The Calix-Shaped Metallocyclophane [Rh{9,10-bis(2-(diphenylphosphino)ethyl)anthracene}-(CO)Cl]$_3$ and Its Solution Behavior

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Summary: The reaction of 9,10-bis(2-(diphenylphosphino)ethyl)anthracene with [Rh(CO)$_2$Cl]$_2$ in dichloromethane at −30 °C by metal-directed self-assembly affords the novel calix-shaped metallocyclophane [Rh{9,10-bis(2-(diphenylphosphino)ethyl)anthracene}(CO)Cl]$_3$, which adopts a cone conformation and possesses a huge cavity. It has special solution behavior and can encapsulate carbon monoxide in a dichoromethane solution, which leads to fluorescent enhancement emission intensity.

Metallocyclophane compounds have been extensively investigated, owing to their unusual chemical and physical properties. Although many cyclic dimers and cyclic tetramers have been prepared and their structures determined, only a small number of cyclic trimers have been reported.[1,2] Herein we wish to describe the preparation, X-ray crystal structure, and solution behavior of the novel calix-shaped metallocyclophane [Rh{9,10-bis(2-(diphenylphosphino)ethyl)anthracene}(CO)-Cl]$_3$ (**1**; Chart 1).

Compound **1**[3] was easily prepared in high yield by reaction of 9,10-bis(2-(diphenylphosphino)ethyl)anthracene[4] with [Rh(CO)$_2$Cl]$_2$ in dichloromethane at −30 °C.

X-ray diffraction grade crystals of compound **1** were grown by slow diffusion of ether into a solution of compound **1** in dichloromethane (Figure 1a).

The resulting X-ray structure[5,6] reveals that this molecule adopts a cone conformation. It belongs to the C_s point group, and there is a mirror plane containing

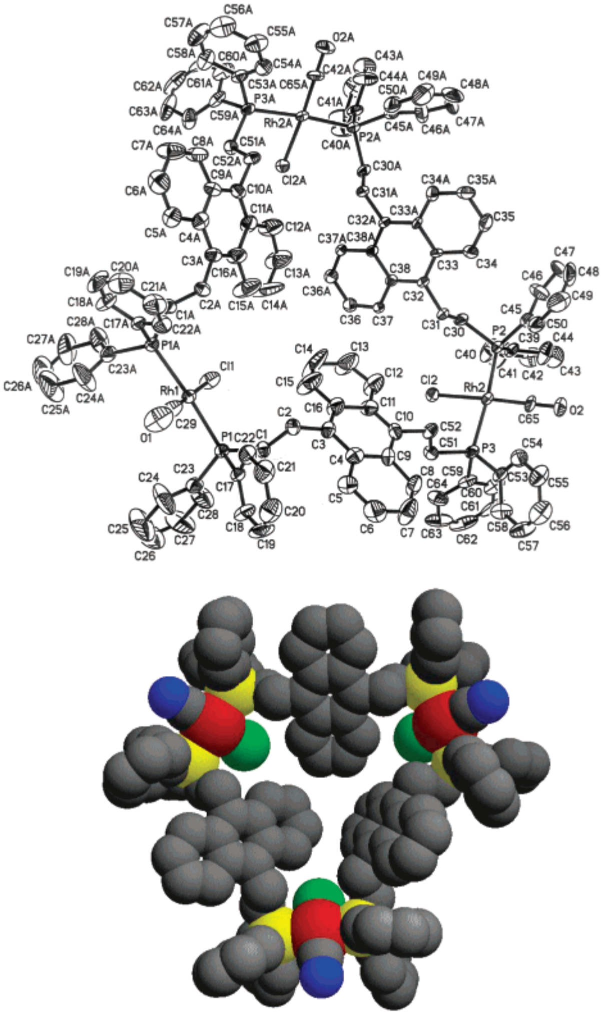
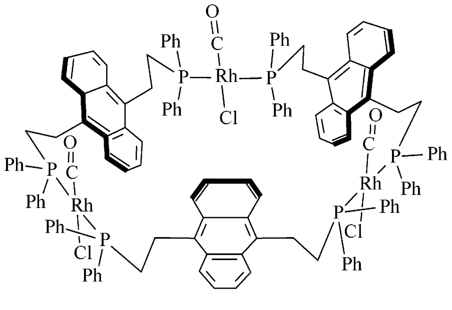


Figure 1. (a, top) ORTEP view and (b, bottom) space-filling view of compound **1**.

Chart 1



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[1] Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289−299.

[2] Olenyuk, B.; Fechtenmkotter, A.; Stang, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1707−1728.

[3] Characterization of compound **1**: ^{31}P NMR δ 26.05, 27.24 ppm, $^{1}J(^{31}P-^{103}Rh) = 120.13$ Hz (CDCl$_3$); IR ν(CO) 1971 cm^{-1}. Anal. Calcd for $C_{129}H_{108}Cl_3O_3P_6Rh_3$: C, 67.30; H, 4.69. Found: C, 67.16; H, 4.72.

[4] Xu, F. B. Ph.D. Thesis, Institute of Elemento-Organic Chemistry, Nankai University, 2001.

[5] Crystal data for $C_{131.25}H_{112.5}Cl_{7.5}O_3P_6Rh_3$: $M_r = 2498.14$; monoclinic, space group $P2_1/m$, $a = 10.592(2)$ Å, $b = 37.929(8)$ Å, $c = 16.505(3)$ Å, $\beta = 95.77(3)°$. $V = 6598(2)$ Å^3, $Z = 2$ (there are 2.25 CH$_2$Cl$_2$ molecules per unit cell), $\rho = 1.258$ g/cm^3. Diffraction experiments were performed on a Bruker Smart 1000 CCD diffractometer employing graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). Of the data, 26 923 were unique and 11 633 ($>2\sigma$(I)) were used to refine the structure employing 708 parameters. The atom positions were determined using direct methods, employing SHELXTL-97 and successive difference Fourier map calculations. The full-matrix least-squares refinement was carried out on F^2. All non-hydrogen atoms were assigned anisotropic temperature factors. Empirical absorption corrections ($\mu = 0.642$ mm^{-1}) were applied to the data sets employing SADABS. Most hydrogen atom positions were calculated and allowed to ride on the carbon to which they were bonded, assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated but not refined (R1 = 0.0675, wR2 = 0.1192, GOF = 0.929).

[6] Sheldrick, G. M. SHELXS97 and SHELXL97; University of Göttingen, Göttingen, Germany, 1997.

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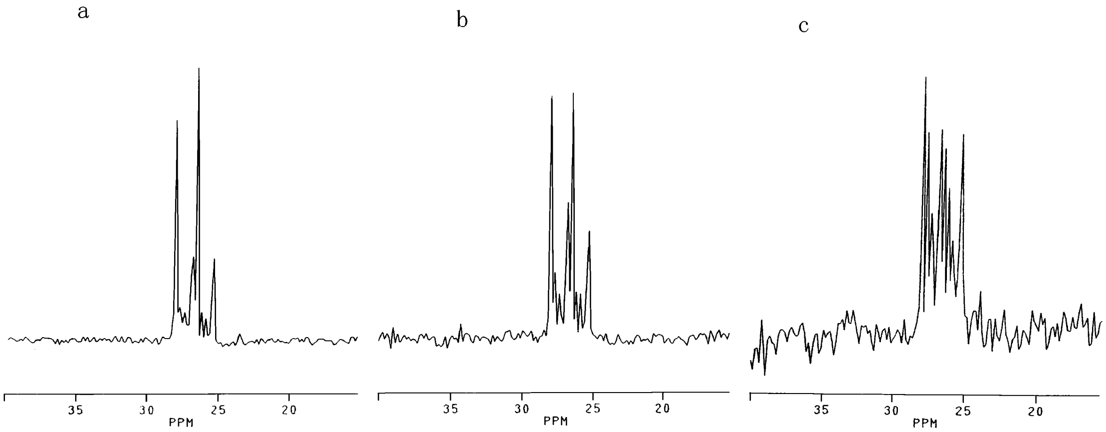

Figure 2. ^{31}P NMR spectra of compound **1** in different concentrations of $CDCl_3$: (a) 2×10^{-2} M; (b) 1×10^{-2} M; (c) 5×10^{-3} M.

atoms Cl(1), Rh(1), C(29), and O(1). All of the P and Rh atoms basically lie in the same plane (the maximum deviation is 0.0972 Å) and the angles of the plane with the three anthracene rings and three OC−Rh bonds are 116, 152, 152° and 138.6, 120.7, 120.7°, respectively. Three carbonyls and three chlorine atoms linked with Rh atoms orient to the upper rim and lower rim, respectively.

While the angle C(29)−Rh(1)−Cl(1) (177.0(6)°) is nearly linear, the angles C(65)−Rh(2)−Cl(2) and C(65A)−Rh(2A)−Cl(2A) (171.8(4)°) exhibit larger deviation. The atoms C(65), Cl(2) and C(65A), Cl(2A) tilt away from the calix cavity. Two Rh−P bond distances (2.324(2) Å) formed at the Rh(1) atoms are equal, but those distances formed at Rh(2) and Rh(2A) (2.324(2), 2.308(2) Å and 2.324(2), 2.308(2) Å) are not.

The areas of the calix top and bottom (calculated by the circle formed through three middle points of the C−C bonds of anthracenes at the upper and lower rims) are ca. 120 and 22 Å^2, respectively. The dihedral angle and the average height between the two planes are ca. 30 °C and 9 Å, respectively. The rough volume of the calix cavity is about 180 Å^3, as shown in Figure 1b, which indicates a large cavity in compound **1**.

The ^{31}P NMR spectrum of compound **1** in $CDCl_3$ mainly shows two double peaks. The chemical shifts are 26.05 and 27.24 ppm, respectively, and heights of peaks strongly depend on the concentration of the compound. Like Fujita's report,[7] our observation shows that there mainly is an equilibrium mixture of two components assignable as cyclic trimer **1** and cyclic tetramer **1′** in $CDCl_3$ solution. At higher concentration the major product is assigned as trimer **1** and at lower concentration the major form shifts to tetramer **1′**. The equilibration is a thermodynamic balance, whereas entropy effects favor the formation of cyclic trimer **1**, since **1** assembles from fewer components than **1′**. Besides, the spectrum also indicates that there are two other minor components, whose ratios increase when the solution is further diluted (Figure 2).

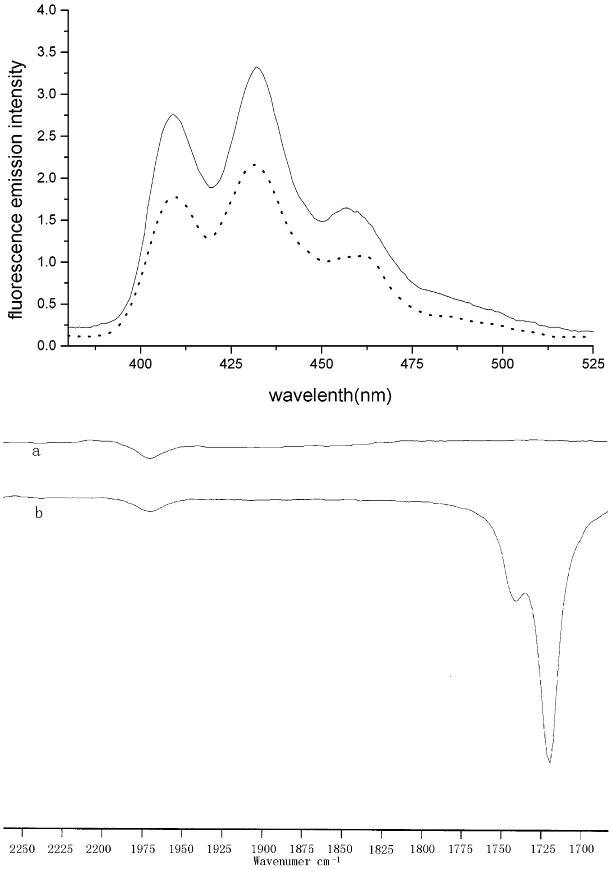

Figure 3. (top) Fluorescence ($\lambda_{ex} = 362$ nm) spectra of (···) the solution of the compound **1** in dichloromethane (concentration, 5×10^{-6} M) and (−) the same solution saturated with CO. (bottom) IR spectra of (a) a solution of compound **1** in dichloromethane (concentration, 5×10^{-3} M) and (b) the same solution saturated with CO.

The fluorescence spectrum of compound **1** in CH_2Cl_2 at room temperature displays the expected emission peak for the anthracenic chromophore centered at 433 nm, and a weak band appears in the IR spectrum at 1971 cm^{-1}, which is the terminal CO stretching frequency. After the same solution of compound **1** was saturated with CO at room temperature, the fluorescence intensity of the solution increased 0.5-fold and two new strong CO bands appeared in the IR spectrum at 1742 and 1721 cm^{-1} (Figure 3). As we know, in metal complexes terminal carbonyls exhibit CO bands in the region 2140−1800 cm^{-1}, while bridging carbonyls appear in the region 1850−1700 cm^{-1}.[8] Formation of two bridging carbonyls at each Rh atom in compound **1** is impossible. Even if were possible, their absorption

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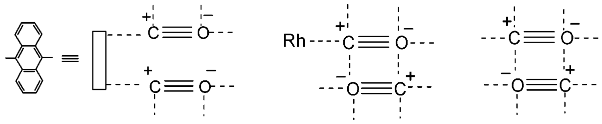
[7] Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun.* **1996**, 1535−1536.

Chart 2



strength under the given solution conditions should be weak and comparable with the terminal CO band (1971 cm^{-1}). Therefore, new CO bond formation at Rh atoms can be excluded unambiguously. While there was a measured weak CO absorption band in heptane at 1725 cm^{-1} (among general organic solvents there is a maximum solubility of CO in heptane at room temperature of 17.24 cm^3/mol[9]), no CO bands were observed in the solvent CH_2Cl_2 or a CH_2Cl_2 solution of the ligand 9,10-bis(2-(diphenylphosphino)ethyl)anthracene after these solvents and the solution were saturated with CO. Besides, it has also been observed that the IR spectrum of *p*-*tert*-butylcalix[6]arene or *p*-*tert*-butylcalix[4]arene (Aldrich) in CH_2Cl_2 (1×10^{-3} M) saturated with CO gives the same medium-intensity CO bands at 1742 and 1720 cm^{-1}. Therefore, the aforementioned CO bands can be assigned to direct and induced dipole–dipole weak interactions between CO molecules and between the anthracene rings and CO due to strong encapsulation of CO in the large cavity of compound **1**. Of course, a weak interaction between CO and Rh atoms may be present as well (Chart 2). Because of the last two weak interactions mentioned above, electron density transfer and photoinduced electron transfer[10,11] processes between them may take place and the enhancement emission intensity can be observed in the CH_2Cl_2 solution of compound **1** saturated with CO. After the solvent and CO are removed and the residue is redissolved, the aforementioned process can be recycled. Therefore, the new discovery shows that compound **1** may be exploited as a potential fluorescent sensor for carbon monoxide.

This report is significant for the following reasons. First, it demonstrates that one can use metal-directed assembly to prepare a new class of calix-shaped metallocyclophanes in simple procedure and high yield. Second, while the solid structure of compound **1** has been firmly confirmed by X-ray crystallography, our work shows that the solution behavior of metallocyclophanes is complicated. Third, our observation shows that compound **1** may act as a potential fluorescent sensor for carbon monoxide. It can be anticipated that, owing to its large cavity, the new compound will exhibit molecular recognition and peculiar photophysical properties. It will provide insight and some exciting opportunities in the aspects of electron transfer and synthetic receptor design and may even act as a microreactor in some catalytic organic reactions.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; Oxford University Press: Oxford, U.K., 1980; p 85.

[9] Wilhelm, E.; Battino, R., *Chem. Rev.* **1973**, *73*, 1–9.

[10] de Silva, A. P.; Gunaratue, H. Q. N.; Gursnlangsson, T.; Huxley, A. J. M.; MeCoy, C. D.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566.

[11] Xu, F. B.; Weng, L. H.; Sun, L. J.; Zhang, Z. Z.; Zhou, Z. F. *Organometallics* **2000**, *19*, 2658–2660.