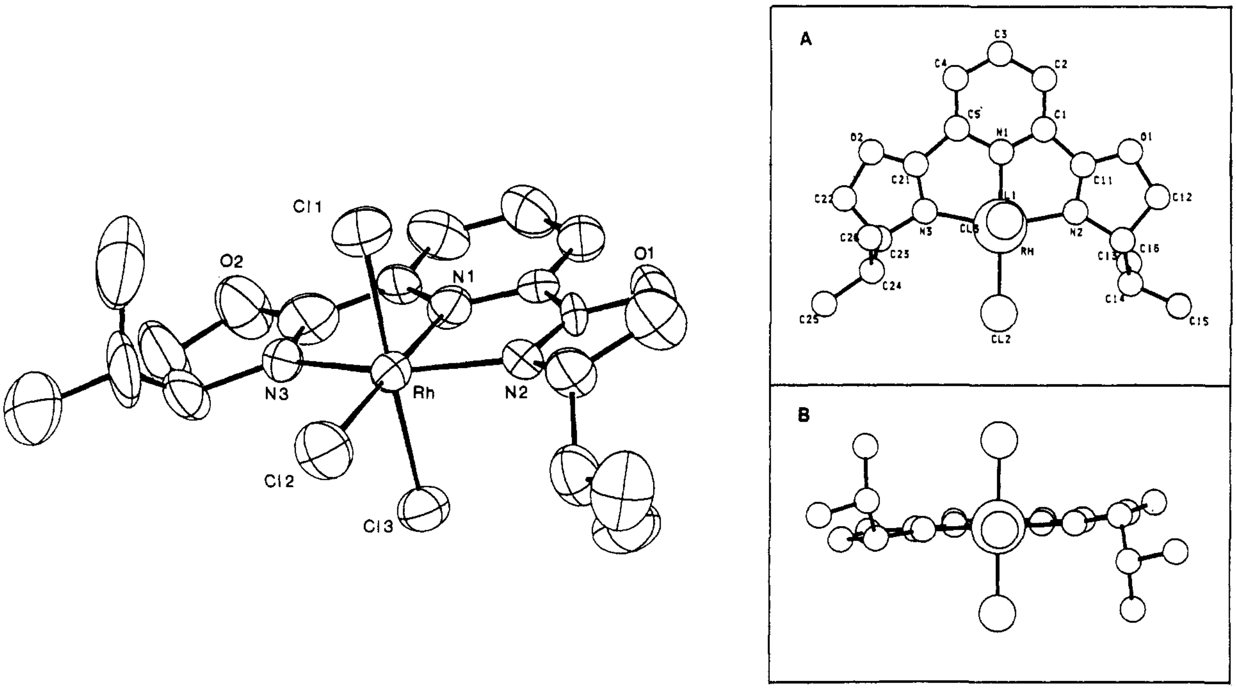
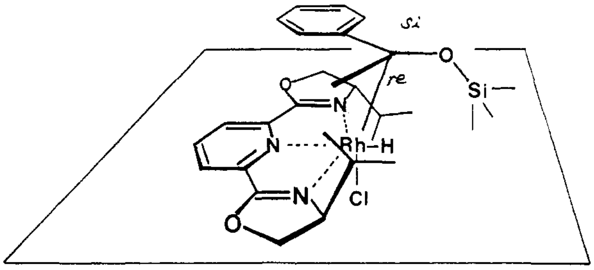


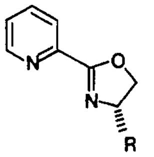
Figure 1. ORTEP drawing of **2a** with 50% probability ellipsoids and PLUTO drawing of **2a** (A, top view; B, front view). Selected bond distances (Å) and angles (deg) are as follows: Rh-N(1), 2.003 (17); Rh-N(2), 2.069 (19); Rh-N(3) 2.083 (17); Rh-Cl(1), 2.334 (6); Rh-Cl(2), 2.352 (7); Rh-Cl(3), 2.342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

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

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Summary: The reaction of $Cu_4(O_2CCF_3)_4{\cdot}2C_6H_6$ with $EtC{\equiv}CEt$ yields the novel tetranuclear complex $Cu_4(O_2CCF_3)_4(\mu\text{-}EtC{\equiv}CEt)_2$ that has been shown in the solid state to contain two $Cu_2(\mu\text{-}EtC{\equiv}CEt)$ 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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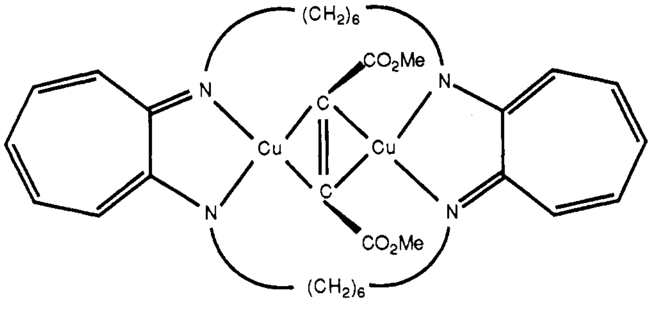
[10] Peyronel, J. F.; Kagan, H. B. *Nouv. J. Chim.* **1978**, *2*, 211. Also see ref 2 and references cited therein.

[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.

Notable exceptions to these are the elements of the copper subgroup. The only dinuclear copper(I) complexes containing bridging alkyne ligands, $[Cu_2(\mu\text{-}RC{\equiv}CR)(tropocoronand)]$ (R = $MeCO_2$ (**1**), $EtCO_2$, Ph, Me), were reported recently by Lippard.[2] These contain a large macrocyclic ligand that coordinates two copper atoms at a distance appropriate for a μ-alkyne ligand. Floriani has reported that the reaction of $Cu_4(O_2CPh)_4$ with $PhC{\equiv}CPh$ yields the dinuclear complex $Cu_2(\mu\text{-}O_2CPh)_2(PhC{\equiv}CPh)_2$ (**2**) which has bridging benzoate ligands but terminally coordinated alkyne ligands.[3] We wish to report the synthesis and solid-state structure of the unusual tetranuclear complex $Cu_4(O_2CCF_3)_4(\mu\text{-}EtC{\equiv}CEt)_2$ (**3**), which contains two alkyne ligands bridging copper atoms not directly bridged by other ligands.



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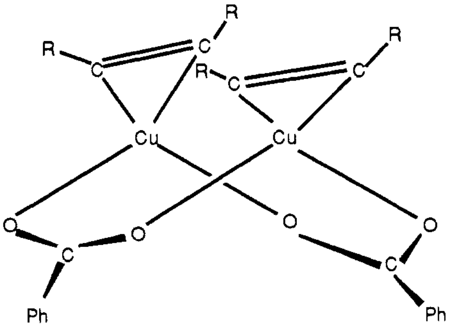


2

Complex **3** was obtained from the reaction of $Cu_4(O_2CCF_3)_4{\cdot}2C_6H_6$[4] with $EtC{\equiv}CEt$ in benzene at ambient temperature.[5] It was also obtained by addition of the alkyne to an equimolar mixture of NaO_2CCF_3 and $[Cu(MeCN)_4]^+$ in acetone. It is soluble in common organic solvents and can be recrystallized from hexane.

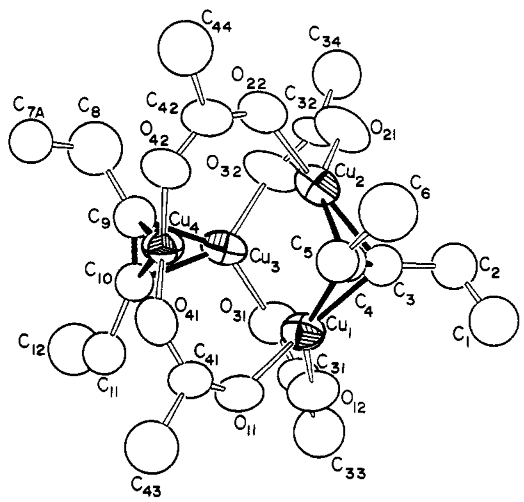
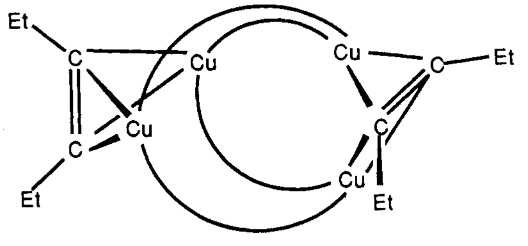


Figure 1. An ORTEP diagram of $Cu_4(O_2CF_3)_4(\mu\text{-}EtC{\equiv}CEt)_2$ (**3**) showing 30% probability thermal ellipsoids. The disordered fluorine atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Cu(1)···Cu(2) = 2.820 (3), Cu(1)···Cu(3) = 3.136 (3), Cu(1)···Cu(4) = 3.130 (3), Cu(2)···Cu(3) = 3.079 (3), Cu(2)···Cu(4) = 3.166 (3), Cu(3)···Cu(4) = 2.799 (3), Cu(1)–C(3) = 1.97 (2), Cu(1)–C(4) = 1.99 (2), Cu(2)–C(3) = 1.97 (3), Cu(2)–C(4) = 2.00 (2), Cu(3)–C(9) = 1.98 (2), Cu(3)–C(10) = 2.00 (2), Cu(4)–C(9) = 1.92 (2), Cu(4)–C(10) = 1.98 (2), C(3)–C(4) = 1.26 (2), C(9)–C(10) = 1.26 (2); C(2)–C(3)–C(4) = 152 (2), C(3)–C(4)–C(5) = 155 (2), C(8)–C(9)–C(10) = 148 (2), C(9)–C(10)–C(11) = 156 (2).

An ORTEP drawing of **3** is shown in Figure 1 along with selected interatomic distances and angles.[6] The structure consists of two $Cu_2(\mu$-alkyne) units held together by bridging trifluoroacetate groups. Each $Cu_2(\mu$-alkyne) unit has a typical butterfly arrangement[1] of the two copper atoms and the bridging acetylenic carbon atoms. The Cu–Cu distances within the butterfly units are 2.820 (3) and 2.799 (3) Å, and these metal atoms are bridged directly only by the alkyne. The two $Cu_2(\mu$-alkyne) units within the molecule are oriented perpendicular with respect to each other. This places the four copper atoms in a pseudotetrahedral arrangement. The Cu–Cu distances between the two halves average at 3.128 (3) Å. The two oxygen and acetylenic carbon atoms form a nearly planar arrangement around each copper atom, but the copper atoms lie, on average, 0.248 Å out of the plane toward the interior of the



3

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[3] Pasquali, M.; Leoni, P.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1982**, *21*, 4324.

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[5] To a benzene (50 mL) solution (under nitrogen) of $[CuO_2CCF_3]_4{\cdot}2C_6H_6$[4a] (1.00 g, 1.16 mmol) was added freshly distilled 3-hexyne (0.19 g, 0.27 mL, 2.4 mmol) via syringe. After the mixture was stirred at room temperature for 1.5 h, the solvent was completely evaporated under vacuum. The white powder was dried overnight in vacuo to give a quantitative yield of crude product. This was recrystallized from warm hexane (0.69 g, 67%): mp 95 °C; ^1H NMR ($CDCl_3$) δ 2.36 (4, q, CH_2), 1.16 (6, t, CH_3); ^{13}C NMR ($CDCl_3$) δ 88.75 (C≡), 16.10 ($CH_2C{\equiv}$), 14.04 ($CH_3CH_2C{\equiv}$); IR (Nujol mull) 1678 (ν(CO)), 1130–1220 ($\nu(CF_3)$); MS *m/e* 434 ($[Cu(O_2CCF_3)]_2$(3-hexyne)), 352 ($[Cu(O_2CCF_3)]_2$), 239 ($Cu_2(O_2CCF_3)$), 82 (3-hexyne). Anal. Calcd for $Cu_4C_{20}H_{20}O_8F_{12}$: C, 27.59; H, 2.30. Found C, 28.15; H, 2.30.

[6] Crystals of **3** were grown from hot-cold hexane. They belong to the monoclinic crystal system; space group $P2_1/a$, a = 12.208 (3) Å, b = 28.391 (7) Å, c = 9.639 (2) Å, β = 108.80 (2)°, Z = 4. The structure was solved by a combination of direct methods and difference Fourier syntheses and was refined with 1956 reflections to the final residuals R = 0.071 and R_w = 0.090. The structure was fraught with disorder in the CF_3 groups, but each CF_3 group was satisfactorily refined with a twofold disorder model with the occupancies of the disordered atoms fixed at 0.5. One of the ethyl groups also exhibited a 50/50 disorder of its methyl group. Data were collected on a Rigaku AFC6 automatic diffractometer using Mo Kα radiation. All calculations were performed on a Digital Equipment Corp. MICROVAX II computer using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX.

tetramer. Thus, the two C_2O_2 planes within each butterfly unit are at a 113.4° angle whereas the two CuC_2 planes form a 97.1° angle.

The short C≡C distances and large C≡C—R bend back angles for **3** both indicate that the alkyne is less perturbed than alkynes in other dinuclear metal complexes.[7] The C≡C—R angles range from 148 (2)° to 156 (2)°. These are much larger than those usually observed for dinuclear complexes and are even larger than those observed in most mononuclear complexes.[8] For comparison with copper structures, these angles are 139.0 (7)° and 138.2 (4)° for **1** and range from 156.6 (14)° to 159.5 (14)° for the two independent molecules in **2**. Both of these structural features imply that back-bonding to the alkyne in **3** is significantly less important than in other dinuclear complexes.

All three complexes show moderately short Cu–Cu distances (considering those within the butterfly units for **3**). Although a normal two-electron bond is not expected between two d^{10} metal centers, calculations have shown that a weak attractive interaction does exist.[9] This may explain the displacement of the copper atoms toward each other out of the O_2C_2 planes for **3**. In both **1** and **2** the geometry about the copper atom is planar.

In view of the known tendency of copper(I) to form high nuclearity aggregates with bridging ligands,[10] it seems likely that a variety of new polynuclear copper complexes containing bridging alkyne ligands may be accessible.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this project (D.L.R.) and the National Science Foundation under Grant No. CHE 86-12862 (R.D.A.).

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (12 pages); a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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1-Sila-3-azacyclobutanes: The Insertion of Isocyanides into Silaaziridines

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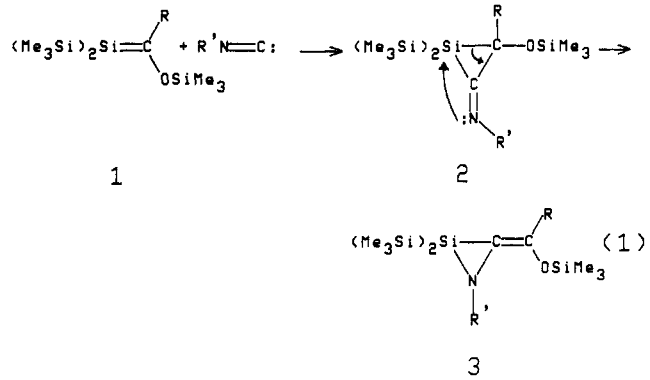
Summary: Stable silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (R = Ad (Ad = 1-adamantyl), Mes (Mes = 2,4,6-trimethylphenyl)) reacted with 2,6-dimethylphenyl isocyanide giving rise to stable compounds shown by X-ray crystallography to be 1-sila-3-azacyclobutanes. Similar four-membered ring compounds were also formed when a silene of this type bearing a mesityl group on the sp^2-hybridized carbon atom reacted with *tert*-butyl isocyanide. The insertion of isocyanide into the Si–N bond of an initially formed silaaziridine is proposed to account for these products.

We have recently reported[1] that the silenes **1** of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (R = *t*-Bu, Ad; Ad = 1-adamantyl) react with alkyl isocyanides R′N≡C: (R′ = *t*-Bu, $CMe_2CH_2CMe_3$ (isooctyl)) to yield solid, relatively stable silaaziridines **3**. Evidence indicated that the initially formed silacyclopropanimines **2** undergo clean rapid thermal rearrangements even at −40 °C to the isomeric silaaziridines (eq 1).[1]



(1)

We have now found that if either the isocyanide bears an aryl group and/or the silene bears an aryl group on the sp^2-hybridized carbon, the first observed isolable products are the result of the reaction of two molecules of isocyanide with each molecule of silene. This family of compounds, whose members **4a–d** have very similar NMR resonances (see Table I), was shown through the X-ray crystal structure of one member (see below) to be 1-sila-3-azacyclobutanes, the first reported examples of this ring system.

Thus, when the silenes **1** (R = Ad or Mes) were generated (by photolysis of the related acylsilane $(Me_3Si)_3SiCOR$ in C_6D_6 using 360-nm radiation at 0 °C) in the presence of the aryl isocyanide R″N≡C: (R″ = 2,6-dimethylphenyl), the compounds obtained were the 1-sila-3-azacyclobutanes **4a** and **4d**, respectively. Similarly the four-membered 1-sila-3-azacyclobutane **4c** was obtained when $(Me_3Si)_2Si{=}C(OSiMe_3)Mes$ was generated in the presence of *t*-BuN≡C:.

Under nonphotochemical conditions, preformed silene **1** (R = Ad), when treated in the dark at −70 °C with 1 equiv of aryl isocyanide, gave a mixture of silaaziridine **3** (R′ = Ar) and 1-sila-3-azacyclobutane **4a** (R′ = Ar), the latter being the major product. This is in contrast to the exclusive formation of silaaziridine **3** (R′ = alkyl) when preformed silene **1** (R = Ad) was treated with an alkyl isocyanide. When silaaziridine **3** (R = Ad, R′ = *t*-Bu) was treated with an equivalent of aryl isocyanide in the dark, no reaction occurred, but reaction occurred slowly when the mixture was photolyzed to give the mixed species **4b** as two geometric isomers in about 3:2 proportions. Only one isomer was observed for each of **4c** and **4d**.

It is evident from the above results that the formation of the silaazacyclobutanes is usually a nonphotochemical process that requires the presence of an aryl group either on the isocyanide or on the sp^2-hybridized carbon of the silene. Delocalization of electron density on the ring ni-

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0276-7333/89/2308-0850$01.50/0