We suggest that the cyclization of **9** and **10** may initially form two stereoisomers, but the less stable cis product undergoes ring opening, and the thermodynamically more stable **12** and **13** are formed exclusively[14] through equilibration.

The present reaction has provided a powerful method to resolve two of the most challenging problems for taxane synthesis: (1) an efficient cyclization of an eight-membered-ring system and (2) complete stereocontrol of two functional groups corresponding to the C-9 and C-10 positions. We are currently pursuing a total synthesis of taxusin and taxinine by applying this methodology.

Acknowledgment. This work was partially supported by grants from the Ministry of Education, Science, and Culture of the Japanese Government. We are also indebted to Prof. H. Suzuki of this Institute for the X-ray crystallographic analysis of **12**.

Supplementary Material Available: Preparation of the starting materials, discussions on the transition states which control the stereochemistry, experimental details on cyclization reactions, and an ORTEP drawing and bond lengths and dihedral angles of typical parts of **12** (9 pages). Ordering information is given on any current masthead page.

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(11) A subsequent treatment of the siloxy enone **7** with $Me_3SiCH(OMe)Li$ and with ${}^tBuOK$ gave **10** (Z:E = 82:18), which, on treatment with $TiCl_4$ at −78 °C for 15 min, gave a mixture of **13** and its cis isomer in 64 and 16% yields, respectively, but when a similar reaction was performed at −78 °C for 45 min and then at −25 °C for 45 min, **13** was obtained exclusively.

(12) Two protons corresponding to C-9 and C-10: **13**, 4.52 and 4.83 (J = 10.0 Hz); the cis isomer, 4.60 and 4.80 (J = 5.8 Hz).

(13) Overall yield of **13** from *m*-methoxybenzaldehyde dimethyl acetal was about 35%.

(14) It has been confirmed by a separate experiment that the cis isomer undergoes isomerization to **13** under similar reaction conditions. By MM2 calculation, the trans isomer **13** has been estimated to be ca. 2.2 kcal/mol more stable than the cis isomer.

A New Coordination Mode for CO. Synthesis and Structure of $Cp_4Mo_2Ni_2S_2(\eta^1,\mu_4\text{-}CO)$

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Coordination modes of CO in organometallic compounds have long served as models of catalytic activation of CO and of coordination of CO on metal surfaces.[1-3] A variety of CO coordination types (η^{1-2},μ_{1-3}) have been recognized either in organometallic compounds or on surfaces of catalysts. However, the only μ_4-CO ligands known are also bonded to the metal framework through the oxygen atom (μ_4,η^2-CO).[4]

In this paper, we report a new sulfido bimetallic cluster, $Cp_4Mo_2Ni_2S_2(CO)$ (**2**), which contains an unprecedented η^1,μ_4-CO ligand, which may serve as a model of CO coordinated in the 4-fold hollows of the 110 surfaces of face-centered cubic (fcc) metals. EHMO calculations support the η^1,μ_4-coordination assignment.

Cluster **2** was synthesized in ca. 20% yield from the reaction of a 1:1 molar ratio of *trans*-$Cp_2Mo_2(SMe)_2(CO)_2$ (**1**) and Cp_2Ni in a refluxing toluene solution (eq 1). The reaction is similar to those we have recently reported for sulfido Mo/late-transition-metal carbonyl clusters, $Cp_2Mo_2M'_{2-3}S_{2-4}(CO)_x$.[5] Compound **2** was characterized by X-ray crystallographic analysis[6] and other spectroscopic methods. ^{1}H NMR spectra gave two equal-intensity peaks for Mo and Ni cyclopentadienyl (Cp) rings at 6.00 and 5.05 ppm in $CDCl_3$. Mass spectra obtained by electron-impact ionization displayed peaks at 662 $[P]^+$ and 634 $[P-CO]^+$. Anal. ($C_{21}H_{20}Mo_2Ni_2OS_2$) C, H, S. Calcd: 38.11, 3.05, 9.69. Found: 38.19, 3.14, 10.21.

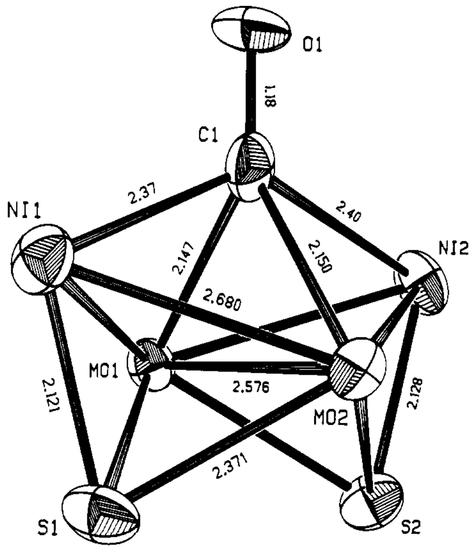
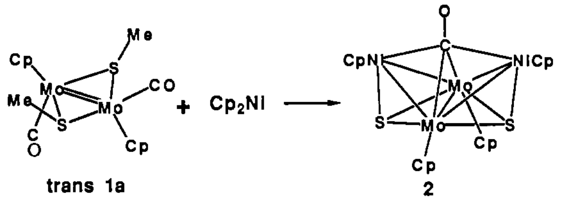


Figure 1. ORTEP plot (50% probability thermal ellipsoids) for the framework structure of $Cp_4Mo_2Ni_2S_2(CO)$.



trans **1a** **2** (1)

The geometrical arrangement of the core (see Figure 1) may be described either as a bicapped trigonal bipyramid with Ni atoms at apex positions and Mo and C atoms in equatorial positions (the carbonyl carbon is regarded as a normal vertex member) or as a butterfly cluster with the carbonyl group bonded to the hinge Mo and wingtip Ni atoms. The Mo-Mo bond distance, 2.576 Å, is shorter than those (2.64-2.67 Å) found in geometrically similar clusters.[5,7,8] The CO ligand is equidistant from both Ni atoms within experimental error. The η^1-CO model is supported by the long Ni-O distances ($d_{Ni-O} > 3.03$ Å) and the unbent CO: the angle between O, C, and the centroid of the Mo-Mo bond is approximately 180°.

The η^1,μ_4-CO assignment is indicated also by the extremely low CO stretching frequency in both the solid state (1654 cm^{-1} in a KBr pellet) and in solution (1653 cm^{-1} in THF) (cf. ν(CO) $\sim$ 1850 cm^{-1} for μ_2-CO and $\sim$1740-1720 cm^{-1} for μ_3-CO). However, the long Ni-CO distances (average 2.39 Å) suggest only a small bonding interaction between the Ni atoms and the carbonyl group. In related cyclopentadienyl Ni dimers and trimers,[9,10] Ni-CO distances average 1.85-1.87 Å for μ_2-CO and 1.93-2.03 Å for μ_3-CO. Since the Ni-CO distance increases with increasing connectivity of the μ_n-CO, a Ni-μ_4-CO distance of 2.39 Å is reasonable. A very long Fe-CO distance (2.63 Å) was also observed in an η^1,μ_3-CO coordination mode.[7,11]

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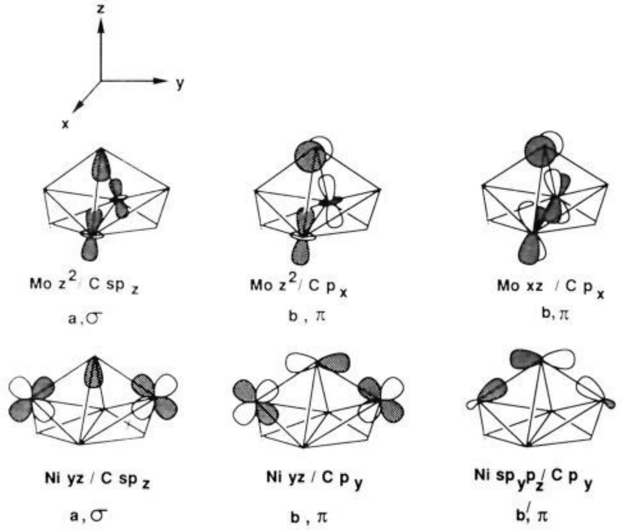

Figure 2. Orbital interactions of M–μ_4-CO in $Cp_4Mo_2Ni_2S_2(CO)$.

Both overlap population and energy matrix analysis from EHMO calculations indicated significant bonding interactions between Ni and CO. The overlap population between Ni and CO is 19% of the total overlap population (1.267) between the metals and the carbonyl carbon. Two unusual bonding features of Ni–CO interactions, related to the electronic saturation on the Ni atoms, were observed. First, bonding molecular orbitals between Ni and CO having Ni 4s and 4p character were found. This is difficult from our calculational results on $Cp_2Mo_2M_{2,3}S_{3,2}L_n$ clusters, in which metal d orbitals only contribute to bonding.[12] Second, two filled Ni–CO orbitals with Ni–C antibonding interactions were calculated.

The orbital interactions of the μ_4-CO are demonstrated in Figure 2. Type a, σ bonding in nature, and type b, multicenter bonding with the CO π-system, are about equally important in the Mo–CO interactions. Types b and b′ (distinguished only by the composition of the Ni atomic orbitals) are dominant (overlap population a:(b + b′) < 1:3) in the Ni–CO interactions. The Ni–CO bonding is best described as a dative bond from Ni to the π* orbitals of the μ_4-CO. The low C–O overlap population (0.95 vs ca. 1.2 for terminal C–O ligands) reflects this additional electron donation into the C–O antibonding orbitals and is consistent with the low ν_{CO} observed.

The framework of **2** may also be viewed as a pentagonal bipyramid in which five atoms (C, Ni, S, S, Ni) are unevenly spread around the Mo–Mo axis. Other clusters having the same framework geometry include $Cp_4Cr_2Ni_2S_2(\mu_4\text{-}S)$,[13] $Cp_2Mo_2Fe_2S_2(\mu_4\text{-}S)(CO)_6$,[8] $Cp_2Mo_2Co_3S_2(CO)_7$,[5] and $(RCp)_2Mo_2Co_2S_2(\mu_4\text{-}S)(CO)_4$.[5,7] A comparison of these clusters shows that the dihedral angle between the MMM′ (M = hinge metal, M′ = wingtip) and the MM(μ_4-X) planes is rather variable, suggesting a soft potential for deformation of the hinge angle or the M′–μ_4-X distance. Thus, it is unlikely that the relatively long Ni–μ_4-CO distance is caused by steric crowding in the M_2M_2' pocket. A series of EHMO calculations in which the CpNiS units were rotated around the Mo–Mo axis showed a shallow-bottomed well with a minimum corresponding to a Ni–μ_4-CO distance of ca. 2.25 Å. Below ca. 2.0 Å, the energy rises rapidly, but no single bonding or antibonding interaction could be identified as the cause of the rapid increase in energy.

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Supplementary Material Available: Tables IS–VIS and VIIIS (list of dihedral angles, crystallographic data, fractional atomic coordinates, thermal parameters, bond distances and angles, and EHMO parameters for **2**) and Figure 1S (labeled ORTEP plot of entire molecule of **2**) (10 pages); Table VIIS (listing of structure factors F_o vs F_c for **2**) (6 pages). Ordering information is given on any current masthead page.

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Investigation of Isomeric Intermediates: Co^+–NH_3 and H–Co^+–NH_2

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One of the prime distinctions between studies of gas-phase and condensed-phase chemistry is that chemical intermediates are rarely isolated in the former, whereas they are routinely studied in the latter. Because of this, gas-phase-ion chemists have resorted to a variety of *indirect* means to study and characterize proposed intermediates in a chemical reaction. These include collision-induced,[1] photon-induced,[2] and metastable[3] dissociations, kinetic energy "sampling",[4] and chemical reactivity studies.[2,5] In this work, we describe the surprising *direct* observation of a long-lived chemical intermediate in a five-atom reaction system, $Co^+ + NH_3$.

Figure 1 shows results obtained by using guided ion beam mass spectrometry to study the reaction of ammonia with Co^+ (as produced by surface ionization at 2300 K, and therefore primarily in the a^3F state). Details of the technique and methods for analyzing the energy dependence of the cross sections can be found elsewhere.[6,7] The dominant product is CoH^+. Analysis of this cross section, $\sigma(CoH^+)$, leads to a threshold of 2.79 ± 0.12 eV. This is within experimental error of the threshold expected for reaction 1, 2.67 ± 0.06 eV, given $D°(NH_2\text{–}H) = 4.69$ eV[8] and

$$Co^+ + NH_3 \rightarrow CoH^+ + NH_2 \qquad (1)$$

$D°(Co^+\text{–}H) = 2.02 \pm 0.06$ eV.[9] This agreement verifies that reaction 1 has no large barriers in excess of the endothermicity.

Below the threshold for reaction 1, formation of $CoNH_2^+$ is the most favorable process and must be due to reaction 2. While

$$Co^+ + NH_3 \rightarrow CoNH_2^+ + H \qquad (2)$$

the logarithmic scale of Figure 1 makes the threshold for this process appear to be near 1 eV, analysis of $\sigma(CoNH_2^+)$ (which accurately accounts for the kinetic and electronic energy distributions of the reactants) shows that the true threshold is 2.0 ± 0.1 eV. This value leads to $D°(Co^+\text{–}NH_2) = 62 \pm 2$ kcal/mol,

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† NSF Presidential Young Investigator, 1984–1989; Alfred P. Sloan Fellow; Camille and Henry Dreyfus Teacher-Scholar, 1988–1993.

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