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Synthesis of Binuclear Complexes Bound in an Enlarged Tetraphosphamacrocycle: Two Diphosphine Metal Units Linked in Front-to-Front Style

Tsutomu Mizuta,* Yuta Inami, Kazuyuki Kubo, and Katsuhiko Miyoshi

Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima, Hiroshima 739-8526, Japan

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A large-hole tetraphosphamacrocycle **2**, with four phosphorus centers separated at the corners of a 3.7 Å wide and 9.7 Å long rectangle, was synthesized by a stepwise cyclization reaction between PCl-bridged [1.1]ferrocenophane and bisphenol A in a 2:2 ratio. The macrocycle **2** could incorporate two Ag^+ or Pt^0 fragments in the hole to provide binuclear complexes, which were identified as μ-**2**-$[Ag(NCMe)_2]_2(BF_4)_2$ (**3**) and μ-**2**-$[Pt(PhCCPh)]_2$ (**5**), respectively, using X-ray and spectroscopic analysis. The X-ray structure of **3** demonstrates that the macrocycle **2** serves as a framework in which two diphosphine silver units are aligned in a front-to-front style, while that of **5** indicates that **2** can also bind two bulky Pt(PhCCPh) fragments by the flexible change of its conformation.

Diphosphine ligands play a crucial role in organometallic chemistry because of their successful application in homogeneous catalysis for organic synthesis and material science.[1,2] On the other hand, there is also a growing interest in polyphosphine ligands that can form binuclear organometallic complexes and exhibit novel and efficient catalytic activity. Most polyphosphine ligands are designed to form a side-by-side-type binuclear complex, in which the two neighboring diphosphine metal fragments are aligned side-by-side, as shown in Figure 1a.[3] However, if the active sites of the two metal fragments face each other, with two diphosphine metal fragments linked to form a macrocyclic framework, as in Figure 1b, the two metal centers can be expected to interact more directly and cooperatively with a substrate. Such a front-to-front-type binuclear complex is known at the active enzyme sites, and several large-azamacrocycle binuclear complexes were prepared in order to mimic the front-to-front-type functionality of such enzymes.[4,5] However, a large phosphamacrocycle that can incorporate two metal fragments in its hole has not been reported to date. This is probably largely because of the inherent air sensitivity of most tervalent phosphorus species and the presence of many possible stereoisomers, which clearly complicates the chemistry of the macrocycle complexes. On the other hand, azamacrocycles readily invert the configuration of the nitrogen centers to give the most stable isomer. We report a novel phosphamacrocycle that is designed to avoid the formation of stereoisomers by the introduction of two doubly chelated diphosphine units, as shown in Figure 1c.

The phosphorus macrocycle was prepared according to the route outlined in Scheme 1, where PCl-bridged [1.1]ferrocenophane (**1**) was employed as the doubly chelated diphosphine unit.[6] Bisphonol A was first protected with a TBS group [TBS = Si(*t*-Bu)Me_2] at one end and then attached to each phosphorus center of **1**. After removal of the

*To whom correspondence should be addressed. E-mail: mizuta@sci.hiroshima-u.ac.jp.

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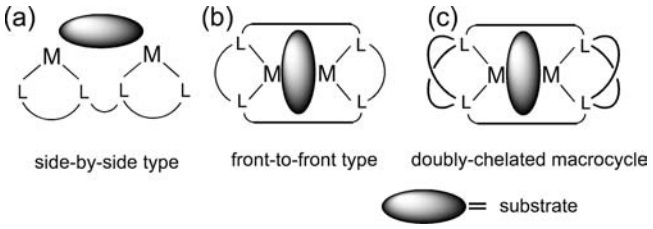
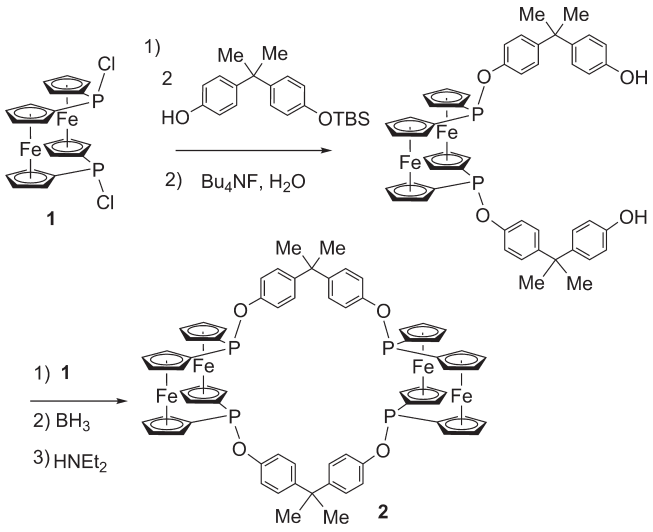


Figure 1. Three types of binuclear complexes: (a) side-by-side type (left); (b) front-to-front type (middle); (c) front-to-front type supported by a doubly chelated macrocycle.

Scheme 1



TBS group, cyclization was carried out by reaction with **1**. This stepwise procedure was necessary because the direct 2:2 reaction of **1** and bisphenol A afforded a 1:1 cyclic product as the major product with only a trace amount of the desired 2:2 product **2**. The macrocycle **2** in Scheme 1 was purified as a BH_3 adduct using preparative-scale gel permeation chromatography equipment, and isolated in 13% yield after removal of BH_3 by reaction with $HNEt_2$. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **2** indicated the absence of stereoisomers and were consistent with the high symmetry expected for the structure of **2**; four Me and C_6H_4 groups, four phosphorus atoms, and eight C_5H_4 groups are all observed as equivalent moieties. For example, the $^{31}P\{^1H\}$ NMR spectrum has a sharp singlet at 112.8 ppm, and 40 cyclopentadienyl carbons provide only five signals, three of which are observed as triplets, because of the through-bond and space couplings with the two phosphorus centers.[7] The molecular structure of the macrocycle **2** was confirmed by X-ray analysis, as shown in Figure 2, where the center of inversion determines each half unit as strictly equivalent, and four phosphorus atoms form a rectangle approximately 3.7 Å wide and 9.7 Å long. The unit cell of the crystal **2** was found to consist of two nonequivalent molecules, of which the other has a 3.6 Å × 10.1 Å rectangular arrangement of the four phosphorus atoms, as shown in Figure S1 in the Supporting Information.

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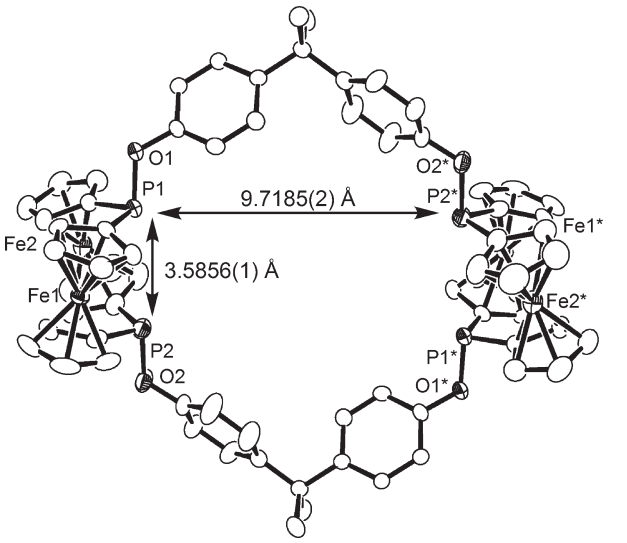

Figure 2. ORTEP diagram of macrocycle **2**. Ellipsoids are shown at 50%. The solvent and hydrogen atoms are omitted for clarity.

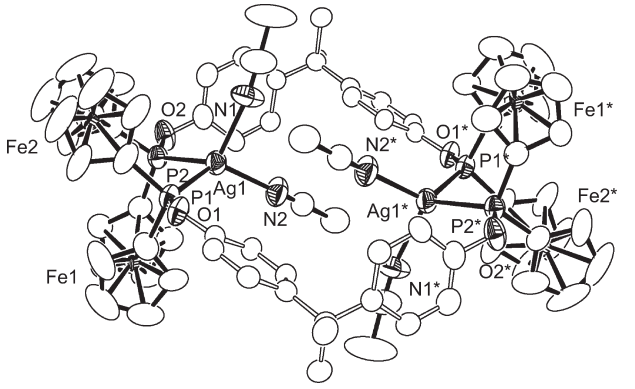

Figure 3. ORTEP diagram of Ag^+ binuclear complex **3**. Ellipsoids are shown at 50%. The solvent, counterion, and hydrogen atoms are omitted for clarity.

Macrocycle **2**, with a large hole in its center, was examined to determine whether it could accommodate two metal fragments. The Ag^I ion was selected as a small metal fragment for this test. A reaction mixture of **2** and 2 equiv of $AgBF_4$ in acetonitrile yielded a product that exhibited a slightly broad doublet in the $^{31}P\{^1H\}$ NMR spectrum at ambient temperature, which became a sharp multiplet at −40 °C with P−Ag couplings ($J_{^{107}Ag-P}$ = 396 Hz and $J_{^{109}Ag-P}$ = 458 Hz). The molecular structure of the silver complex μ-**2**-$[Ag(NCMe)_2]_2(BF_4)_2$ (**3**) was determined by X-ray analysis, as shown in Figure 3. Macrocycle **2** incorporates two Ag^I ions as expected, with two diphosphinesilver fragments aligned in a front-to-front style. Each Ag^I ion forms pseudotetrahedral geometry with two coordinated acetonitrile ligands, which are responsible for the dynamic behavior observed in the $^{31}P\{^1H\}$ NMR spectra.

In contrast, when macrocycle **2** was reacted with d^8 metal fragments, such as $PtCl_2$(cod) and $[RhCl(cod)]_2$ (cod = 1, 5-cyclooctadiene), insoluble precipitates were formed, although they could not be characterized because of their low solubility in common solvents. On the other hand, the reaction of **2** with Pt^0 fragments afforded a soluble product. From the reaction with $Pt(PPh_3)_4$, the $^{31}P\{^1H\}$ NMR spectrum of the product after workup displayed a doublet and a

triplet at 162.1 and 58.1 ppm, respectively, which coupled to one another with J_{P-P} = 147 Hz. The former signal can be assigned to macrocycle **2** and the latter to PPh_3. These signals had satellite signals arising from ^{195}Pt with $J_{^{195}Pt-P}$ = 5064 and 4538 Hz, respectively. The large $J_{^{195}Pt-P}$ coupling constants and the P−P coupling patterns indicate a three-coordinate Pt^0 complex with a PtP_2P' spin system, which is consistent with the formula μ-**2**-$[Pt(PPh_3)]_2$ (**4**), in which two $Pt(PPh_3)$ fragments coordinate to respective diphosphine units. Structure **4** is of interest in that PPh_3 is so bulky that macrocycle **2** cannot accommodate two $PtPPh_3$ fragments in its hole. An X-ray structure was not available for the product because of the thermal instability of the product; however, the structure is expected to be similar to that of a diphenylacetylene analogue of **4** (vide infra).

Diphenylacetylene is expected to serve as an electron-withdrawing ligand that thermodynamically stabilizes the Pt^0 complex; therefore, the reaction of **2** with $Pt(PhCCPh)(PPh_3)_2$ in place of $Pt(PPh_3)_4$ was carried out to give μ-**2**-$[Pt(PhCCPh)]_2$ (**5**) after workup. Complex **5** had a single $^{31}P\{^1H\}$ NMR signal at 133.6 ppm with ^{195}Pt satellites ($J_{^{195}Pt-P}$ = 4053 Hz) and was stable at ambient temperature under a nitrogen atmosphere. The molecular structure of **5** determined by X-ray analysis is given in Figure 4, where each diphosphine unit directs its binding site to above or below the mean plane of the macrocyclic ring, so as to bind the bulky Pt(PhCCPh) fragments. A similar conformational deformation of **2** is expected for the PPh_3 analogue **4**.

In conclusion, a large tetraphosphorus macrocycle **2** was designed so as to incorporate two metals and avoid the formation of stereoisomers. The prepared macrocycle **2** provided a coordination space in which the front-to-front-type alignment was realized for a small metal fragment such as $Ag(NCMe)_2$. Macrocycle **2** could also accommodate a sterically bulky fragment by flexibly changing its conformation. The front-to-front alignment realized with **2** is currently being applied to a new metal−substrate interaction that is useful for the cleavage of a thermally inactive bond.

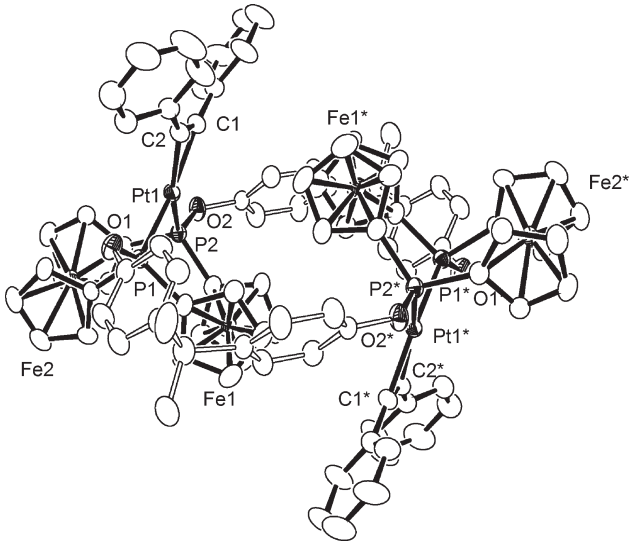

Figure 4. ORTEP diagram of Pt binuclear complex **5**. Ellipsoids are shown at 50%. The solvent and hydrogen atoms are omitted for clarity.

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Supporting Information Available: Experimental details of the syntheses and catalyses, ORTEP drawings, and crystallographic data for **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.