632 *Organometallics* **2004,** *23,* 632−634

Bimetallocyclophanes Formed by the $\pi-\pi$ Stacking Interaction Approach and Fluorescent Chemosensing Behavior

Feng-Bo Xu,* Qing-Shan Li, Xian-Shun Zeng, Xue-Bing Leng, and
Zheng-Zhi Zhang*

*State Key Laboratory of Elemento-Organic Chemistry, Nankai University,
Tianjin 300071, People's Republic of China*

Received June 19, 2003

*Summary: A new high-yielding synthetic approach for the preparation of bimetallic cyclophane has been achieved through the $\pi-\pi$ stacking interaction approach from the flexible ligand **1** and group 11 metal M^+. The Cu complex **2a** can act as a fluorescent chemosensor for benzenediacetonitrile.*

Metallocyclophane is an important kind of compound in supramolecular chemistry due to its particular molecular recognition properties and potential applications in chemosensing and molecular electronics.[1] In the preparation of metallocyclophanes three general and high-yielding synthetic approaches have been presented in the literature,[2] which include (1) the directional-bonding approach,[3] (2) the symmetry-interaction approach, and (3) the weak-link approach.[4] Herein we offer a new high-yielding synthetic strategy to prepare bimetallocyclophane from a new flexible phosphine ligand with an anthracene fluorophore and group 11 metal M(I) ion starting materials by a $\pi-\pi$ stacking interaction. In contrast to the weak link approach, the new approach does not need two coordination positions to a metal center in the flexible ligand. These new compounds possess other weakly coordinated ligands and vacant coordination sites at the metal centers, which are available for further chemistry and molecule-responsible fluorescent chemosensing research.

The new flexible phosphine ligand **1** was prepared by a Mannich reaction from Ph_2PH, $(CH_2O)_n$, and 9,10-bis(*n*-propaminomethyl)anthracene (Scheme 1). Spectroscopic data for solution of **1** are completely consistent with the proposed structure.

The bimetallocyclophanes **2** were prepared in >90% yield by the reaction of ligand **1** with $M(CH_3CN)_4(ClO_4)$ (M = Cu, Ag) or $Au(SMe_2)Cl$ in a 1:1 stoichiometric ratio. These reactions were driven by the $\pi-\pi$ stacking interaction between the anthracene units in the two ligands **1**. The complexes **2a**,[5] **2b**,[6] and **2c**[7] have been fully characterized in solution, and the crystal structures of **2a**[5] and **2c**[7] have been determined by X-ray diffraction studies.

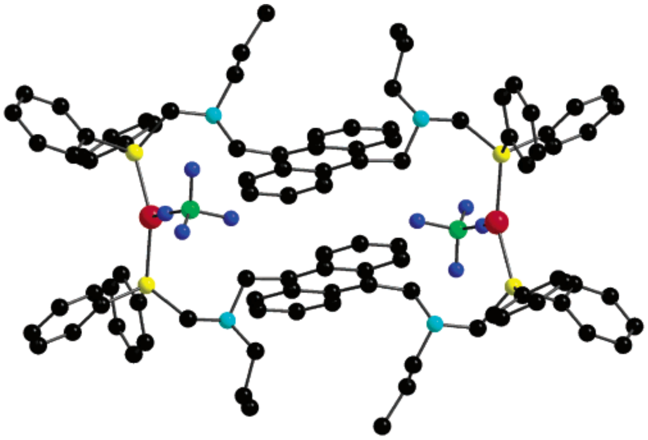


Figure 1. ORTEP view of complex **2a**.

Figure 1 shows the molecular structure of **2a**. The coordination environment around the Cu atom is trigonal planar with two P atoms from the two ligands **1** and one O atom from the anion ClO_4^-. The distance of the two anthracene rings in **2a** is 3.5626 Å, which exhibits

---

(1) (a) Jones, C. J. *Chem. Soc, Rev*. **1998**, *27*, 289−299. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev*. **2000**, *100*, 853−908. (c) Xu, F. B.; Li, Q. S.; Zeng, X. S.; Leng, X. B.; Zhang, Z. Z. *Organometallics* **2002**, *21*, 4894−4896. (d) Xu, F. B.; Li, Q. S.; Wu, L. Z.; Leng, X. B.; Li, Z. C.; Zeng, X. S.; Chow, Y. L.; Zhang, Z. Z. *Organometallics* **2003**, *22*, 633−640.

(2) (a) Review: Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed*. **2001**, *40*, 2022−2043. (b) Eisenberg, A. H.; Ovchinnikov, M. V.; Mirkin, C. A. *J. Am. Chem. Soc*. **2003**, *125*, 2836−2837. (c) Holliday, B. J.; Jeon, Y. M.; Mirkin, C. A.; Stern, C. L.; Incarvito, C. D.; Zakharov, L. N.; Sommer, R. D.; Rheingold, A. L. *Organometallics* **2002**, *21*, 5713−5725.

(3) Hogarth, G.; Norman, T. *J. Chem. Soc., Dalton Trans*. **1996**, 1077−1085.

(4) (a) Hartshorn, C. M.; Steel, P. J. *Inorg. Chem*. **1996**, *35*, 6902−6903. (b) Hartshorn, C. M.; Steel, P. J. *J. Chem. Soc., Dalton Trans*. **1998**, 3927−3933. We have noted that Steel's work is not included in Mirkin's review.[2a] In fact, however, it should also belong to the weak-link synthetic approach.

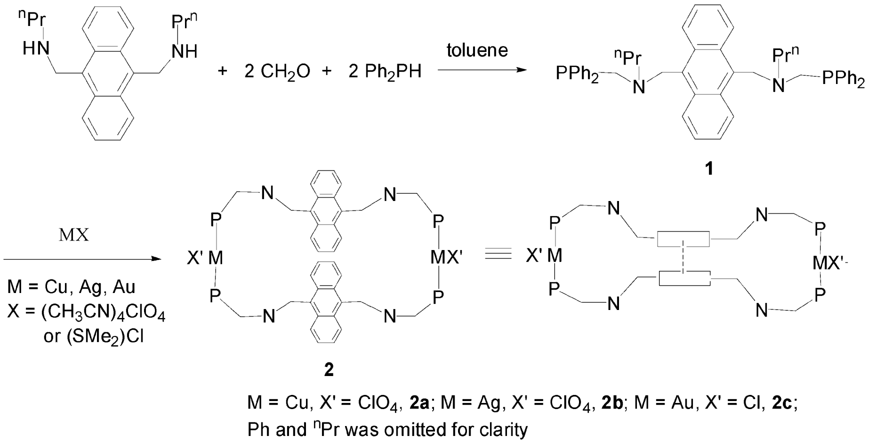
(5) **2a**: mp 152−154 °C; ^1H NMR ($CDCl_3$) δ 0.79−0.83 (t, 12H, $4CH_3$, ^nPr), 1.51−1.57 (m, 8H, $4CH_2$, ^nPr), 2.83−2.88 (m, 8H, $4CH_2$, ^nPr), 3.79 (s, 8H, $4N-CH_2-P$), 4.75 (s, 8H, $4An-CH_2-N$), 6.61−6.65 (m, 16H, $8C_6H_5$), 7.04−7.09 (m, 16H, $8C_6H_5$), 7.23−7.33 (m, 8H, $8C_6H_5$), 7.77−7.81 (m, 8H, 2An), 8.71−8.74 (m, 8H, 2An) ppm; ^{31}P NMR ($CDCl_3$) δ −10.443 ppm. Anal. Calcd for $C_{96}H_{100}Cl_2N_4O_8P_4Cu_2$: C, 64.52; H, 5.84; N, 3.27. Found: C, 64.81; H, 6.01; N, 3.09. Crystal data: 0.20 × 0.20 × 0.30 mm, monoclinic, space group $P2_1/n$, a = 11.2322(8) Å, b = 21.6175(14) Å, c = 19.4727(13) Å, β = 92.6520(10)°, V = 4723.1(6) Å, ρ_{calcd} = 1.257 Mg m^{-3}, $2\theta_{max}$ = 50.06°, T = 298 K, μ = 0.631 mm^{-1}, 19 512 measured reflections, of which 8346 reflections are independent, 541 parameters, R1 = 0.0615, wR2 = 0.2131 (all data, refined against $|F^2|$), largest residual peak 0.845 e Å^{-3}.

(6) **2b**: mp 124−125 °C; ^{31}P NMR ($CDCl_3$) δ −6.05 ppm. Anal. Calcd for $C_{96}H_{100}Cl_2N_4O_8P_4Ag_2$: C, 60.25; H, 5.38; N, 2.90. Found: C, 60.40; H, 5.28; N, 3.24.

(7) **2c**: mp 134−136 °C; ^{31}P NMR ($CDCl_3$) δ 23.94 ppm. Anal. Calcd for $C_{96}H_{100}Cl_2N_4P_4Au_2$: C, 56.91; H, 5.07; N, 2.71. Found: C, 56.34; H, 4.87; N, 2.52. Crystal data: 0.25 × 0.20 × 0.20 mm, triclinic, space group $P\bar{1}$, a = 13.5464(11) Å, b = 14.1715(11) Å, c = 15.7734(13) Å, α = 78.810(2)°, β = 67.0000(10)°, γ = 62.225(2)°, V = 2465.9(3) Å, ρ_{calcd} = 1.474 Mg m^{-3}, $2\theta_{max}$ = 50.06°, T = 298 K, μ = 3.326 mm^{-1}, 10 278 measured reflections, of which 8602 reflections are independent, 550 parameters, R1 = 0.0371, wR2 = 0.0923 (all data, refined against $|F^2|$), largest residual peak 0.960 e Å^{-3}.

10.1021/om0340037 CCC: $27.50

Scheme 1. Preparation of Complexes 2



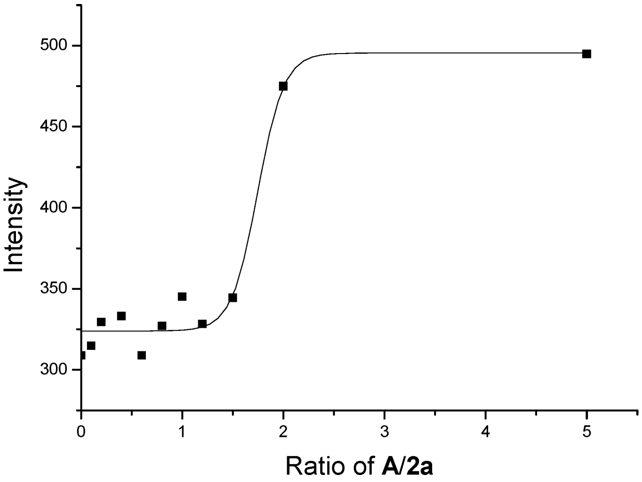


Figure 2. Plot of the recorded relation of fluorescence intensities at 435 nm against the ratio of **A** to **2a** ([**2a**] = 1×10^{-5} M) in dichloromethane.

a π−π stacking interaction. The Cu and N separation is in the range of 3.861−4.129 Å, which indicates that there is no interaction between them. The Cu···Cu separation is 11.430 Å. The whole molecule of **2a** possesses a dumbbell shape. The complex **2c** has a similar structure with **2a** (see the Supporting Information), but each gold center possesses a linear two-coordinate geometry with two P atoms. The distance of the Au atom from the anion Cl^- is 2.953 Å, which can be considered as a very weak interaction,[8] and the Au···Au separation is 11.726 Å. The formation of bimetallocyclophane by the π−π stacking interaction approach, to a great extent, depends on the rational topological design of the flexible ligand.

When a solution of **2a** in dichloromethane was titrated with 1,4-benzenediacetonitrile (**A**), the fluorescence intensity gave rise to a noticeable change. The plot of fluorescence intensity versus equivalents of **A** gives a sigmoid curve (Figure 2), which indicates that two probable chemical processes take place sequentially (Scheme 2). At the beginning the 1:1 copolymer **3** was formed by the substitution of two cyano groups in **A** for two anions ClO_4^- between the two macrocycles **2a**, as shown in Scheme 2. The further reaction of the complex **3** with **A** afforded the 1:2 copolymer **4** through **A** sequestering into the macrocycles in **3**. While there is no change of the fluorescence intensity in the conversion of **2a** to **3**, due to the untouched structure of the part of bimetallocyclophane in **3**, the conversion of **3** into **4** is accompanied by an increase in the fluorescence intensity due to the structural change of the macrocycle by the formation of the tetrahedrally coordinated polymer, which causes a decrease in the though-space interaction between the two fluorophores.[9] When the **2a**/**A** ratio is around 1:2, the fluorescence enhancement reaches the maximum. In the emission spectra of **2a** before and during the titration with **A** no excimer emissions are observed. Spectroscopic data and elemental analysis of **4** completely support the proposed structure.[10] In the IR spectrum of **4** two CN stretching vibrations (2362 and 2330 cm^{-1}) are observed, which are caused by coordination of **4** inside and outside the macrocycle and are at higher wavenumbers than that of **A** (2246 cm^{-1}), owing to the donation of antibonding electrons of the CN group to the copper atom.[11] In the ^{31}P NMR spectrum the 1.7 ppm upfield shifts of **4** with respect to the resonance of **2a** may be attributed to the coordination of **A** molecules to the Cu atoms, which increase the electron density at the P atoms. Owing to the decrease of through-space interaction between the two anthracene rings, the proton resonances of anthracene rings in **4** are 0.167 and 0.275 ppm upfield shifts from those in **2a**. Many attempts failed to obtain crystals of **4** suitable for an X-ray diffraction study.

In contrast, when the solution of **2a** in dichloromethane was titrated with acetonitrile or 1,3-dicyanopropane, no noticeable change in the fluorescene signal of **2a** was shown and no new complex was formed, due to the basicity of acetonitrile or 1,3-dicyanopropane

---

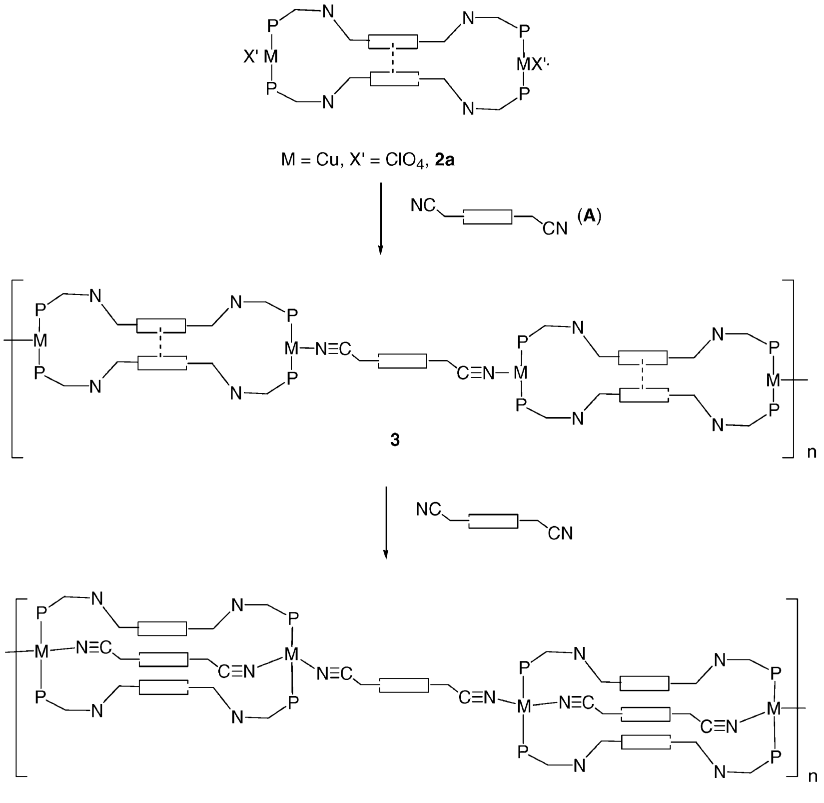
(8) Schmidbaur, H.; Pollok, T.; Herr, R.; Wagner, F. E.; Bau, R.; Riede, J.; Muller, G. *Organometallics* **1986**, *5*, 566−574.

(9) (a) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Sacchi, D.; Taglietti, A.; *Analyst* **1996**, *121*, 1763−1768. (b) Fabbrizzi, L.; Faravelli, I.; Francese, G.; Licchelli, M.; Perotti, A.; Taglietti, A. *Chem. Commun.* **1998**, 971−972.

(10) Complex **4**: mp >140 °C dec, FT-IR (KBr disk) ν_{CN} 2362 and 2330 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76−0.81 (t, 12H, $4CH_3$, ^nPr), 1.54−1.61 (m, 8H, $4CH_2$, ^nPr), 2.60−2.65 (m, 8H, $4CH_2$, ^nPr), 3.80 (s, 8H, $4N-CH_2-P$), 3.92 (s, 8H, $4NC-CH_2$), 4.72 (s, 8H, $4An-CH_2-N$), 6.60−6.62 (m, 16H, $8C_6H_5$), 7.02−7.07 (m, 20H, $8C_6H_5$ and $2C_6H_4$), 7.19−7.26 (m, 12H, $8C_6H_5$ and $2C_6H_4$), 7.50−7.53 (m, 8H, 2An), 8.54−8.58 (m, 8H, 2An) ppm; ^{31}P NMR ($CDCl_3$) δ −12.143 (s) ppm. Anal. Calcd for $C_{116}H_{116}Cl_2Cu_2N_4O_8P_4$: C, 67.24; H, 5.64; N, 5.41. Found: C, 66.94; H, 5.80; N, 5.32.

(11) Nakamoto, K. *Infrared and Roman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978; p 266.

Scheme 2



being weaker than that of **A**.[12] The titration experiment of **2a** with benzeneacetonitrile also does not give a sigmoid curve of fluorescence change.

In conclusion, we have demonstrated that a new high-yielding synthetic approach can be used for the preparation of bimetallocyclophanes. The solution of **2a** exhibits chemosensing behavior for 1,4-benzenediacetonitrile. The expansion of the types of transition metals that can be utilized in the $\pi-\pi$ stacking interaction approach for the preparation of bimetallocyclophane is underway.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant No. 20342006).

Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for compounds **2a** and **2c** and figures giving NMR spectra of complexes **2a** and **4** and the fluorescence emission spectra of **2a** in order of increasing **A** in dichloromethane. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0340037

---

[12] Larson, R. C.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1960**, *82*, 3526–3527.