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Synthesis and Reactivity of Diphosphine-Bridged Diruthenium Complexes

Yoshihiro Miyake, Yohei Nomaguchi, Masahiro Yuki, and Yoshiaki Nishibayashi*

Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku,
Tokyo 113-8656, Japan

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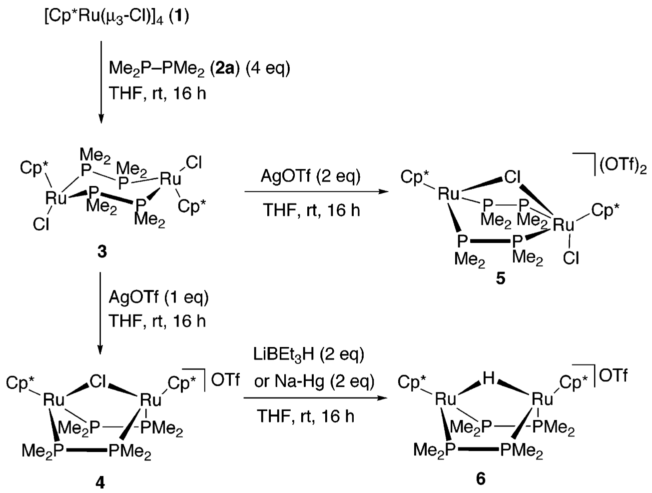
Summary: Treatment of a chloride-bridged tetraruthenium complex with tetramethyldiphoshine and tetraphenyldiphosphine affords a different type of diphosphine-bridged diruthenium complexes, which are further transformed into the corresponding cationic complexes by treatment with silver trifluoromethanesulfonate. Some diphosphine-bridged diruthenium complexes show a catalytic activity toward the quantitative cyclotrimerization of ethyl propiolate to two regioisomeric benzene derivatives.

Introduction

The synthesis and reactivity of multinuclear complexes have attracted considerable attention because of their potential applicability to effective organic transformations.[1,2] The choice of suitable bridging ligands is a very important factor to construct the desirable multinuclear skeletons effectively. For example, bis(diorganophosphino)methanes such as dppm (1,1-bis(diphenyl)phosphinomethane ($Ph_2PCH_2PPh_2$)) are known to work as bridging ligands to give the dinuclear complexes[3] that provide suitable reactive sites to facilitate the simultaneous activation and transformation of substrate molecules. On the other hand, tetraorganodiphosphines (R_2P-PR_2) are often used as other types of bridged ligands, where two metal centers coordinated by tetraorganodiphosphines can be fixed in closer proximity because the two phosphorus atoms in tetraorganodiphosphines are connected directly. A variety of diphosphine-bridged dinuclear complexes are known, but most of them are limited to the complexes bearing carbonyl ligands and their analogues.[4] In addition, the reactivity of the diphosphine-bridged dinuclear complexes has not yet been investigated in detail up to now. Herein, we report the synthesis and characterization of diphosphine-bridged diruthenium complexes together with their stoichiometric and catalytic activity for some organic transformations.

Scheme 1



Results and Discussion

Treatment of a chloride-bridged tetraruthenium(II) complex $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$) with 4 equiv of tetramethyldiphosphine (**2a**; Me_2P-PMe_2) in tetrahydrofuran (THF) at room temperature for 16 h afforded the corresponding diphosphine-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}Me_2P-PMe_2)]_2$ (**3**) in 53% isolated yield (Scheme 1). The use of 2 equiv of **2a** resulted in the formation of **3** in only 22% isolated yield. The complex **3** was revealed to be thermally very stable, and no phosphorus−phosphorus bond cleavage occurred even when a solution of **3** in 1,4-dioxane was heated at 100 °C for 16 h. Next, treatment of **3** with 1 equiv of silver trifluoromethanesulfonate (AgOTf; $OTf = SO_3CF_3$) in THF at room temperature for 16 h afforded the corresponding monocationic chloride-bridged diruthenium complex $[Cp^*Ru(\mu_2\text{-}Cl)(\mu_2\text{-}Me_2P-PMe_2)_2RuCp^*]OTf$ (**4**) in 89% isolated yield. Unexpectedly, the reaction of **3** with 2 equiv of AgOTf under the same reaction conditions gave the corresponding dicationic chloride-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}Cl)(\mu_2\text{-}Me_2P-PMe_2)_2RuCp^*](OTf)_2$ (**5**) in 56% isolated yield together with the formation of

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(1) (a) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998. (b) *Metal-Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Ed.; Plenum: New York, 1990.

(2) Recently, we have reported a novel catalytic activity of chalcogenolate-bridged diruthenium complexes for many organic transformations. For recent examples, see: (a) Nishibayashi, Y.; Uemura, S. *Curr. Org. Chem.* **2006**, *10*, 135. (b) Yamauchi, Y.; Onodera, G.; Sakata, K.; Yuki, M.; Miyake, Y.; Uemura, S.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 5175. (c) Inada, Y.; Yoshikawa, M.; Milton, M. D.; Nishibayashi, Y.; Uemura, S. *Eur. J. Org. Chem.* **2006**, 881. (d) Nishibayashi, Y.; Shinoda, A.; Miyake, Y.; Matsuzawa, H.; Sato, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4835. (e) Nishibayashi, Y.; Milton, M. D.; Inada, Y.; Yoshikawa, M.; Wakiji, I.; Hidai, M.; Uemura, S. *Chem.−Eur. J.* **2005**, *11*, 1433. (f) Inada, Y.; Nishibayashi, Y.; Uemura, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7715. (g) Ammal, S. C.; Yoshikai, N.; Inada, Y.; Nishibayashi, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 9428. (h) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 26.

(3) For reviews, see: (a) Anderson, G. K. *Adv. Organomet. Chem.* **1993**, *35*, 1. (b) Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W. *Polyhedron* **1990**, *9*, 2767. (c) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191. (d) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

(4) For recent examples, see: (a) Mizuta, T.; Kunikata, S.; Miyoshi, K. *J. Organomet. Chem.* **2004**, *689*, 2624. (b) Gelger, W. E.; Order, N.; Pierce, D. T.; Bitterwolf, T. E.; Rheingold, A. L.; Chasteen, N. D. *Organometallics* **1991**, *10*, 2403. (c) Chau, C.; Yu, Y.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *Organometallics* **1987**, *6*, 308. (d) Calderazzo, F.; Poli, R.; Vitali, D.; Korp, J. D.; Bernal, I.; Pelizzi, G.; Atwood, J. L.; Hunter, W. E. *Gazz. Chim. Ital.* **1983**, *113*, 761. (e) Atwood, J. L.; Newell, J. K.; Hunter, W. E.; Bernal, I.; Calderazzo, F.; Mavani, I. P.; Vitali, D. *J. Chem. Soc., Dalton Trans.* **1978**, 1189.

10.1021/om070216a CCC: $37.00

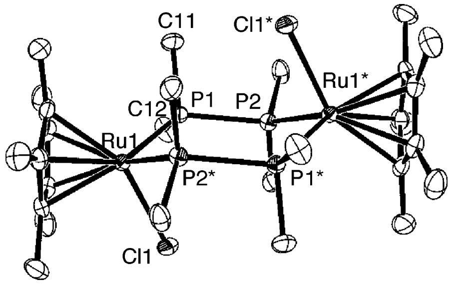


Figure 1. ORTEP drawings of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å), angles (deg), and torsion angles (deg): Ru1−Cl1, 2.4700(13); Ru1−P1, 2.2885(12); Ru1−P2*, 2.2854(9); P1−P2, 2.2490(13); P1−Ru1−P2*, 94.43(4); Cl1−Ru1−P1, 89.77(4); Ru1−P1−P2, 124.22(5); Cl1−Ru1−P1−C11, −175.98(15); Cl1−Ru1−P1−C12, 67.71(17).

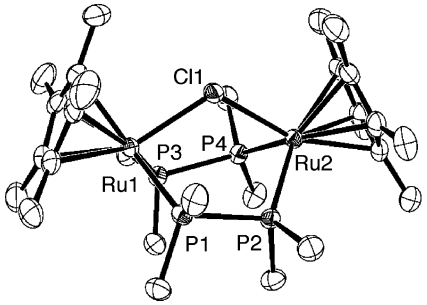
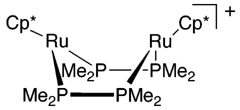


Figure 2. ORTEP drawings of **4**. Hydrogen atoms and OTf anion are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å), angles (deg), and torsion angles (deg): Ru1−Cl1, 2.451(1); Ru1−P1, 2.301(1); P1−P2, 2.261(2); P1−Ru1−Cl1, 83.22(4); P3−Ru1−Cl1, 90.37(4); P3−Ru1−P1, 91.44(4); Ru1−P1−P2, 115.52(5); Ru1−Cl1−Ru2, 115.09(4); P1−Ru1−Cl1−Ru2, 50.09(3); Cl1−Ru2−P2−P1, 11.03(5); Ru1−P1−P2−Ru2, 21.80(8).

4 in 38% yield. The formation of **5** means that oxidation from Ru(II)−Ru(II) to Ru(III)−Ru(III) proceeded in place of the removal of the chloride ligand with AgOTf. The reaction of **4** with 2 equiv of $LiBEt_3H$ in THF at room temperature for 16 h gave the corresponding hydride-bridged diruthenium complex [Cp*Ru(μ_2-H)(μ_2-$Me_2P{-}PMe_2$)$_2$RuCp*]OTf (**6**) in 46% isolated yield. When **4** was treated with 2 equiv of Na−Hg at room temperature, the complex **6** was also obtained in 70% isolated yield. In the latter case, it is considered that one-electron reduction of **4** with Na−Hg results in the initial formation of the Ru(I)−Ru(II) mixed-valence intermediate **7**, which abstracts a hydrogen atom from THF.



7

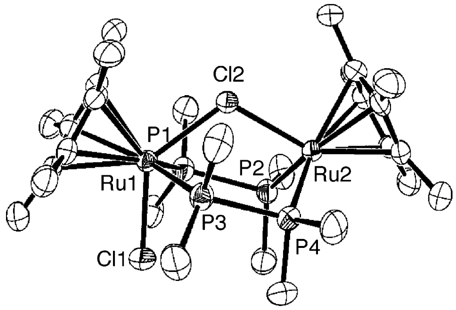


Figure 3. ORTEP drawings of **5**. Hydrogen atoms and OTf anions are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å), angles (deg), and torsion angles (deg): Ru1−Cl1, 2.403(1); Ru1−Cl2, 2.409(1); Ru1−P1, 2.383(1); Ru2−P2, 2.293(1); P1−P2, 2.235(2); P1−Ru1−Cl2, 76.23(4); P3−Ru1−P1, 118.48(6) Ru1−P1−P2, 111.16(6); Cl2−Ru1−Cl1, 128.88(5); Cl1−Ru1−Cl2−Ru2, 0.46(6); Cl1−Ru1−P1−P2, −81.79(5); Cl2−Ru1−P1−P2, −60.9(2).

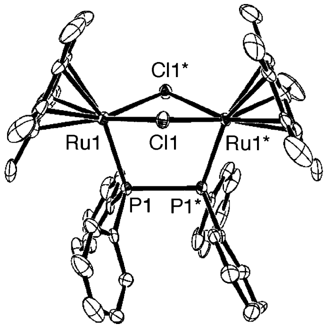
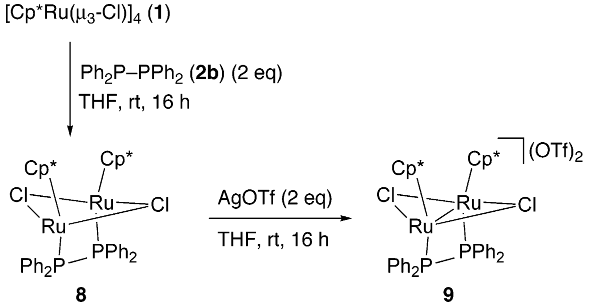


Figure 4. ORTEP drawings of **8**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ru1−P1, 2.315(2); Ru1−Cl1, 2.4732(13); P1−P1*, 2.321(2); Cl1−Ru1−Cl1*, 81.41(4); Cl1−Ru1−P1, 85.74(5); Ru1−P1−P1*, 106.97(7).

Scheme 2



The diphosphine-bridged diruthenium complexes (**3**−**5**) were characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and the molecular structure of the diruthenium complexes was confirmed by X-ray analysis.[5−7] ORTEP drawings of diruthenium complexes (**3**−**5**) are shown in Figures 1−3, respectively. As shown in Figure 1, the diruthenium complex **3** has a chairlike six-membered ring including two Ru atoms and two diphosphine skeltons, and the two Cp* and two chloride ligands are present in *trans*-configuration to each other. As shown in Figures 2 and 3, the diruthenium complexes **4** and **5** have boatlike and half-chairlike six-membered rings, respectively, where two Cp*Ru units are bridged by two diphosphines and a chloride ligand. In both cases, two Cp* and the bridging chloride ligands are

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(5) Crystal data for **3**: $C_{28}H_{54}Cl_2P_4Ru_2$, fw = 787.68, triclinic, $P\bar{1}$, a = 8.3837(4) Å, b = 8.8397(4) Å, c = 12.2277(4) Å, α = 103.4234(16)°, β = 99.937(2)°, γ = 106.0421(11)°, V = 819.50(6) Å^3, Z = 1, 7885 reflections measured, 3665 unique (R_{int} = 0.039), R_1 = 0.0380, wR_2 = 0.0840, GOF = 1.02.

(6) Crystal data for **4**·0.5Et$_2$O: $C_{31}H_{59}ClF_3O_{3.5}P_4Ru_2S$, fw = 938.35, triclinic, $P\bar{1}$, a = 11.0196(7) Å, b = 11.3090(9) Å, c = 16.559(1) Å, α = 94.454(3)°, β = 94.477(3)°, γ = 102.337(3)°, V = 2000.4(3) Å^3, Z = 2, 18900 reflections measured, 9056 unique (R_{int} = 0.054), R_1 = 0.044, wR_2 = 0.113, GOF = 1.071.

(7) Crystal data for **5**·2CH$_2$Cl$_2$: $C_{32}H_{58}Cl_6F_6O_6P_4Ru_2S_2$, fw = 1255.67, triclinic, $P\bar{1}$, a = 11.9463(2) Å, b = 13.3412(1) Å, c = 17.3660(5) Å, α = 72.970(2)°, β = 78.210(2)°, γ = 67.329(1)°, V = 2423.86(8) Å^3, Z = 2, 10868 reflections measured, 10858 unique (R_{int} = 0.074), R_1 = 0.048, wR_2 = 0.117, GOF = 1.05.

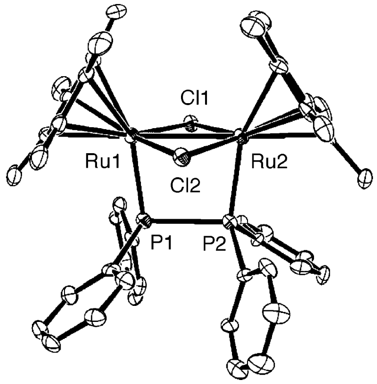
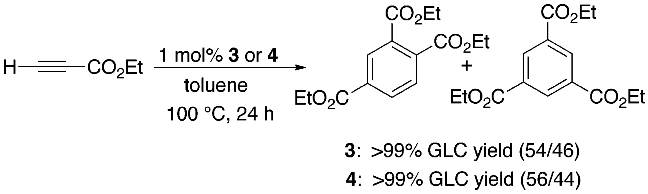


Figure 5. ORTEP drawings of **9**. Hydrogen atoms and OTf anion are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ru1−Ru2, 2.8837(1); Ru1−Cl1, 2.381(2); Ru1−P1, 2.343(2); P1−P2, 2.303(3); Ru1−Cl1−Ru2, 74.45(16); Ru1−Ru2−P2, 82.66(6); Ru1−P1−P2, 97.14(10).

Scheme 3



arranged in *syn*-position. Although the distance between the two ruthenium atoms in **4** and **5** (**4**: 4.14 Å; **5**: 4.07 Å) is shorter than that in **3** (5.18 Å), no ruthenium−ruthenium bonds are observed in all cases. The hydride-bridged diruthenium complex **6** was characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy along with a preliminary X-ray analysis. Complex **6** has a similar boatlike structure to that of complexes **4**.

On the other hand, treatment of [Cp*Ru(μ_3-Cl)]$_4$ (**1**) with 2 equiv of tetraphenyldiphosphine (**2b**; Ph_2P-PPh_2) afforded the diphosphine- and chloride-bridged diruthenium complex (**8**) in 68% yield (Scheme 2). When the reduction of **8** with $LiBEt_3H$ or Na−Hg in THF was investigated, no reduced complex was isolated and only the recovery of unreacted **8** was confirmed by ^{31}P{^{1}H} NMR spectroscopy. The reaction of **8** with 2 equiv of AgOTf in THF at room temperature for 16 h gave the corresponding dicationic diruthenium complex (**9**) in 68% isolated yield. No abstraction of the bridging chloride ligand in **8** was observed even when an excess of AgOTf was employed, and the oxidation from Ru(II)−Ru(II) to Ru(III)−Ru(III) occurred. These diruthenium complexes (**8** and **9**) were characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and their molecular structure was confirmed by X-ray analysis.[8,9] ORTEP drawings of **8** and **9** are shown in Figures 4 and 5, respectively. The molecular structure of **8** is similar to that of the reported tetraphenyldiphosphine-bridged diruthenium complexes such as [Mn(CO)$_3$(μ_2-Br)$_2$(μ_2-Ph_2P-PPh_2)Mn(CO)$_3$][4d] and [Re(CO)$_3$(μ_2-Br)$_2$(μ_2-Ph_2P-PPh_2)Re(CO)$_3$].[4e] The bond distance between the two ruthenium atoms in **8** was revealed to be 3.68 Å, indicating the absence of a ruthenium−ruthenium bond between them. In contrast, the bond distance between the two ruthenium atoms in **9** (2.88 Å) is shorter than that of **8** and is typical for a Ru−Ru single bond (2.71−3.02 Å).[10]

Some chemical reactivities of the produced diphosphine-bridged diruthenium complexes were next examined. The stoichiometric reactions of these diruthenium complexes with terminal alkynes did not give the corresponding vinylidene or alkyne complexes, but some diruthenium complexes such as **3** and **4** were revealed to have a catalytic activity toward the cyclotrimerization of ethyl propiolate, giving benzene derivatives. Thus, the use of 1 mol % of the diruthenium complex **3** or **4** as a catalyst at 100 °C for 24 h in toluene afforded them quantitatively as a mixture of two regioisomers. Some mononuclear ruthenium complexes such as [Cp*RuCl(cod)] (cod = 1,5-cyclooctadiene) have already been known to catalyze the facile cyclotrimerization of activated terminal alkynes.[11] Although the reactivity was lower in our case, this is the first successful example of the catalytic reaction promoted by diphosphine-bridged diruthenium complexes.

In summary, we have prepared a new type of diphosphine-bridged diruthenium complexes by using tetramethyl- and tetraphenyldiphosphines. Some diruthenium complexes have been found to promote the catalytic quantitative cyclotrimerization of ethyl propiolate to the corresponding benzene derivatives.

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Supporting Information Available: Experimental procedures including X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data for **8**: $C_{44}H_{50}Cl_2P_2Ru_2$, fw = 913.87, trigonal, $P3_121$, a = 18.0110(14) Å, c = 12.1888(10) Å, V = 3424.3(5) Å^3, Z = 3, 33261 reflections measured, 5230 unique (R_{int} = 0.058), R_1 = 0.031, wR_2 = 0.0953, GOF = 1.005.

(9) Crystal data for **9**·0.5Et$_2$O: $C_{48}H_{55}Cl_2F_6O_{6.5}P_2Ru_2S_2$, fw = 1249.06, monoclinic, $P2_1/c$, a = 16.56(2) Å, b = 20.274(5) Å, c = 16.741(12) Å, β = 111.20(2)°, V = 5241(8) Å^3, Z = 4, 46608 reflections measured, 11976 unique (R_{int} = 0.083), R_1 = 0.0724, wR_2 = 0.0960, GOF = 1.005.

(10) (a) Gao, Y.; Jennings, M. C.; Puddephatt, R. J.; Jenkins, H. A. *Organometallics* **2001**, *20*, 3500. (b) Engel, D. W.; Moodley, K. G.; Subramony, L.; Haines, R. J. *J. Organomet. Chem.* **1988**, *349*, 393, and references threin.

(11) For recent examples of ruthenium-catalyzed cyclotrimerization of alkynes, see: (a) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143. (b) Ruba, E.; Schmid, R.; Kirchner, K.; Calhorda, M. J. *J. Organomet. Chem.* **2003**, *682*, 204. (c) Becker, E.; Mereiter, K.; Puchberger, M.; Schmid, R.; Kirchner, K.; Doppiu, A.; Salzer, A. *Organometallics* **2003**, *22*, 3164.