Metallaligands

DOI: 10.1002/ange.201309986

Formation, Expansion, and Interconversion of Metallarings in a Sulfur-Bridged Au^{I}Co^{III} Coordination System**

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Abstract: *A novel Au^{I}Co^{III} coordination system that is derived from the newly prepared [Co(D-nmp)$_2$]$^-$ (**1**$^-$; D-nmp = N-methyl-D-penicillaminate) and a gold(I) precursor Au^{I} is reported. Complex **1**$^-$ acts as a sulfur-donating metallaligand and reacts with the gold(I) precursor to give [Au$_2$Co$_2$(D-nmp)$_4$] (**2**), which has an eight-membered Au$^{I}_2$Co$^{III}_2$ metallaring. Treatment of **2** with [Au$_2$(dppe)$_2$]$^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane) leads to the formation of [Au$_4$Co$_2$(dppe)$_2$(D-nmp)$_4$]$^{2+}$ (**3**$^{2+}$), which consists of an 18-membered Au$^{I}_4$Co$^{III}_2$ metallaring that accommodates a tetrahedral anion (BF$_4^-$, ClO$_4^-$, ReO$_4^-$). In solution, the metallaring structure of **3**$^{2+}$ is readily interconvertible with the nine-membered Au$^{I}_2$Co^{III} metallaring structure of [Au$_2$Co(dppe)(D-nmp)$_2$]$^+$ (**4**$^+$); this process depends on external factors, such as solvent, concentration, and nature of the counteranion. These results reveal the lability of the Au–S and Au–P bonds, which is essential for metallaring expansion and contraction.*

The development of efficient strategies for the synthesis of coordination compounds that show reversible changes in their structural and physicochemical properties in response to external factors has attracted much attention in recent years.[1] These compounds are of fundamental importance not only because of their sophisticated molecular designs but also because of their potential application as switching devices and molecular machines.[2] Among the structural motifs of coordination compounds, discrete metallarings are suitable candidates for creating switchable systems, owing to the flexibility of the coordination bonds around their metal centers. In general, a coordination-driven self-assembly of predesigned metal acceptor units and bridging organic ligands is employed to construct metallaring structures,[3] the sizes and geometries of which are often controlled by the introduction of templating molecules or ions.[4,5] Although this approach is highly effective for the construction of homometallic rings of higher symmetry, functional heterometallic rings with lower symmetry are rarely obtained using this approach. An alternative method that may overcome this limitation is the use of metallaligands that can link metal ions in a cyclic manner.[6,7]

We previously showed that [Co(D-pen)$_2$]$^-$ (D-pen = D-penicillaminate) serves as a bridging metallaligand for gold(I) centers to produce the sulfur-bridged Au$^{I}_3$Co$^{III}_3$ hexanuclear complex [Au$_3$Co$_3$(D-pen)$_6$].[8] In this complex, three octahedral [Co(D-pen)$_2$]$^-$ units are linked by three linear Au^{I} ions to form a twelve-membered heterometallic ring. Unfortunately, further studies on the stability and reactivity of [Au$_3$Co$_3$(D-pen)$_6$] in solution could not be conducted owing to its poor solubility in most common solvents. This property is ascribed to multiple intermolecular hydrogen bonds that are formed between the amine and carboxylate groups of D-pen, which results in the construction of a rigid 2D sheet-like structure in the solid state. Therefore, we thought it worthwhile to employ [Co(D-nmp)$_2$]$^-$ (**1**$^-$; D-nmp = *N*-methyl-D-penicillaminate) as a metallaligand instead of [Co(D-pen)$_2$]$^-$ for the synthesis of a related Au^{I}Co^{III} heterometallic complex. It was anticipated that this complex would possess sufficient solubility for an assessment of its behavior in solution because of the presence of the methyl groups on each amine, which should prevent the formation of intermolecular NH···O hydrogen bonds. Thus, [Co(D-nmp)$_2$]$^-$ (**1**$^-$) was prepared and subsequently reacted with a gold(I) precursor. Contrary to our anticipation, this reaction did not give an Au$^{I}_3$Co$^{III}_3$ hexanuclear complex analogous to [Au$_3$Co$_3$(D-pen)$_6$], but produced the Au$^{I}_2$Co$^{III}_2$ tetranuclear complex [Au$_2$Co$_2$(D-nmp)$_4$] (**2**), which is soluble in various solvents. Remarkably, **2** shows good reactivity toward [Au$_2$(dppe)$_2$]$^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane) in solution, affording the larger Au$^{I}_4$Co$^{III}_2$ metallaring structure [Au$_4$Co$_2$(dppe)$_2$(D-nmp)$_4$]$^{2+}$ (**3**$^{2+}$), which accommodates an appropriate inorganic anion inside the ring. Furthermore, this Au$^{I}_4$Co$^{III}_2$ metallaring was found to be interconvertible with the smaller Au$^{I}_2$Co^{III} metallaring structure [Au$_2$Co(dppe)(D-nmp)$_2$]$^+$ (**4**$^+$) in response to several external factors. Herein, we describe this fascinating Au^{I}Co^{III} coordination system that is derived from **1**$^-$ and a gold(I) species, and which is an example of the rational creation, expansion, and interconversion of heterometallic ring structures (Scheme 1).

The starting complex, Na[Co(D-nmp)$_2$] (Na-**1**), which was expected to act as a sulfur-donating metallaligand, was obtained as a brown powder by the reaction of Na$_3$[Co(CO$_3$)$_3$] with D-H$_2$nmp (2 equiv) in water.[9] Complex Na-**1** was characterized using IR, ^{1}H NMR, electronic absorption, and CD spectroscopy (Supporting Information, Figure S1–S3) and elemental analysis.[9] The structure of the potassium salt of **1**$^-$ was determined by single-crystal X-ray analysis.[10] As shown in Figure 1a, **1**$^-$ has a normal octahedral structure in

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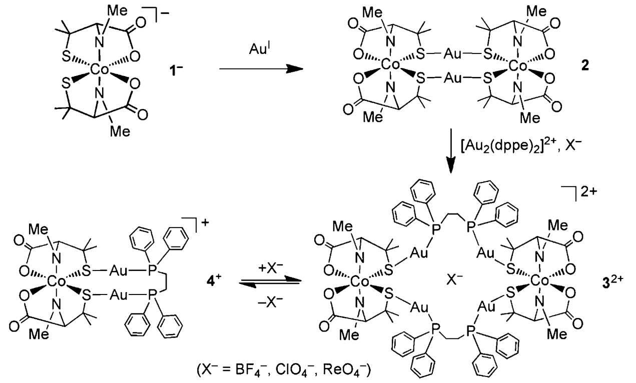
[**] This work was supported in part by Grants-in-Aid for Science Research (23350026) from the Ministry of Education, Culture, Sports, Science and Technology of Japan (T.K.).

Supporting information for this article, including experimental details, crystal structures, and spectroscopic data, is available on the WWW under http://dx.doi.org/10.1002/anie.201309986.



Scheme 1. Synthetic route to **2** and **3**$^{2+}$ and interconversion between **3**$^{2+}$ and **4**$^{+}$.

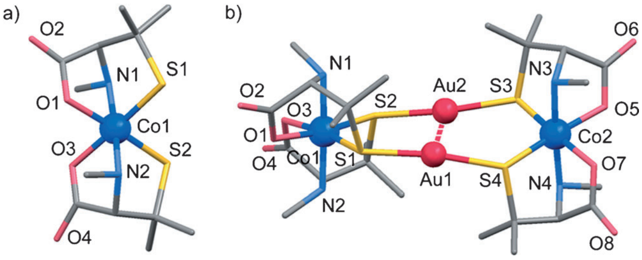


Figure 1. a, b) Perspective views of **1**$^{-}$ (a) and **2** (b). A minor portion of the disordered atoms and the hydrogen atoms are omitted for clarity.

which two D-nmp ligands coordinate to a Co^{III} center through the nitrogen, oxygen, and sulfur atoms. The geometrical configuration of **1**$^{-}$ entails the nitrogen atoms in a *trans* arrangement (*trans*(N)), which is the same as that of [Co(D-pen)$_2$]$^{-}$.[11] Furthermore, the two nitrogen donor atoms in **1**$^{-}$ are chiral centers with an *S* configuration.

To investigate the coordination ability of **1**$^{-}$ towards gold(I) species, Na-**1** was reacted with [AuCl{S(CH$_2$CH$_2$OH)$_2$}] (1 equiv) in water. This reaction gave a dark brown solution from which a brown powder (**2**) was isolated in a satisfactory yield.[9] X-ray fluorescence spectroscopy indicated that **2** contains cobalt and gold as the metal components. The presence of [Co(D-nmp)$_2$]$^{-}$ as a constitutional unit in **2** is suggested by the absorption spectrum, which resembles that of **1**$^{-}$ over the entire region, although each band for **2** is slightly shifted to higher energy compared with the corresponding bands for **1**$^{-}$ (Figure S3).[9] This conclusion is also supported by the IR spectrum of **2**, which is very similar to that of **1**$^{-}$ and shows a strong band at 1637 cm^{-1}, which is characteristic of coordinated COO^{-} groups (Figure S1).[9,12] On the basis of these results and elemental analysis data, **2** was assigned to be a 1:1 adduct of **1**$^{-}$ and gold(I) cations. Single-crystal X-ray analysis revealed that **2** has a sulfur-bridged Au$^{I}_2$Co$^{III}_2$ tetranuclear structure with the formula [Au$_2$Co$_2$(D-nmp)$_4$] (Figure 1 b).[10] In this complex, two [Co(D-nmp)$_2$]$^{-}$ units are linked by two linearly coordinated gold(I) ions (average distance for Au–S: 2.29 Å, average angle for S-Au-S: 166.7°), forming an Au$_2$Co$_2$S$_4$ eight-membered metallaring. Each [Co(D-nmp)$_2$]$^{-}$ unit has a *trans*(N)-N$_2$O$_2$S$_2$ octahedral geometry with *S*-configured nitrogen donors (average distances: Co–N: 1.97 Å, Co–O: 1.96 Å, Co–S, 2.23 Å), indicating that the geometry of **1**$^{-}$ is retained during the reaction. This retention of geometry is in contrast to observations for the reaction of [Co(D-pen)$_2$]$^{-}$ with Au^{I}, which is accompanied by a change from *trans*(N) to *trans*(O), affording a sulfur-bridged Au$^{I}_3$Co$^{III}_3$ hexanuclear structure with the formula [Au$_3$Co$_3$(D-pen)$_6$].[8] The presence of a methyl group on each nitrogen donor in the [Co(D-nmp)$_2$]$^{-}$ unit appears to prevent the formation of a sterically crowded *trans*(O) geometry with *cis* configured nitrogen donor atoms. Furthermore, the four bridging sulfur atoms in **2** are also chiral, and all of them adopt the *S* configuration so as to form an aurophilic interaction between the two Au^{I} atoms (Au⋯Au = 2.8991(3) Å).[13] The ^{1}H NMR spectrum of **2** in D$_2$O shows only a single set of signals owing to the D-nmp ligands (Figure S2),[9] which suggests that on average, the sulfur-bridged Au$^{I}_2$Co$^{III}_2$ tetranuclear structure with D_2 symmetry is retained in solution. It should also be noted that the CD spectrum of **2** in H$_2$O is largely different from that of **1**$^{-}$ (Figure S3),[9] and corroborates the retention of a tetranuclear structure in solution that possesses additional chirality owing to the bridging sulfur atoms.

We recently found that a {Au(dppm)}$^{+}$ moiety (dppm = bis(diphenylphosphino)methane) is inserted into the sulfur-bridged Au$^{I}_2$Ni^{II} structure in [Au$_2$Ni(dppm)(D-pen)$_2$] upon treatment with [Au$_2$(dppm)$_2$]$^{2+}$, which leads to an expansion of the eight-membered metallaring to a twelve-membered metallaring.[14] Prompted by this result, **2** was treated with [Au$_2$(dppe)$_2$](BF$_4$)$_2$ (1 equiv) in methanol with the expectation that two {Au(dppe)}$^{+}$ moieties would be inserted into **2** to create a larger metallaring. Indeed, brown crystals (**3**-(BF$_4$)$_2$) were isolated in good yield from this reaction.[9] The presence of D-nmp, dppe, and BF$_4^{-}$ in this product was confirmed by its IR spectrum (Figure S1), which shows characteristic bands at 1648 (COO^{-}), 1436 (Ph), 1103 (P–Ph), and 1061 cm^{-1} (BF$_4^{-}$).[9,12] Furthermore, the elemental analysis data were consistent with the formation of a 1:1 adduct of **2** and [Au$_2$(dppe)$_2$](BF$_4$)$_2$. Single-crystal X-ray analysis established that **3**$^{2+}$ has an Au$^{I}_4$Co$^{III}_2$ hexanuclear structure with the formula [Au$_4$Co$_2$(dppe)$_2$(D-nmp)$_4$]$^{2+}$, in which two [Co(D-nmp)$_2$]$^{-}$ units are connected by two {Au$_2$(dppe)}$^{2+}$ linkers to form an Au$_4$Co$_2$S$_4$P$_4$C$_4$ 18-membered metallaring (Figure 2 and Figure S4).[9,10] As in **2**, each [Co(D-nmp)$_2$]$^{-}$ unit has a *trans*(N)-N$_2$O$_2$S$_2$ octahedral geometry with

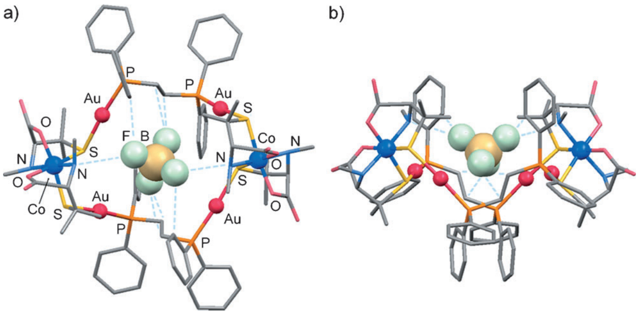


Figure 2. a, b) Perspective views of **3**$^{2+}$ accommodating a BF$_4^{-}$ ion; top view (a) and side view (b). Hydrogen atoms are omitted. Dotted lines represent the interactions between the complex cation and BF$_4^{-}$.

S-configured nitrogen donors (average distances: Co–N: 1.97 Å, Co–O: 1.90 Å, Co–S: 2.26 Å). This result implies that two $\{Au_2(dppe)\}^{2+}$ moieties that originate from $[Au_2(dppe)_2]^{2+}$ were inserted into two Au–S bonds in **2**, with retention of the geometry of the $[Co(\text{D-nmp})_2]^-$ units. Furthermore, each Au^I atom is in a nearly linear arrangement with a sulfur atom of $[Co(\text{D-nmp})_2]^-$ and a phosphorus atom of dppe (average values: Au–P: 2.26 Å, Au–S: 2.31 Å, P-Au-S = 174°), and the two asymmetric bridging sulfur atoms in each $[Co(\text{D-nmp})_2]^-$ unit adopt the *R* and *S* configurations to form a C_2-symmetric metallaring structure. Furthermore, the intramolecular separation between the nearest two gold(I) centers in $\mathbf{3}^{2+}$ is 5.141 Å, which is indicative of the absence of an aurophilic interaction. Notably, one BF_4^- anion is accommodated in the cavity of the 18-membered metallaring in $\mathbf{3}^{2+}$ and forms hydrogen bonds with D-nmp and dppe ligands (N···F: 3.221 Å, average distance for C···F: 3.16 Å), whereas the other BF_4^- anion is positioned outside of the ring (Figure S5).[9]

In the ^1H NMR spectrum of $\mathbf{3}$-$(BF_4)_2$ in CD_2Cl_2, two sets of signals are found for the four D-nmp ligands in the complex (Figure 3 a and Figure S6 a).[9] Furthermore, two fluorine signals that arise from the BF_4^- anions are observed in its ^{19}F NMR spectrum (Figure S7).[9] These spectral features are compatible with a C_2-symmetric metallaring structure for $\mathbf{3}^{2+}$ in which one BF_4^- ion is accommodated inside the ring, whereas the other ion is located outside of the ring. However, the NMR spectra of $\mathbf{3}$-$(BF_4)_2$ in CD_3OD and D_2O do not reflect such a structure; a single set of signals is predominantly observed at different chemical shifts in CD_3OD, and the signals for $\mathbf{3}^{2+}$ are significantly less intense (Figure 3 b and Figure S6 b). Meanwhile, in D_2O (Figure 3 c and Figure S6 c), only this single set of signals is observed.[9] These observations imply that in the polar solvents CD_3OD and D_2O, $\mathbf{3}^{2+}$ is converted into a species $\mathbf{4}^+$ that has high symmetry, whereas $\mathbf{3}^{2+}$ is structurally stable in nonpolar CD_2Cl_2.[15] The 2D diffusion-ordered ^1H NMR spectrum (DOSY) in CD_3OD revealed that the diffusion coefficient for $\mathbf{4}^+$ ($\log D \approx 4.1$) is larger than that for $\mathbf{3}^{2+}$ ($\log D \approx 3.3$; Figure S9);[9] therefore, the molecular size of $\mathbf{4}^+$ is considered to be smaller than that of $\mathbf{3}^{2+}$. Furthermore, the ESI mass spectrum of $\mathbf{3}$-$(BF_4)_2$ in methanol/water (1:1) gave a major signal for a monocationic species at $m/z = 1173.10$, which corresponds to the formula of the $Au^I_2Co^{III}$ trinuclear complex, $[Au_2Co(dppe)(\text{D-nmp})_2]^+$ (Figure S10).[9] On the basis of these results, it was concluded that, upon dissolution in a polar solvent, the $Au^I_4Co^{III}_2$ hexanuclear structure of $\mathbf{3}^{2+}$ is converted into the $Au^I_2Co^{III}$ trinuclear structure in $[Au_2Co(dppe)(\text{D-nmp})_2]^+$ ($\mathbf{4}^+$), in which a $[Co(\text{D-nmp})_2]^-$ unit is spanned by a $[Au_2(dppe)]^{2+}$ moiety through two Au–S bonds. Given that the metallaring structure of $\mathbf{3}^{2+}$ is stabilized by the accommodation of a BF_4^- ion inside its cavity, it is reasonable to assume that the solvation of BF_4^- by a polar solvent leads to the removal of the accommodated BF_4^- in $\mathbf{3}^{2+}$, which is then converted into the thermodynamically more stable, compact, and rigid $Au^I_2Co^{III}$ trinuclear structure of $\mathbf{4}^+$. Unfortunately, attempts to isolate a salt of $\mathbf{4}^+$ were unsuccessful. Instead, we obtained reddish brown crystals (**4′**) when tetrabutylammonium chloride was added to an acetonitrile solution containing $\mathbf{3}^{2+}$. Single-crystal X-ray analysis revealed that **4′** has an acyclic $Au^I_2Co^{III}$ trinuclear structure with the formula $[Au_2CoCl(dppe)(\text{D-nmp})_2]$, in which one of the two Au^I atoms in the $[Au_2(dppe)]^{2+}$ moiety is bound by a $[Co(\text{D-nmp})_2]^-$ unit, and the other Au^I atom is bound to a chloride ion (Figure S11).[9,10] Interestingly, the ^1H NMR spectrum of **4′** in CD_3OD is coincident with that of $\mathbf{4}^+$, implying that the acyclic $Au^I_2Co^{III}$ trinuclear structure in **4′** is converted into the cyclic $Au^I_2Co^{III}$ trinuclear structure in $\mathbf{4}^+$ in the absence of excess Cl^- ions in solution. This conversion occurs with replacement of a Cl^- donor in **4′** by a non-bridging sulfur donor in the $[Co(\text{D-nmp})_2]^-$ unit (Scheme 2).

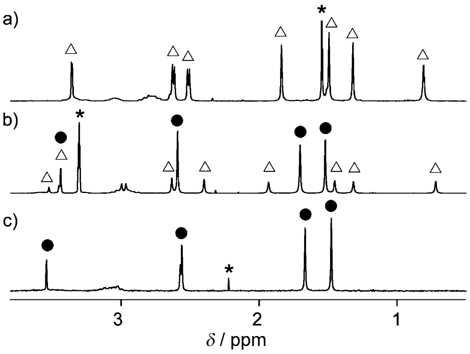
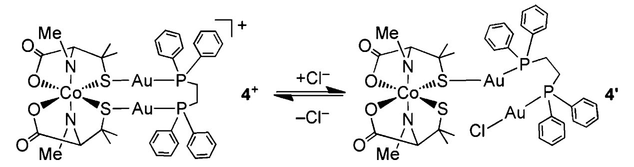


Figure 3. a–c) ^1H NMR spectra of $\mathbf{3}$-$(BF_4)_2$ in CD_2Cl_2 (a), CD_3OD (b), and D_2O (c). The methyl signals of $\mathbf{3}^{2+}$ and $\mathbf{4}^+$ are represented by △ and ●, respectively. δ Values are given relative to tetramethylsilane (TMS; a, b) or sodium 4,4′-dimethyl-4-silapentane-1-sulfonate (DSS; c).



Scheme 2. Interconversion between $\mathbf{4}^+$ and **4′**.

Next, to examine the influence of coexisting anions on the stability of the $Au^I_4Co^{III}_2$ metallaring structure in $\mathbf{3}^{2+}$ in solution, $\mathbf{3}$-$(BF_4)_2$ was dissolved in CD_3OD (1.5×10^{-3} M), and its ^1H NMR spectrum was measured immediately after the addition of an excess of various salts (10 equiv; Figure 4 and Figure S12). Whereas the integration ratio of the ^1H NMR signals for $\mathbf{3}^{2+}$ and $\mathbf{4}^+$ was 1:40 without added salt, the ratio changed to 1:10 (increase in the signals for $\mathbf{3}^{2+}$) upon addition of NH_4BF_4 (Figure 4 b), indicating that the $Au^I_4Co^{III}_2$ structure of $\mathbf{3}^{2+}$ was stabilized by BF_4^- anions. A marked increase in the intensity of the signals for $\mathbf{3}^{2+}$ was also observed when NH_4ClO_4 or NH_4ReO_4 were added to the solution (Figure 4 c, d).[16] On the other hand, the addition of NH_4PF_6 or NH_4OTf (OTf = trifluoromethanesulfonate) had little effect on the signal ratio.[9,17] It is assumed that the tetrahedral geometry of BF_4^-, ClO_4^-, and ReO_4^- enables these anions to fit into the cavity of the metallaring of $\mathbf{3}^{2+}$ to form multiple hydrogen bonds that sustain its structure. Indeed, X-ray

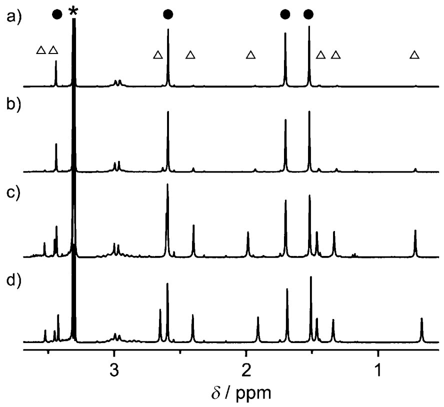


Figure 4. a–d) ^{1}H NMR spectra of **3**-$(BF_4)_2$ (a) and **3**-$(BF_4)_2$ with added NH_4BF_4 (b), NH_4ClO_4 (c), and NH_4ReO_4 (d) in CD_3OD. The methyl signals of $\mathbf{3}^{2+}$ and $\mathbf{4}^{+}$ are represented by △ and ●, respectively. δ Values are given relative to TMS.

analysis of **3**-Cl(ClO_4), which was obtained from **2** and $[Au_2(dppe)_2]Cl_2$ in MeOH following the addition of tetrabutylammonium perchlorate, confirmed the presence of a ClO_4^- ion inside the cavity of the metallaring in $\mathbf{3}^{2+}$ (Figure S13) and the formation of multiple hydrogen bonds (N···O: 3.179 Å; average distance for C···O: 3.23 Å) that appear to be stronger that those found in **3**-$(BF_4)_2$.[9] The equilibrium between $\mathbf{3}^{2+}$ and $\mathbf{4}^{+}$ is affected by the solution concentration; the intensity of the ^{1}H NMR signals for $\mathbf{3}^{2+}$ increases in a concentrated CD_3OD solution of **3**-$(BF_4)_2$ compared to that in a dilute solution (Figure S14).[9] This behavior is believed to be due to the more effective solvation of the BF_4^- anions in a more diluted solution, which prevents the accommodation of a BF_4^- ion in the cavity of the metallaring of $\mathbf{3}^{2+}$.

In summary, we have shown that *trans*(N)-$[Co(\text{D-nmp})_2]^-$ ($\mathbf{1}^-$) functions as a sulfur-donating metallaligand toward a gold(I) center with retention of its geometry, and that the presence of a methyl group on each nitrogen donor leads to the formation of $[Au_2Co_2(\text{D-nmp})_4]$ (**2**), which is soluble in various solvents. The solubility of **2** enabled the investigation of its reaction with $[Au_2(dppe)_2]^{2+}$, which revealed a unique expansion of the eight-membered $\mathrm{Au^{I}_{2}Co^{III}_{2}}$ ring in **2** to the 18-membered $\mathrm{Au^{I}_{4}Co^{III}_{2}}$ ring in $[Au_4Co_2(dppe)_2(\text{D-nmp})_4]^{2+}$ ($\mathbf{3}^{2+}$), which selects and accommodates a tetrahedral anion inside the ring. Remarkably, $\mathbf{3}^{2+}$ is readily interconvertible with a nine-membered $\mathrm{Au^{I}_{2}Co^{III}}$ ring in $[Au_2Co(dppe)(\text{D-nmp})_2]^+$ ($\mathbf{4}^{+}$) in solution; this process depends on several external factors, such as solvent, concentration, and counteranion. To the best of our knowledge, such an interconversion between heteroleptic and heterometallic rings is unprecedented, although several examples of the interconversion of homoleptic and homometallic rings have been reported.[5a,f,g] The interconversion between $\mathbf{3}^{2+}$ and $\mathbf{4}^{+}$, together with the conversion of **2** into $\mathbf{3}^{2+}$, confirms the lability of the Au–S and Au–P bonds, which is essential for the observed metallaring expansion and contraction events. Finally, the present study should provide insight into the development of metallaring coordination systems with tunable and switchable structures and properties.

Received: November 18, 2013

Keywords: heterometallic complexes · metallacycles · ring expansion · S ligands · template synthesis

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[1] a) M.-S. Wang, G. Xu, Z.-J. Zhang, G.-C. Guo, *Chem. Commun.* **2010**, *46*, 361–376; b) J. Tao, R.-J. Wei, R.-B. Huang, L.-S. Zheng, *Chem. Soc. Rev.* **2012**, *41*, 703–737; c) H. Miyake, H. Tsukube, *Chem. Soc. Rev.* **2012**, *41*, 6977–6991; d) O. S. Wenger, *Chem. Rev.* **2013**, *113*, 3686–3733; e) E. Coronado, G. M. Espallargas, *Chem. Soc. Rev.* **2013**, *42*, 1525–1539.

[2] a) *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCY, Weinheim, **2001**; b) A. C. Benniston, *Chem. Soc. Rev.* **2004**, *33*, 573–578; c) J.-P. Collin, V. Heitz, J.-P. Sauvage, *Top. Curr. Chem.* **2005**, *262*, 29–62; d) S. Bonnet, J.-P. Collin, M. Koizumi, P. Mobian, J.-P. Sauvage, *Adv. Mater.* **2006**, *18*, 1239–1250; e) F. Durola, J.-P. Sauvage, O. S. Wenger, *Coord. Chem. Rev.* **2010**, *254*, 1748–1759.

[3] a) B. J. Holliday, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 2076–2097; *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2043; b) S. J. Lee, W. Lin, *Acc. Chem. Res.* **2008**, *41*, 521–537; c) B. H. Northrop, H.-B. Yang, P. J. Stang, *Chem. Commun.* **2008**, 5896–5908; d) M. A. Halcrow, *Dalton Trans.* **2009**, 2059–2073; e) B. H. Northrop, Y.-R. Zheng, K.-W. Chi, P. J. Stang, *Acc. Chem. Res.* **2009**, *42*, 1554–1563; f) B. Lippert, P. J. S. Miguel, *Chem. Soc. Rev.* **2011**, *40*, 4475–4487.

[4] a) M. D. Lankshear, P. D. Beer, *Coord. Chem. Rev.* **2006**, *250*, 3142–3160; b) N. Gimeno, R. Vilar, *Coord. Chem. Rev.* **2006**, *250*, 3161–3189; c) J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh, R. T. McBurney, *Angew. Chem.* **2011**, *123*, 9428–9499; *Angew. Chem. Int. Ed.* **2011**, *50*, 9260–9327; d) J.-C. Chambron, J.-P. Sauvage, *New J. Chem.* **2013**, *37*, 49–57.

[5] a) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi, K. Ogura, *Chem. Commun.* **1996**, 1535–1536; b) S. B. Lee, S. Hwang, D. S. Chung, H. Yun, J.-I. Hong, *Tetrahedron Lett.* **1998**, *39*, 873–876; c) M. Schweiger, S. R. Seidel, A. M. Arif, P. J. Stang, *Inorg. Chem.* **2002**, *41*, 2556–2559; d) C. S. Campos-Fernández, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsa, J. M. Koomen, D. H. Russell, K. R. Dunbar, *J. Am. Chem. Soc.* **2005**, *127*, 12909–12923; e) P. Diaz, J. A. Tovilla, P. Ballester, J. Benet-Buchholz, R. Vilar, *Dalton Trans.* **2007**, 3516–3525; f) Y. M. Na, T. H. Noh, I. S. Chun, Y.-A. Lee, J. Hong, O.-S. Jung, *Inorg. Chem.* **2008**, *47*, 1391–1396; g) C. R. Kim, H. J. Kang, C. W. Kim, K. H. Yoo, O.-S. Jung, *Transition Met. Chem.* **2009**, *34*, 579–584; h) *Anion Coordination Chemistry* (Eds.: K. Bowman-James, A. Bianchi, E. García-España), Wiley-VCY, Weinheim, **2012**.

[6] a) A. Mayr, J. Guo, *Inorg. Chem.* **1999**, *38*, 921–928; b) Y.-F. Han, W.-G. Jia, Y.-J. Lin, G.-X. Jin, *Angew. Chem.* **2009**, *121*, 6352–6356; *Angew. Chem. Int. Ed.* **2009**, *48*, 6234–6238; c) A. Baniodeh, I. J. Hewitt, V. Mereacre, Y. Lan, G. Novitchi, C. E. Anson, A. K. Powell, *Dalton Trans.* **2011**, *40*, 4080–4086; d) G. N. Newton, M. Nihei, H. Oshio, *Eur. J. Inorg. Chem.* **2011**, 3013–3042; e) V. Vajpayee, Y. H. Song, Y. J. Yang, S. C. Kang, T. R. Cook, D. W. Kim, M. S. Lah, I. S. Kim, M. Wang, P. J. Stang, K.-W. Chi, *Organometallics* **2011**, *30*, 6482–6489; f) S.-L. Huang, Y.-J. Lin, T. S. A. Hor, G.-X. Jin, *J. Am. Chem. Soc.* **2013**, *135*, 8125–8128.

[7] a) T. Konno, Y. Chikamoto, K. Okamoto, T. Yamaguchi, T. Ito, M. Hirotsu, *Angew. Chem.* **2000**, *112*, 4264–4267; *Angew. Chem. Int. Ed.* **2000**, *39*, 4098–4101; b) T. Konno, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 627–648; c) A. Toyota, T. Yamaguchi, A. Igashira-Kamiyama, T. Kawamoto, T. Konno, *Angew. Chem.* **2005**, *117*, 1112–1116; *Angew. Chem. Int. Ed.* **2005**, *44*, 1088–1092; d) A.

Igashira-Kamiyama, T. Konno, *Dalton Trans.* **2011**, *40*, 7249–7263; e) R. Lee, A. Igashira-Kamiyama, M. Okumura, T. Konno, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 908–920.

[8] T. Konno, M. Hattori, T. Yoshimura, M. Hirotsu, *Chem. Lett.* **2000**, *29*, 852–853.

[9] See the Supporting Information.

[10] CCDC 967556 (K-**1**), 967557 (**2**), 967558 (**3**-(BF4)2), 967559 (**4′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For experimental details of the X-ray crystal structure determination, see the Supporting information.

[11] K. Okamoto, K. Wakayama, H. Einaga, S. Yamada, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 165.

[12] a) G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley, Chichester, **1980**; b) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, **1997**.

[13] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597–636.

[14] Y. Hashimoto, K. Tsuge, T. Konno, *Chem. Lett.* **2010**, *39*, 601–603.

[15] Consistently, the absorption and CD spectra of **3**-$(BF_4)_2$ in water are quite different from those in CH_2Cl_2 (Figure S8).

[16] The integration ratios of the ^{1}H NMR signals for $\mathbf{3}^{2+}$ and $\mathbf{4}^{+}$ after the addition of NH_4BF_4, NH_4ClO_4, and NH_4ReO_4 are 1:10, 1:1.8, and 1:1.6, respectively. This implies that the larger ClO_4^- and ReO_4^- anions more effectively stabilize the ring structure in $\mathbf{3}^{2+}$ because of the stronger binding of these anions to $\mathbf{3}^{2+}$.

[17] The addition of $KMnO_4$ to a solution of **3**-$(BF_4)_2$ in MeOH led to a quick color change to give an unidentified precipitate owing to the decomposition of $\mathbf{3}^{2+}$ by oxidation with MnO_4^-.