ORGANOMETALLICS

Volume 20, Number 18, September 3, 2001

Communications

Synthesis and Structure of New Binuclear Organopalladium Macrocyclic Complexes

Taro Tsubomura,* Takayuki Tanihata, Tetsuya Yamakawa, Rakuko Ohmi,
Tsuyoshi Tamane, Akon Higuchi, Akira Katoh, and Ken Sakai[†]

*Department of Applied Chemistry, Seikei University, Kichijoji-kitamachi, Musashino,
Tokyo 180-8633, Japan*

Received May 11, 2001

Summary: A new macrocyclic ligand and the binuclear palladium(II) complex of the ligand have been prepared and characterized. The two 2,6-bis(diaminomethyl)-phenyl units coordinate to the Pd(II) centers with N,C,N donor atoms. Two conformational isomers of the complex were isolated and characterized by X-ray and NMR.

There has been considerable interest in cyclometalated complexes containing anionic terdentate ligands.[1] The bis(2,6-diaminomethyl)phenyl chelate (N∧C∧N) is one of the well-known ligands,[2] but other S∧C∧S and P∧C∧P chelates[3] have been studied. In recent years, the complexes have also been used as catalysts for Karasch addition,[4] hydrocarbon activation,[5] Michael addition,[6] and the Heck reaction.[7] Other studies of the units include the preparation of the bimetallic complexes using a connecting ligand that contains the two N∧C∧N units.[8] The resulting complex polymers prepared could be specialty materials with interesting electronic and/or optical properties.[9] Furthermore, some macrocyclic complexes containing the terdentate N∧C∧N[10] or S∧C∧S[11] unit have been reported. The macrocyclic complexes are of interest, because they serve as receptors for specific molecules[11] and as potential catalysts for selective reactions.

We have reported the synthesis and reactivity of a series of macrocyclic metal complexes containing bis(aminomethyl)pyridyl (or bis(iminomethyl)pyridyl) groups as donating groups.[12] As an extension of our study, we

---

[*] To whom correspondence should be addressed. E-mail: tsubo@ch.seikei.ac.jp. Fax: +81-422-37-3871.

[†] Current address: Department of Applied Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku, Tokyo 162-8601, Japan.

(1) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New J. Chem* **1997**, *21*, 751.

(2) (a) van Koten, G.; Jastrzenbski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C. *J. Organomet. Chem.* **1978**, *148*, 233. (b) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589. (c) Grove, D. M.; van Koten, G.; Aoet, R.; Murrall, N. W.; Welch, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 1379. (d) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609.

(3) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

(4) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659.

(5) (a) Vifalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539. (b) Gupta, M.; Hage, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840.

(6) Stark, M. A.; Jones, G.; Richards, C. J. *Organometallics* **2000**, *19*, 1282.

(7) (a) Bergbreiter, D. E.; Osburn, P. L.; Liu, U.-S. *J. Am. Chem. Soc.* **1999**, *121*, 9538. (b) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687.

(8) (a) Steenwinkel, P.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1998**, *17*, 5411. (b) Lagunas, M.-C.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 731.

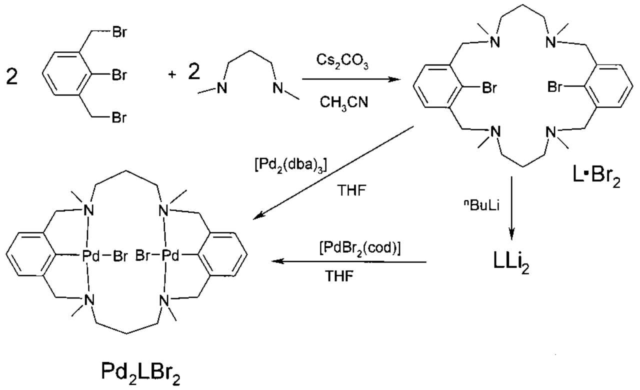
(9) James, S. L.; Verspui, G.; Spek, A. L.; van Koten, G. *Chem. Commun.* **1996**, 1309.

(10) (a) Hiraki, K.; Tsutsumida, J.; Fuchita, Y. *Chem. Lett.* **1986**, 337. (b) Hiraki, K.; Fuchita, Y.; Ohta, Y.; Tsutsumida, J.; Hardcastle, K. I. *J. Chem. Soc., Dalton Trans.* **1992**, 833.

(11) Kickham, J. E.; Loeb, S. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1848.

10.1021/om0103862 CCC: $20.00

Scheme 1



designed a novel macrocycle which contains two N∧C∧N coordinating units. The macrocyclic ligand (L•Br_2 shown in Scheme 1) is expected to incorporate two late transition metals in the N∧C∧N coordinating units. In this work, we prepared and characterized the ligand and the two conformational isomers of the palladium complex of this ligand.

The macrocycle L•Br_2 was prepared by a condensation reaction of 2,6-bis(bromomethyl)bromobenzene with *N*,*N*'-dimethyl-1,3-diaminopropane in the presence of Cs_2CO_3 in acetonitrile solution.[13] The ligand was obtained as colorless crystals in 30% yield. As shown in Scheme 1, two methods were tried to synthesize the palladium(II) complex of the macrocycle. In the first method, the ligand was treated with ^{n}BuLi and the lithium complex obtained was then mixed with dibromo(1,5-cyclooctadiene)palladium(II). The pale yellow compound Pd_2Br_2L crystallized from chloroform solution.[14] The ^{1}H NMR spectrum of the compound showed (1) a considerable high-field shift of the phenyl protons and (2) AB doublets at near 4 ppm, which were ascribed to the inequivalent methylene protons connected at the 2,6-position of the phenyl groups. The latter feature means the complex has a nonplanar structure. The compound was further characterized by X-ray studies.[15] Figure 1 shows the Z-shaped structure of the dipalladium complex. A center of inversion is located at the center of the dinuclear complex. One of the methyl groups in an asymmetric unit is axially oriented and the other equatorially. The NMR data show that the two methyl groups are equivalent in solution.

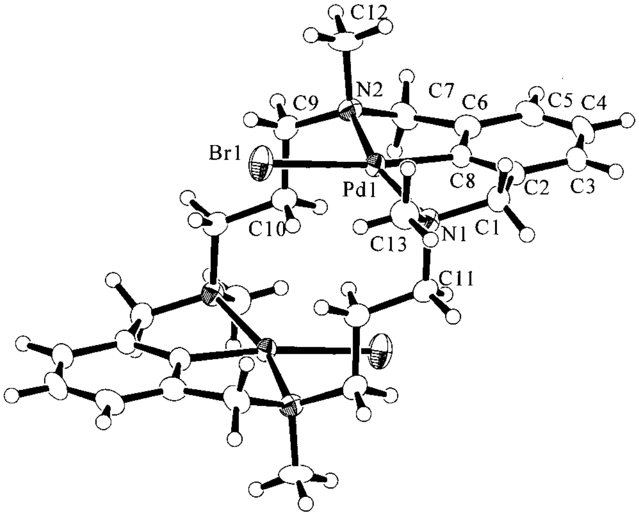


Figure 1. ORTEP drawing of the macrocyclic palladium(II) complex of the Z-shaped conformer. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (deg): Pd1−Br1 = 2.5691(9), Pd1−N1 = 2.131(4), Pd1−N2 = 2.122(4), Pd1−C8 = 1.919(5); Br1−Pd1−N1 = 101.2(1), Br1−Pd1−N2 = 96.3(1), Br1−Pd1−C8 = 173.7(2).

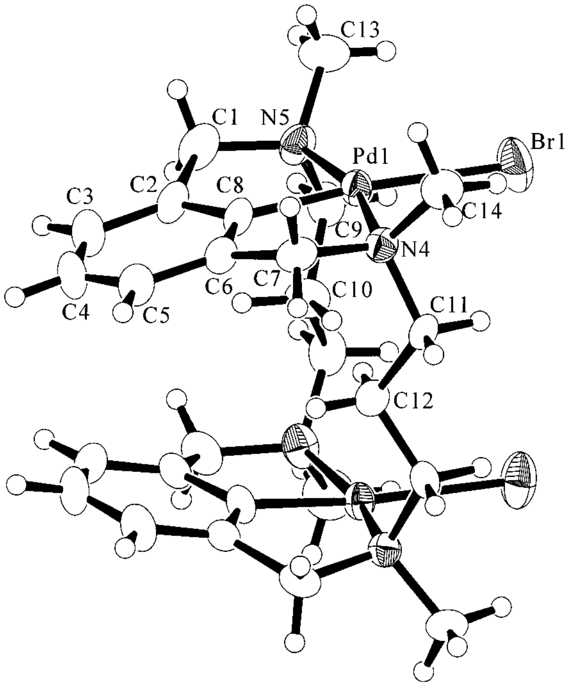


Figure 2. ORTEP drawing of the macrocyclic palladium(II) complex of the U-shaped conformer. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (deg): Pd1−Br1 = 2.5617(9), Pd1−N4 = 2.104(6), Pd1−N5 = 2.136(6), Pd1−C8 = 1.914(6); Br1−Pd1−N4 = 97.6(1), Br1−Pd1−N5 = 96.8(2), Br1−Pd1−C8 = 173.9(2)°.

In the second method, direct reaction of a Pd(0) complex, $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone), with the ligand was conducted. The product was shown to be a mixture of two isomers. One is the same Z-shaped complex that is obtained in the first method. The other compound, which was isolated in 10% yield as pale yellow crystals, shows an NMR pattern similar to that of the Z-shaped conformer, but it gives different chemical shifts and coupling constants.[16] The structure of the latter isomer was also clarified by X-ray studies.[17] As shown in Figure 2, this isomer has an interesting

---

(12) (a) Tsubomura, T.; Ezawa, M.; Sato, T.; Sakai, K. *Inorg. Chim. Acta* **2000**, *31*, C265. (b) Sato, T.; Sakai, K.; Tsubomura, T. *Supramol. Chem.* **1996**, *7*, 157. (c) Tsubomura, T.; Yasaku, K.; Sato, T.; Morita, M. *Inorg. Chem.* **1992**, *31*, 447.

(13) The macrocyclic ligand L•Br_2 was obtained as colorless crystals. The ligand was characterized by CHN analysis and ^{1}H NMR. See the Supporting Information for details.

(14) A very small amount of good crystals was obtained in ca. 1% yield. Mass spectrum (FAB+; *m*/*z*): 699 $(Pd_2BrL)^+$, 654, 609, 551, 397, 313. NMR spectra of the reaction mixture showed unidentified products in addition to the isolated complex.

(15) X-ray data for the Z-shaped conformer: $C_{26}H_{38}N_4Pd_2Br_2$, 779.2, monoclinic, $P2_1/a$, $a = 16.545(7)$ Å, $b = 10.210(3)$ Å, $c = 8.428(3)$ Å, $\beta = 104.77(4)°$, $V = 1376.6(9)$ Å^3, $Z = 2$, $T = 23.0$ °C, Rigaku AFC-5S diffractometer, $\omega-2\theta$ scan, 4010 observations, $R = 0.084$, $R_w = 0.103$ (based on F^2).

(16) These complexes give signals characteristic of AB methylene protons, which are assigned as the methylene protons attached to the phenyl rings. For the Z-shaped complex, the signals were at 4.27 and 3.90 ppm ($J_{AB} = 14.8$ Hz) from TMS, but for the U-shaped complex, they were at 4.05 and 3.95 ppm (15.8 Hz) (δ in $CDCl_3$). See the Supporting Information for details.

U-shaped structure. There is a crystallographic mirror plane passing through the C10 and C12 atoms. This U-shaped molecule has pseudo C_{2v} symmetry.

Both isomers of the palladium complex are fairly stable in air, even in solution. The coordination geometries around the Pd atoms are approximately square planar in both complexes. The Pd−C distances are 1.921(4) and 1.915(7) Å, respectively, for Z-shaped and U-shaped complexes. There are no unusual bond lengths and angles in the complexes. The Pd−Pd distances are 4.80 and 5.19 Å in the Z-shaped and U-shaped complexes, respectively, and there is negligible interaction between the Pd atoms.

NMR data show remarkable inequivalency in some methylene protons. In addition to the AB signal of the methylene groups described above, distinct signals of two protons on the methylene groups C9 (C11) in the Z-shaped conformer and C9 (C10) in the U-shaped conformer are observed. Furthermore, a very large difference in the chemical shift values of the two methylene protons on C10 (C12) in the U-shaped conformer is found (δ 4.26 and 2.34). The result of the X-ray study supports the inequivalency. There is a 12-membered metallacycle in the complex. In the U-shaped conformer, one of the two protons on the C12 methylene group is directed toward the inside of the metallacyle, but the other proton connects axially to the ring. The distance between the former proton and the palladium atom is only 2.79 Å. The U shape of the complex enforces the two bromide ions to be in the same direction in the binuclear complex. This structure should be important for use as a potential catalyst.

In this work, two structures of the new macrocycle complex have been clarified. Our method, i.e., incorporation of two terdentate N∧C∧N coordination groups into a macrocycle, enables us to obtain interesting complexes that contain two noble metals at specific sites in macrocyclic molecules. The method should be useful for designing potential catalysts and new molecular devices.

Acknowledgment. This work was financially supported by The Promotion and Mutual aid Corporation for Private Schools of Japan and the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (C).

Supporting Information Available: Text giving details of the preparation and characterization data for the ligand and the complexes and tables giving X-ray data of the two conformers. X-ray data for the two conformers are also given as electronic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0103862

---

(17) X-ray data for the U-shaped conformer: $C_{26}H_{38}N_4Pd_2Br_2{\cdot}CHCl_3$, 898.6, orthorhombic, *Pnma*, $a = 14.445(2)$ Å, $b = 17.928(2)$ Å, $c = 12.903(2)$ Å, $V = 3341.3(5)$ Å^3 , $Z = 4$, $T = 23.0$ °C, Rigaku AFC5S diffractometer, $\omega-2\theta$ scan, 3958 observations, $R = 0.093$, $R_w = 0.115$ (based on F^2).