form the following secondary (*S*)-alcohols.[8]



*Temp., time; a, 0°C, 7 h; b, -5°C, 7 h; c, -5°C, 6 h; d, 5°C, 24 h; e, 20°-25°C, 16 h; f, -5°C, 24 h.

Ethyl levelinate is reduced more selectively than reported before,[9] and the linear aliphatic ketones 2-octanone and 6-methyl-5-hepten-2-one give 59% ee and 70% ee, respectively.

(4) The amino alcohols were prepared by reduction of the corresponding optically pure amino acids, L-valine, L-isoleucine, and L-*tert*-leucine (Dai-ichikagaku Yakuhin Inc.) with $LiAlH_4$ in THF. See: Itsuno, S.; Hirao, A.; Nakahama, S.; Yamazaki, N. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1673. L-*tert*-Leucinol: bp 117–120 °C (57 mmHg), $[\alpha]^{25}_D$ = +37.24° (*c* = 1.02 in EtOH).

(5) From pyridine-2,6-dicarboxylic acid: (1) $SOCl_2$, reflux, 10 h; (2) the amino alcohol (3.0 equiv), Et_3N, room temperature, 1 day; (3) $SOCl_2$, reflux, 3 h; (4) NaOH, MeOH–H_2O, room temperature, 1–3 days. **1a**: mp 152–153 °C, $[\alpha]^{26}_D$ = −116.8° (*c* = 1.01 in CH_2Cl_2). **1b**: mp 143–144 °C, $[\alpha]^{19}_D$ = −105.5° (*c* = 1.24 in CH_2Cl_2). 1c: mp 242–243 °C, $[\alpha]^{26}_D$ = −114.8° (*c* = 1.07 in CH_2Cl_2).

(6) The rhodium complexes were purified by silica gel column chromatography with methanol and ethyl acetate as eluents. **2a** includes a half mole of dichloromethane by precipitation from dichloromethane and ether.

(7) Crystal data for **2a**: $C_{17}H_{23}N_3O_2RhCl_3(H_2O)$; fw 528.65 (orange prisms), which was obtained by recrystallization from EtOH–H_2O; orthorhombic, space group $P2_12_12_1$; a = 12.597 Å, b = 16.694 Å, c = 11.821 Å, V = 2485 (7) Å^3; Z = 4, D(calcd) = 1.387 g/cm^3. The data ($2 < 2\theta < 40°$) were collected on a Rigaku AFC-5 diffractometer by using Mo Kα radiation (0.71068 Å); total observations, 2620; criteria for selecting data used in refinement $|F_o| > 3\sigma(|F_o|)$; number of data used in refinement, 1337; final R = 0.064 and R_w = 0.066 ($\sum w(|F_o| - |F_c|)/\sum w|F_o|$). The crystal decomposed during the data collection. The absolute configuration was assigned on the basis of that of the starting amino acid L-(*S*)-valine.

(8) Isolated yields. The enantiomeric excess were determined by optical rotation and ^1H NMR study of their MTPA esters. For the values of $[\alpha]_D$, see ref 2. Collyer, T. A.; Kenyon, J. *J. Chem. Soc.* **1940**, *143*, 676. Balfe, M. P.; Downer, E. A. W.; Evans, A. A.; Kenyon, J.; Poplett, R.; Searle, C. E.; Tarnoky, A. L. *Ibid.* **1946**, 797. Pickard, R. H.; Kenyon, J. *Ibid.* **1907**, *91*, 2058. Mori, K. *Tetrahedron* **1975**, *31*, 3011.

(9) The product alcohol ethyl (*S*)-4-hydroxypentanoate (95% ee by the MTPA ester) was converted to γ-valerolactone by treatment with *p*-toluenesulfonic acid. The lactone shows −31.7° of $[\alpha]^{20}_D$ (neat) and −31.6° (*c* = 0.86, CH_2Cl_2). See ref 2 and: Levene, P. A.; Haller, H. L. *J. Biol. Chem.* **1926**, *69*, 165. $[\alpha]^{22}_D$ = −27.75° (neat): Mori, K. *Tetrahedron* **1975**, *31*, 3011. $[\alpha]^{23}_D$ = −29.6° (*c* = 1.29, CH_2Cl_2).

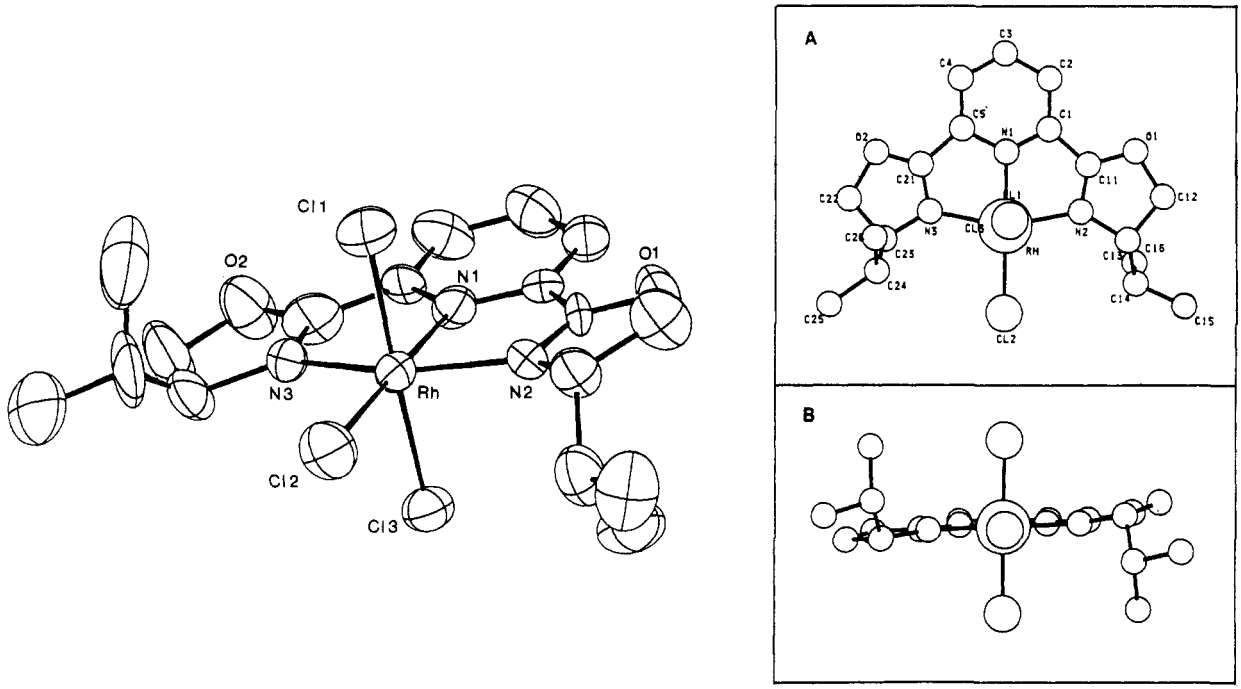
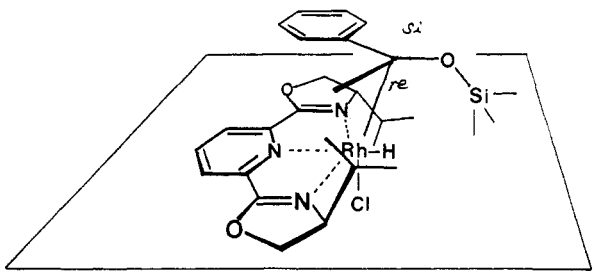


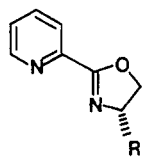
Figure 1. ORTEP drawing of **2a** with 50% probability ellipsoids and PLUTO drawing of **2a** (A, top view; B, front view). Selected bond distances (Å) and angles (deg) are as follows: Rh-N(1), 2.003 (17); Rh-N(2), 2.069 (19); Rh-N(3) 2.083 (17); Rh-Cl(1), 2.334 (6); Rh-Cl(2), 2.352 (7); Rh-Cl(3), 2.342 (8); N(1)-Rh-N(2), 78.5 (8); N(1)-Rh-N(3), 80.2 (8); N(2)-Rh-Cl(2), 101.5 (6); N(3)-Rh-Cl(2), 99.7 (5).

Thus we have attained highly enantioselective reduction of several ketones in hydrosilylation with the rhodium catalysts having the chiral terdentate ligands *bis(oxazolinylpyridines)*. According to the reported mechanism for hydrosilylation,[10] the insertion reaction of a ketone occurs preferably at the Rh-Si bond and not at the Rh-H bond. Therefore, although we have no evidence for our catalytic system, we have assumed a following intermediate selecting the *re* face of acetophenone to produce the *S* absolute configuration.



We have also examined, for comparison, *mono(oxazolinylpyridines)* (pymox) **3a** and **3b**.[11] The reduction of acetophenone with **3a** (5 mol %), Rh(COD)Cl/2 (0.5 mol %), and Ph_2SiH_2 (1.6 equiv) gave the (*R*)-alcohol in 60% ee (88% yield) at −5 °C for 7 days. The same reduction with **3b** (tb-pymox) gave the (*R*)-alcohol in 91% ee at −5 °C for 1 day.[12]

It is interesting that in contrast to the formation of (*S*)-alcohols with the bis(oxazolinyl) derivatives, the mono(oxazolinyls) produce (*R*)-alcohols in high optical yields; the origin of chirality is derived from the same *S* configuration of starting L-valinol and L-leucinols.



3a (R=i-Pr)

3b (R=t-Bu)

Acknowledgment. We thank Dr. M. Akita, Prof. H. Suzuki, and Prof. Y. Moro-oka (Tokyo Institute of Technology) for assistance with X-ray analysis.

Supplementary Material Available: Synthetic and spectroscopic data for the ligands and the rhodium complexes and tables of atomic coordinates, bond angles and distances, and anisotropic thermal parameters (9 pages); a listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

(10) Peyronel, J. F.; Kagan, H. B. *Nouv. J. Chim.* **1978**, *2*, 211. Also see ref 2 and references cited therein.

(11) The pyridines were prepared by treatment of picolinic acid with $SOCl_2$, and then the corresponding amino alcohols followed by cyclization with $SOCl_2$. Brunner, H.; Obermann, U.; Wimmer, P. *J. Organomet. Chem.* **1986**, *316*, C1-C3.

(12) The combination of **1a** (3 mol %) and Rh(COD)Cl/2 (0.05 mmol %) with Ph_2SiH_2 reduced acetophenone in 76% ee (88% product yield) at 0 °C for 28 h to give the (*S*)-alcohol.

A Novel Copper(I) Complex with Bridging Alkyne Ligands. The Synthesis and Structural Characterization of $[Cu_4(O_2CCF_3)_4(\mu\text{-EtC}{\equiv}\text{CEt})_2]$

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Summary: The reaction of $Cu_4(O_2CCF_3)_4{\cdot}2C_6H_6$ with EtC≡CEt yields the novel tetranuclear complex $Cu_4(O_2CCF_3)_4(\mu\text{-EtC}{\equiv}\text{CEt})_2$ that has been shown in the solid state to contain two $Cu_2(\mu\text{-EtC}{\equiv}\text{CEt})$ units held together by four bridging trifluoroacetate ligands.

Metal complexes containing bridging alkyne ligands are abundant for most elements of the transition series.[1]

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