Novel Monophosphido-Bridged Diruthenium Complexes: Efficient Preparative Method and Catalytic Activity toward Reactions of Propargylic Alcohols with Aromatic Compounds

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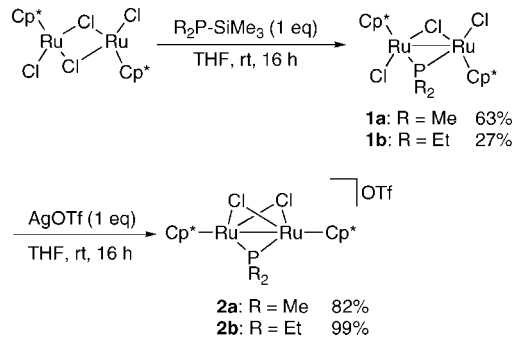
Summary: Reactions of a chloride-bridged diruthenium(III) complex with (dialkylphosphino)trimethylsilanes afford novel monophosphido-bridged diruthenium complexes, which are further transformed into the corresponding cationic complexes by treatment with silver trifluoromethanesulfonate. The dimethylphosphido-bridged complex is found to work as a dual catalyst toward the redox isomerization of propargylic alcohols to α,β-unsaturated ketones and sequential Friedel−Crafts reactions with heteroaromatic compounds.

Considerable attention has recently been paid to multimetallic complexes bridged by heteroatom ligands, because of their potential applicability to various organic transformations.[1] Recently, we disclosed the unique catalytic activity of thiolato- and selenolato-bridged diruthenium complexes toward propargylic substitution reactions of propargylic alcohols with a variety of nucleophiles.[2,3] In sharp contrast, tellurolato-bridged diruthenium complexes did not work as effective catalysts for these reactions,[3] suggesting that the nature of the bridging ligands plays an important role in the catalysis of these diruthenium complexes. These results prompted us to design and prepare other heteroatom-bridged diruthenium complexes. Herein, we report the novel synthetic method and the characterization of some monophosphido-bridged diruthenium complexes[4] together with their catalytic activity toward reactions of propargylic alcohols with aromatic compounds.

Scheme 1



Results and Discussion

To date, a variety of phosphido-bridged multinuclear complexes have been prepared by three methods: deprotonation of primary or secondary phosphines,[4a,c,d,5c,d] oxidative addition of the P−H bond of primary or secondary phosphines to low-valent metal species, [5a,b] and P−C bond cleavage of tertiary phosphines by multinuclear complexes.[4b,e] We have now found that silylphosphines ($R_2P-SiMe_3$) can be also used as useful reagents for the synthesis of phosphido-bridged diruthenium complexes.[6] Thus, treatment of the chloride-bridged diruthenium(III) complex $[Cp^*RuCl(\mu_2\text{-}Cl)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with 1 equiv of $Me_2P-SiMe_3$, generated in situ from the reaction of tetramethyldiphosphine (Me_2P-PMe_2) with potassium metal followed by quenching with chlorotrimethylsilane, in tetrahydrofuran (THF) at room temperature afforded the corresponding monophosphido-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}Cl)(\mu_2\text{-}PMe_2)RuClCp^*]$ (**1a**) in 63% yield (Scheme 1). The diethylphosphido-bridged diruthenium complex **1b** was also obtained in 27% yield under the same reaction conditions. In addition, reactions of **1** with 1 equiv of silver trifluoromethanesulfonate (AgOTf; OTf = SO_3CF_3) in THF at room temperature proceeded smoothly to give the corresponding monocationic dichloride-bridged diruthenium complexes $[Cp^*Ru(\mu_2\text{-}Cl)_2(\mu_2\text{-}PR_2)RuCp^*]OTf$ (**2a**, R = Me; **2b**, R = Et) in 82% and 99% yields, respectively (Scheme 1).

The monophosphido-bridged diruthenium complexes **1** and **2** were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy,

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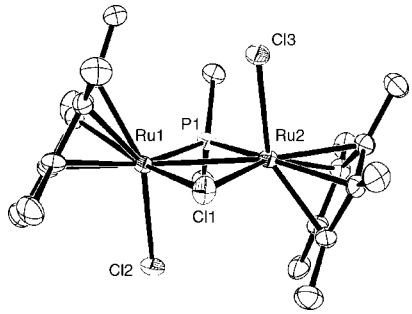


Figure 1. ORTEP drawing of **1a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and torsion angle (deg): Ru1−Ru2, 2.8485(7); Ru1−Cl1, 2.3792(16); Ru1−P1, 2.2844(16); Ru2−P1, 2.2908(16); Ru1−Cl2, 2.4512(18); Ru1−P1−Ru2, 77.01(5); Ru1−Cl1−Ru2, 73.46(4); Cl2−Ru1−Ru2−Cl3, 146.14(3).

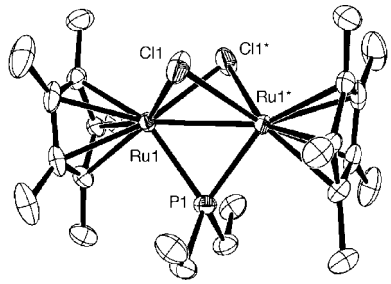
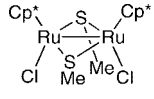


Figure 2. ORTEP drawing of **2b**. The structure of one of the two crystallographically independent molecules is shown. The structures of the two independent molecules are almost the same. Hydrogen atoms and the counteranion (OTf) are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ru1−Ru1*, 2.7047(2); Ru1−Cl1, 2.7738(7); Ru1−P1, 2.2831(6).

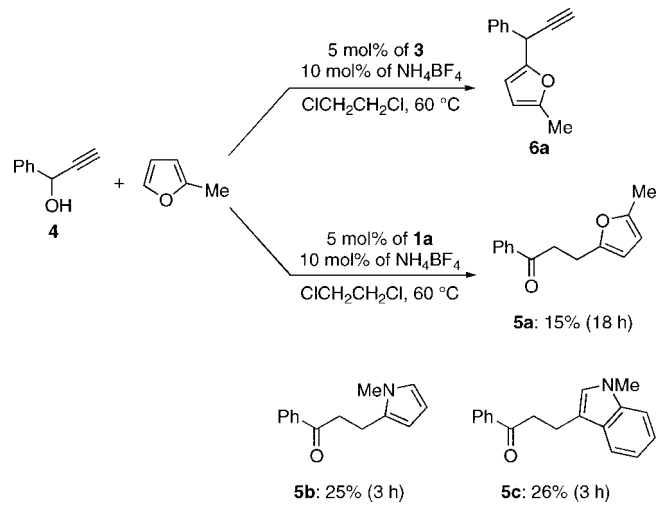
and the molecular structures of **1a** and **2b** were confirmed by X-ray analysis. An ORTEP drawing of **1a** is shown in Figure 1. As shown in Figure 1, both the two Cp* ligands and two chloride ligands of the complex **1a** are trans to each other. The bond distance between the two ruthenium atoms in **1a** (2.8485(7) Å) is similar to that of the methanethiolate-bridged diruthenium complex $[Cp^*RuCl(SMe)]_2$ (**3**) (2.8354(7) Å),[3a] and it is in accord with the generally known Ru−Ru single bond (2.71−3.02 Å).[7] An ORTEP drawing of one of the two independent molecules of the complex **2b** in each unit cell is shown in Figure 2. Complex **2b** contains one phosphido and two chloride ligands, and both Cp* rings lie on a horizontal axis, as shown in Figure 2. The bond distance between the two ruthenium atoms in **2b** (2.70 Å (average)) is shorter than that of the thiolate-bridged complex **3**, as the two ruthenium atoms in **2b** are connected strongly by three bridging ligands.



3

The redox properties of **1a** are found to be quite different from those of **3**.[8] The cyclic voltammogram of **1a** showed only one reversible oxidation wave at $E_{1/2} = +0.09$ V, while that of **3** exhibited two reversible oxidation waves at $E_{1/2} = -0.04$ and $+0.89$ V. From this result, **1a** is expected to show a catalytic activity different from that of **3**.

Scheme 2



Next, we investigated the catalytic activity of **1** and **2** toward propargylic alcohols. Treatment of 1-phenyl-2-propyn-1-ol (**4**) with 2-methylfuran in $ClCH_2CH_2Cl$ in the presence of a catalytic amount of **1a** at 60 °C for 18 h afforded the corresponding β-arylated ketone **5a** in 15% isolated yield without any formation of the propargylated product **6a**, while the reaction of propargylic alcohol **4** with 2-methylfuran in the presence of a catalytic amount of **3** afforded **6a** in an excellent yield (Scheme 2).[2c] Separately, we observed the complete consumption of **4** after the reaction, together with some unidentified byproducts. Use of 1-methylpyrrole and 1-methylindole in place of 2-methylfuran gave similar β-arylated ketones **5b**,**c** in 25% and 26% yields, respectively (Scheme 2). However, when reactions of **4** with 1-methylindole were carried out in the presence of a catalytic amount of **1b** and **2a**, no formation of **5c** was observed in both cases.

To obtain some information on the reaction pathway, we monitored the reaction of **4** with 1-methylindole in the presence of a catalytic amount of **1a**. At first, the formation of phenyl vinyl ketone (**7**) was observed by GC-MS in the reaction mixture. In addition, we detected the formation of **7** by GC-MS when the reaction of **4** in the presence of a catalytic amount of **1a** was carried out in the absence of aromatic compounds. Separately, we confirmed that **7**[9] reacts with 1-methylindole under the same reaction conditions to give **5c** in 43% yield. These results indicate that the formation of **5** proceeds via an initial isomerization of **4** into **7**, followed by Friedel−Crafts reaction of **7** with heteroaromatic compounds (Scheme 3). Isomerization of propargylic alcohols into α,β-unsaturated carbonyl compounds with the transposition of the oxygen[10–12] is well-known as a Meyer−Schuster rearrangement. On the other

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(8) A Pt stick as the working electrode and a Pt wire as a counter electrode were used in CH_2Cl_2 containing 0.1 M $^nBu_4NClO_4$ at room temperature. All potentials were measured against an Ag/Ag^+ reference electrode and converted to the values vs Fc/Fc^+.

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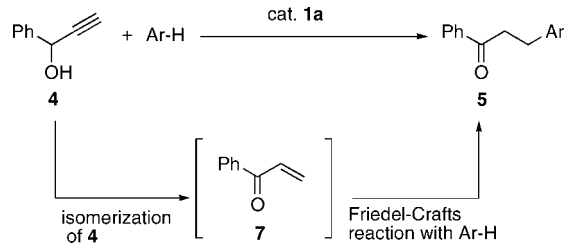
(11) Ruthenium-catalyzed Meyer−Schuster type isomerization reactions of propargylic alcohols have been reported: (a) Cadierno, V.; García-Garrido, S. E.; Gimeno, J. *Adv. Synth. Catal.* **2006**, *348*, 101. (b) Cadierno, V.; Díez, J.; García-Garrido, S. E.; Gimeno, J. *Chem. Commun.* **2004**, 2716.

Scheme 3



hand, examples of redox isomerization such as the transformation of **4** into **7** are relatively limited.[13] It is interesting that the monophosphido-bridged complex **1a** works as a dual catalyst toward the redox isomerization of propargylic alcohols to α,β-unsaturated ketones and their Friedel−Crafts reactions with heteroaromatic compounds, although the product yields were unfortunately not so high.

Conclusion

We have newly prepared monophosphido-bridged diruthenium complexes **1** and **2** from a chloride-bridged diruthenium complex and (dialkylphosphino)trimethylsilanes. This synthetic method may be applied to the preparation of other phosphido-bridged bimetallic complexes bearing a metal−metal bond. We have also found that the monophosphido-bridged diruthenium complex **1a** works as a dual catalyst toward the redox isomerization of propargylic alcohols and sequential Friedel−Crafts reaction with heteroatomatic compounds. Further studies on the application of these monophosphido-bridged diruthenium complexes to other organic transformations are now in progress.

Experimental Section

General. The ^{1}H NMR (270 MHz) and ^{31}P NMR (109 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvents. Elemental analyses were performed at the Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. The chloride-bridged diruthenium(III) complex [Cp*RuCl(μ_2-Cl)]$_2$[14] and tetramethyldiphosphine[15] were prepared according to the literature procedures. The β-arylated ketone **5a** is a known compound.[16]

Preparation of the Monophosphido-Bridged Diruthenium-(III) Complex 1. A typical experimental procedure for **1a** is described below. To a solution of tetramethyldiphosphine (183 mg, 1.50 mmol) in THF (1.0 mL) was added potassium metal (117 mg, 3.00 mmol), and the mixture was stirred at room temperature. After 16 h, a solution of chlorotrimethylsilane (326 mg, 3.00 mmol) in THF (6.0 mL) was added, and the mixture was stirred for an additional 1 h. To the resulting solution was added [Cp*RuCl(μ_2-Cl)]$_2$ (1.84 g, 3.00 mmol), and the mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (50 mL). The extract was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2−*n*-hexane to give dark green blocks of **1a** (1.20 g, 1.88 mmol, 63%). ^{1}H NMR (CD_2Cl_2): δ 1.65 (d, 30H, J = 1.1 Hz), 2.29 (d, 6H, J = 10.8 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 270.3 (s). Anal. Calcd for $C_{22}H_{36}Cl_3PRu_2$: C, 41.29; H, 5.67. Found: C, 41.05; H, 5.61.

Diethylphosphido-Bridged Diruthenium(III) Complex 1b. Yield: 27%. Dark green blocks. ^{1}H NMR (CD_2Cl_2): δ 1.49 (quint, 6H, J = 7.6 Hz), 1.63 (s, 30H), 2.25−2.50 (m, 2H), 2.65−2.90 (m, 2H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 297.0 (s). Anal. Calcd for $C_{24}H_{40}Cl_3PRu_2$: C, 43.15; H, 6.04. Found: C, 42.93; H, 5.90.

Preparation of the Cationic Monophosphido-Bridged Diruthenium(III) Complex 2. A typical experimental procedure for **2a** is described below. To a solution of **1a** (61.4 mg, 0.096 mmol) in THF (3.0 mL) was added AgOTf (23.9 mg, 0.093 mmol), and the mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2−*n*-hexane to give brown blocks of **2a** (59.5 mg, 0.079 mmol, 82%). ^{1}H NMR (acetone-d_6): δ 1.87 (d, 30H, J = 1.4 Hz), 2.84 (d, 6H, J = 10.8 Hz). ^{31}P{^{1}H} NMR (acetone-d_6): δ 305.7 (s). HRMS for $C_{22}H_{36}Cl_2PRu_2$: *m*/*z* calcd for [M−OTf] 605.0023, found 605.0031.

Cationic Diethylphosphido-Bridged Diruthenium(III) Complex 2b. Yield: 99%. Dark red blocks. ^{1}H NMR (CD_2Cl_2): δ 1.08 (t, 3H, J = 7.4 Hz), 1.15 (t, 3H, J = 7.4 Hz), 1.79 (d, 30H, J = 1.0 Hz), 3.05−3.20 (m, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 369.1 (s). HRMS for $C_{24}H_{40}Cl_2PRu_2$: *m*/*z* calcd for [M−OTf] 637.0327, found 637.0262.

Ruthenium-Catalyzed Reaction of Propargylic Alcohols with Heteroaromatic Compounds. A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**4**) with 2-methylfuran in the presence of **1a** is described below. In a 20 mL flask were placed **1a** (16.0 mg, 0.025 mmol) and NH_4BF_4 (5.2 mg, 0.050 mmol) under N_2. Anhydrous and degassed 1,2-dichloroethane (5.0 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of 1-phenyl-2-propyn-1-ol (**4**; 66.1 mg, 0.50 mmol) and 2-methylfuran (410 mg, 5.0 mmol), the reaction flask was kept at 60 °C for 16 h. The resulting mixture was filtered through Florisil and Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, eluent *n*-hexane/ethyl acetate 5/1) to give **5a** (16.3 mg, 0.076 mmol, 15% yield) as a brown oil.[16] ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 3H), 3.05 (t, 2H, J = 7.6 Hz), 3.25−3.35 (m, 2H), 5.84−5.86 (m, 1H), 5.91−5.92 (m, 1H), 7.42−7.52 (m, 3H), 7.94−8.02 (m, 2H).

Data for **5b** are as follows. Yield: 25%. A yellow solid. ^{1}H NMR ($CDCl_3$): δ 3.01 (t, 2H, J = 8.0 Hz), 3.35 (t, 2H, J = 8.0 Hz), 3.60 (s, 3H), 5.94−5.96 (m, 1H), 6.08 (t, 1H, J = 3.0 Hz), 6.59 (t, 1H, J = 3.0 Hz), 7.46−7.52 (m, 2H), 7.56−7.62 (m, 1H), 7.99−8.02 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 20.6, 33.6, 37.7, 105.3, 106.6, 121.4, 128.0, 128.6, 132.0, 133.1, 136.8, 199.1. HRMS for $C_{14}H_{15}NO$: *m*/*z* calcd for [M] 213.1154, found 213.1159.

Data for **5c** are as follows. Yield: 26%. A yellow solid. ^{1}H NMR ($CDCl_3$): δ 3.19 (t, 2H, J = 8.0 Hz), 3.36 (t, 2H, J = 8.0 Hz), 3.71 (s, 3H), 6.88 (s, 1H), 7.07−7.13 (m, 1H), 7.21−7.29 (m, 2H), 7.40−7.45 (m, 2H), 7.50−7.55 (m, 1H), 7.60−7.62 (m, 1H), 7.93−7.97 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 19.6, 32.5, 39.6, 109.2, 113.9, 118.7, 118.8, 121.5, 126.5, 127.6, 128.0, 128.5, 132.9, 137.0, 199.8. HRMS for $C_{18}H_{17}NO$: *m*/*z* calcd for [M] 263.1310, found 263.1319.

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(13) For representative examples, see: (a) Haak, E. *Eur. J. Org. Chem.* **2007**, 2815. (b) Tanaka, K.; Shoji, T.; Hirano, M. *Eur. J. Org. Chem.* **2007**, 2687. (c) Trost, B. M.; Livingston, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 9586, and references cited therein.

(14) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.

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(16) Alder, K.; Schmidt, C.-H. *Ber. Dtsch. Chem. Ges.* **1943**, *76B*, 18.

(17) SIR97: Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(18) Crystal Structure Analysis Package; Rigaku and Rigaku/MSC, 2000−2005.

Table 1. Summary of Crystallographic Data

	1a	**2b**
formula	$C_{22}H_{36}PCl_3Ru_2$	$C_{25}H_{40}O_3F_3PSCl_2Ru_2$
fw	640.00	781.66
cryst size/mm	0.70 × 0.50 × 0.20	0.45 × 0.35 × 0.30
color, habit	black plate	dark red block
cryst syst	*monoclinic*	*tetragonal*
space group	$P2_1/n$ (No. 14)	$P4_2/n$ (No. 86)
a/Å	8.8726(4)	19.1907(4)
b/Å	14.5203(7)	
c/Å	19.0631(7)	16.3113(4)
β/deg	96.1559(17)	
V/Å^3	2441.79(18)	6007.2(2)
Z	4	8
d_c/g cm^{-3}	1.741	1.728
μ(Mo Kα)/cm^{-1}	16.380	13.507
no. of data collected	20 078	43 603
no. of unique data	5555 (R_{int} = 0.071)	6881 (R_{int} = 0.030)
$R1^a$ ($I > 2\sigma$(I))	0.0613	0.0223
$wR2^b$	0.1789	0.0497
goodness of fit indicator^c	0.999	1.000
largest shift/esd, final cycle	0.000	0.000
residual electron density/e Å^{-3}	+2.62/−2.27	+0.85/−0.70

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2]^2]^{1/2}$, where $w = 1/[0.0037F_o^2 + \sigma(F_o^2)]/(4F_o^2)$. ^{c} $[\sum w(F_o^2 - F_c^2)^2/(N_{observns} - N_{params})]^{1/2}$.

X-ray Crystallography. Crystallographic data for **1a** and **2b** are summarized in Table 1. The crystals were immersed in oil (Sigma-Aldrich, Cat. Code I0890) on a nylon loop and mounted on a Rigaku RAXIS RAPID imaging plate. Data were collected at −100 °C under a cold nitrogen stream using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Empirical absorption corrections were applied. Structures were solved by the direct method,[17] and refined on F^2 by full-matrix least squares using the Crystal Structure software package.[18] Anisotropic thermal parameters were introduced for all non-hydrogen atoms. All hydrogen atoms were generated at calculated positions (d_{C-H} = 0.97 Å) and treated as riding atoms with isotropic thermal factors. Crystallographic data are also given in the Supporting Information as a CIF file.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 19028013, "Chemistry of Concerto Catalysis" and No. 18066003, "Molecular Theory for Real Systems") and for Young Scientists (S) (No. 19675002) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Figures giving spectroscopic data for **2** and CIF files giving crystallographic data for **1a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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