Rotational Isomers of a 1,2-Diphenyl-3,4-diphosphinidenecyclobutene

Masaaki Yoshifuji,* Yoshito Ichikawa, Kozo Toyota, Eiji Kasashima,† and Yoshio Okamoto†
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-77
†*Department of Applied Chemistry, School of Engineering, Nagoya University, Chikusa, Nagoya 464-01*

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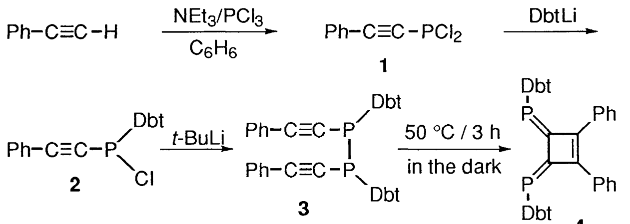
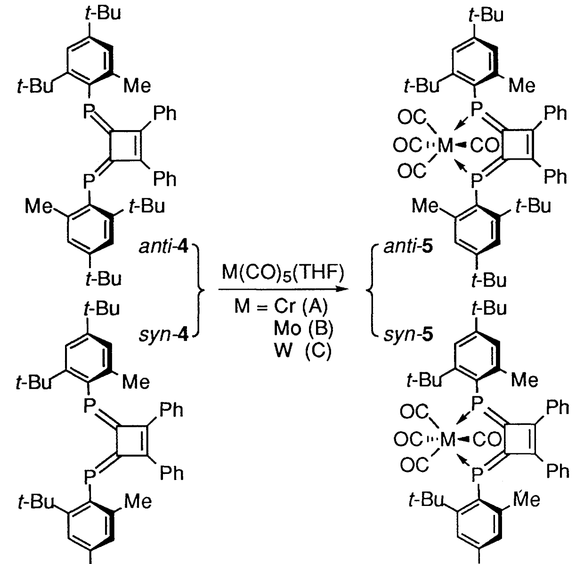
The group-6 metal tetracarbonyl complexes of 3,4-diphosphinidenecyclobutenes protected with the 2,4-di-*t*-butyl-6-methylphenyl group were prepared and one of the rotamers, ligated with W(CO)$_4$, was confirmed by X-ray analysis while the other was analyzed by a chiral HPLC column.

Using an extremely bulky 2,4,6-tri-*t*-butylphenyl group (hereafter, abbreviated to the Ar group), we were successful in preparation of several unusual organophosphorus compounds[1] such as diphosphenes,[2a] phosphaalkenes,[2b] and phosphacumulenes[2c,d] as stable species. Appel,[3] Märkl,[4] and we[5] prepared some sterically protected diphosphinidenecyclobutenes as an additional example of low coordinated phosphorus compounds, which belongs to a phosphorus analogue of dimethylenecyclobutene. Furthermore, we have reported on the preparation and structures of the group-6 metal(0)[6] and palladium(II)[7]. complexes of diphosphinidenecyclobutenes ligating as a bidentate ligand. On the other hand, we have developed several protecting groups other than the Ar group and found that the 2,4-di-*t*-butyl-6-methylphenyl (hereafter abbreviated to Dbt) group is useful to stabilize some unsymmetrical diphosphene[8] and phosphaethenes.[9,10] We made a further application of the Dbt group to the diphosphinidenecyclobutene system and found conformational isomerism due to the restricted rotation around the two P–Dbt bonds at the edges of the system.



Scheme 1. Dbt = 2,4-*t*-Bu$_2$-6-MeC$_6$H$_2$

The diphosphinidenecyclobutene was prepared as described in Scheme 1. Phenylacetylene was converted to phenylethynylphosphonous dichloride **1** (δ_P = 122)[11] in 24% and **1** was allowed to react with DbtLi to give the corresponding phosphinous chloride **2** (δ_P = 46). The chloride **2** was then allowed to react with equimolar amount of *t*-butyllithium to give 1,2-bis(2,4-di-*t*-butyl-6-methylphenyl)-1,2-bis(phenylethynyl)diphosphane **3** (δ_P = –53). When the diphosphane **3** was heated in the dark for 3 h, 3,4-bis(2,4-di-*t*-butyl-6-methylphenylphosphinidene)-1,2-diphenylcyclobutene **4** was obtained. It is interesting to note that the compound **4** consists of two rotamers, *syn*-**4** and *anti*-**4**, the ^{31}P NMR of which appeared as two singlets, δ_P at 169.1 and 168.4 in a ratio of 1 : 2, but attempts to separate these rotamers were unsuccessful.



Scheme 2.

After addition of M(CO)$_5$(THF) to this mixture, where M equals Cr (**A**), Mo (**B**), and W (**C**), the ^{31}P NMR of the reaction products appeared as two singlets again in a ratio of about 1 : 2, respectively, due to *syn*-**5** and *anti*-**5** with complete retention of conformation (Scheme 2). The compounds **5A–C** were purified through column chromatography to give dark purple complexes and were analyzed by spectroscopic data.[12]

Furthermore, the structure of *syn*-**5C** was unambiguously determined by X-ray analysis.[13,14] Figure 1 depicts a molecular structure of *syn*-**5C**, which clearly shows the ligand on the tungsten metal is in the *syn*-configuration. The atoms W, P(1), C(1), C(2), and P(2) are on the same plane with a mean deviation of 0.01 Å and the atoms C(1), C(2), C(3), and C(4) are coplanar with a mean deviation of 0.01 Å making a dihedral angle of 2.9°, each other. Thus, the diphosphinidenecyclobutene framework including the W atom is almost coplanar. The two Dbt rings (C(5)–C(10) and C(20)–C(25)) are almost perpendicular to the WPCCP plane making interplanar angles of 100° and 94°, respectively. The two phenyl rings, C(35)–C(40) and C(41)–C(46), make dihedral angles of 37.2° and 18.7°, with the cyclobutene ring, respectively. The six ligands around the W atom are located forming a slightly distorted octahedron. The P=C bond lengths (1.669(6) Å for P(1)–C(1) and 1.662(6) Å for P(2)–C(2), respectively) are close to the values for the corresponding complexes as reported for 3,4-bis(2,4,6-tri-*t*-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutene (**6**) (1.678(6) and 1.676(5) Å),[6b] and the bond length C(1)–C(2) for *syn*-**5C** is 1.507(8) Å, whereas that for **6**•[Mo(CO)$_4$] is 1.483(6) Å.[6b] The X-ray analysis indicated that

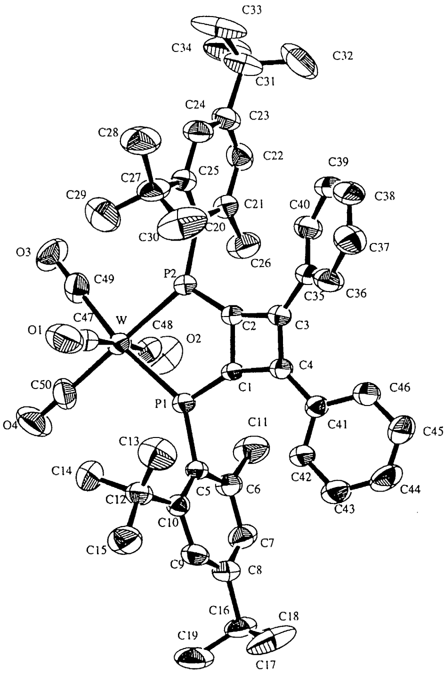


Figure 1. Molecular structure of tungsten complex *syn*-**5C**. Benzene as a solvent was omitted for clarity.

diphosphinidenecyclobutene **4**, as well as the group-6 metal carbonyl complexes **5**, is less suffering from steric congestion compared with the Ar derivatives.

On the other hand, *anti*-**5C** was analyzed by HPLC using a Daicel chiral column (Chiralcel OD) and a baseline separation was atained.[15] Each separated enantiomer showed the symmetrical CD spectrum as shown in Figure 2.

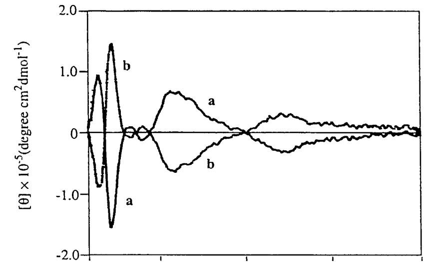


Figure 2. CD spectrum of the separated enantiomers of *anti*-**5C** (a: first-eluted isomer; b: second-eluted isomer; JASCO J-720, hexane, 1-cm cell).

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12 *anti*-**5A**: δ_P = 189.5; *syn*-**5A**: δ_P = 187.5. *anti*-**5B**: δ_P = 169.4; *syn*-**5B**: δ_P = 168.0. *anti*-**5C**: dark purple solid, δ_P = 146.5 (J_{PW} = 254 Hz); *syn*-**5C**: dark purple, mp 212 °C (decomp.), δ_P = 145.1 (J_{PW} = 254 Hz); *anti*-**5C**+*syn*-**5C**: 37% yield based on **1** (0.62 g, 3.1 mmol, employed). The peaks due to the carbonyl carbon in ^{13}C NMR were diagnostic of the structure of the complexes and the major one was assigned to the *anti*-type which has two apical CO's and two equatorial CO's, whereas the minor one was assinged to the *syn*-type, which has two equatorial CO's and two apical non-equivalent CO's.

13 Crystal Data for *syn*-**5C**: Recrystallized from benzene-hexane. $C_{50}H_{56}O_4P_2W \cdot 1/2C_6H_6$, Mr = 1005.84, prismatic, a = 11.485(3) Å, b = 21.434(3) Å, c = 11.270(2) Å, α = 95.83(2)°, β = 112.85(2)°, γ= 97.02(2)°,V = 2503(1) Å^3, $P\bar{1}$ (#2), Z = 2, T = 296 K, R = 0.045, Rw = 0.043; 7430 unique reflections with $I > 3\sigma(I)$. The structure was solved with SHELXS86; G. M. Sheldrick, *SHELX86, Programs for the Automatic Solution of Crystal Structures*, University of Göttingen, Germany (1986). Further details of the crystal structure investigation for *syn*-**5C** are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK).

14 Some selected bond lengths (Å) and angles (°) of *syn*-**5C**: W–P(1), 2.515(2); W–P(2), 2.489(2); W–C(47), 1.955(9); W–C(48), 1.930(9); W–C(49), 1.986(8); W–C(50), 2.014(9); P(1)–C(1), 1.669(6); P(1)–C(5), 1.833(6); P(2)–C(2), 1.662(6); P(2)–C(20), 1.821(7); C(1)–C(2), 1.507(8); C(1)–C(4), 1.483(8); C(2)–C(3), 1.466(8); C(3)–C(4), 1.410(9); P(1)–W–P(2), 77.73(6); P(1)–W–C(47), 90.7(2); P(1)–W–C(48), 91.0(2); P(1)–W–C(49), 169.9(2); P(1)–W–C(50), 99.4(2); P(2)–W–C(47), 90.2(2); P(2)–W–C(48), 94.5(3); P(2)–W–C(49), 92.2(2); P(2)–W–C(50), 173.5(3); C(47)–W–C(48), 175.2(4); C(47)–W–C(49), 89.9(3); C(47)–W–C(50), 83.9(4); C(48)–W–C(49), 89.2(3); C(48)–W–C(50), 91.4(4); C(49)–W–C(50), 90.6(3); W–P(1)–C(1), 111.5(2); W–P(1)–C(5), 137.7(2); C(1)–P(1)–C(5), 110.1(3); W–P(2)–C(2), 112.1(2); W–P(2)–C(20), 135.6(2); C(2)–P(2)–C(20), 111.8(3); P(1)–C(1)–C(2), 118.9(4); P(1)–C(1)–C(4), 153.2(5); C(2)–C(1)–C(4), 87.8(5); P(2)–C(2)–C(1), 119.7(5); P(2)–C(2)–C(3), 151.9(5); C(1)–C(2)–C(3), 88.4(5); C(2)–C(3)–C(4), 92.3(5); C(2)–C(3)–C(35), 130.0(6); C(4)–C(3)–C(35), 137.2(6); C(1)–C(4)–C(3), 91.5(5); C(1)–C(4)–C(41), 132.8(6); C(3)–C(4)–C(41), 135.7(6); P(1)–C(5)–C(6), 113.4(5); P(1)–C(5)–C(10), 126.2(5).

15 Column: Chiralcel OD 25 × 0.46 (i.d.) cm (Daicel); eluent: hexane; flow speed: 0.5 ml/min; tempearture: RT. *anti*-**5C** was dissolved in a mixture of hexane-isopropyl alcohol (9:1) in 0.1 mg/mL. First peak appeared at 10.4 min and the second one at 11.6 min.