ORGANOMETALLICS

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# Synthesis and Reactivity of Hybrid Phosphido- and Hydrosulfido-Bridged Diruthenium Complexes: Transformations into Diruthenium and Tetraruthenium Complexes Bridged by Phosphido and Sulfido Ligands

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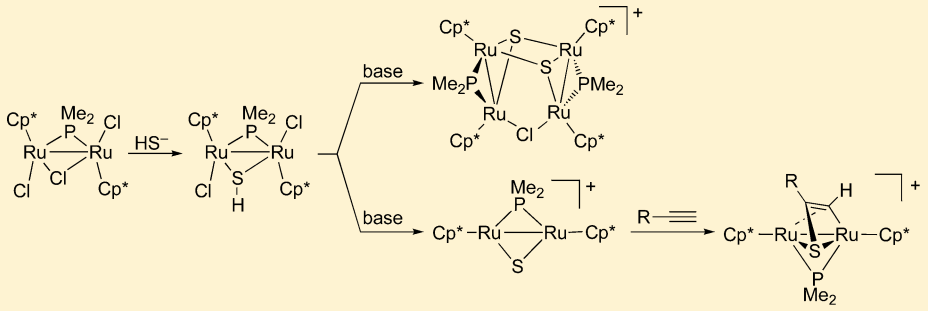
Supporting Information




**ABSTRACT:** The reaction of the monophosphido-bridged diruthenium(III) complex [Cp*RuCl($\mu$-PMe$_2$)($\mu$-Cl)RuClCp*] with sodium hydrogen sulfide affords the hybrid phosphido- and hydrosulfido-bridged diruthenium(III) complex [Cp*RuCl($\mu$-PMe$_2$)($\mu$-SH)RuClCp*]. The hydrosulfido-bridged diruthenium(III) complex can be further converted into the corresponding sulfido-bridged multinuclear ruthenium(III) complex via deprotonation of the hydrosulfido ligand. The hydrosulfido-bridged diruthenium(III) complex also reacts with bases to afford a coordinatively unsaturated diruthenium(III) complex, where insertion of terminal alkynes further occurs to form phosphido-bridged diruthenium(III) complexes bearing ruthenathiacyclobutene moieties.

## INTRODUCTION

Multimetallic complexes bridged by heteroatom ligands have been developed as potentially useful catalysts for organic transformations, where the nature of the bridging ligands is expected to play an important role in the reactivity of multimetallic complexes.[1] We have already found a unique catalytic activity of the alkanethiolato-bridged diruthenium complexes [Cp*RuCl($\mu$-SR)]$_2$ (Cp* = $\eta^5$-C$_5$Me$_5$)[2,3] toward a variety of organic transformations, including propargylic substitution reactions[4] via ruthenium−allenylidene intermediates.[5,6] More recently, we have prepared the monophosphido-bridged diruthenium complex [Cp*RuCl($\mu$-PMe$_2$)($\mu$-Cl)RuClCp*] (**1**) and found that its catalytic activity is different from that of [Cp*RuCl($\mu$-SR)]$_2$.[7] In addition, **1** is expected to work as a useful precursor for diruthenium complexes bridged by different heteroatoms, because **1** has a bridging chloride ligand which may be easily substituted with a variety of heteroatom ligands. In fact, we have succeeded in the preparation of a variety of hybrid phosphido- and thiolato-bridged complexes [Cp*RuCl($\mu$-PMe$_2$)($\mu$-SR)RuClCp*].[8]

As an extension of our study on the preparation and reactivity of diruthenium complexes, we have now envisaged to prepare diruthenium complexes bridged by phosphido and hydrosulfido ligands. The hydrosulfido ligand (SH$^-$) belongs to the family of sulfur donor ligands, while hydrosulfido transition-metal complexes are known to be convertible into sulfido complexes via deprotonation of the hydrosulfido ligand.[9] Herein, we describe the preparation of a hybrid phosphido- and hydrosulfido-bridged diruthenium complex **2** from the reaction of **1**, as well as transformations of **2** into diruthenium and tetraruthenium complexes bridged by phosphido and sulfido ligands.

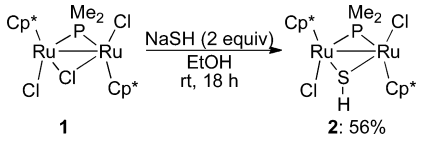
## RESULTS AND DISCUSSION

Treatment of **1** with 2 equiv of sodium hydrosulfide (NaSH) in ethanol (EtOH) at room temperature for 18 h afforded the corresponding hybrid phosphido- and hydrosulfido-bridged diruthenium complex [Cp*RuCl($\mu$-PMe$_2$)($\mu$-SH)RuClCp*] (**2**) in 56% isolated yield (Scheme 1). The IR spectrum of **2** shows a weak $\nu$(SH) band at 2459 cm$^{-1}$, which is similar to that of the dihydrosulfido-bridged diruthenium complex [Cp*RuCl($\mu$-SH)]$_2$ (2462 cm$^{-1}$).[10] The $^1$H NMR spectrum of **2** displays one doublet signal ($J_{P-H}$ = 0.8 Hz) at 4.16 ppm assignable to the proton of the bridging hydrosulfido ligand, while the other $^1$H NMR resonances due to Cp* moieties and dimethylphosphido

**Received:** February 15, 2012
**Published:** March 27, 2012

**Scheme 1. Synthesis of 2**




1 2: 56%

and hydrosulfido ligands appear with an intensity ratio of 30:6:1, showing that two Cp*Ru fragments are bridged by one dimethylphosphido and one hydrosulfido ligand. Furthermore, $^1$H NMR resonances attributable to both the Cp* and dimethylphosphido ligands are observed to be split into a pair of doublets, apparently arising from the sp$^3$ hybridization on the sulfur atom of the bridging hydrosulfido ligand, which creates slightly different environments for the two Cp* and methyl groups. The molecular structure of **2** was confirmed by an X-ray analysis. As shown in the ORTEP drawing of **2** depicted in Figure 1, the two Cp* ligands and two chloride ligands of **2** are located anti to each other, while the hydrogen atom of the hydrosulfido ligand is disordered into two symmetrical positions, which is in accordance with the spectroscopic observations in solution. The interatomic distance between two ruthenium atoms in **2** (2.8567(3) Å) is slightly shorter than those in the phosphido- and thiolato-bridged diruthenium complex [Cp*RuCl($\mu$-PMe$_2$)($\mu$-SR)RuClCp*] (R = $^i$Pr, 2.8839(5) Å; R = Ph, 2.86682(15) Å)[8] but is in accord with generally known Ru−Ru single-bond distances (2.71−3.02 Å).[11] In addition, the bond distances between ruthenium and sulfur (2.3003(6) Å) and between ruthenium and phosphorus atoms (2.2924(6) Å) are also similar to those in [Cp*RuCl($\mu$-PMe$_2$)($\mu$-SR)-RuClCp*].[8]

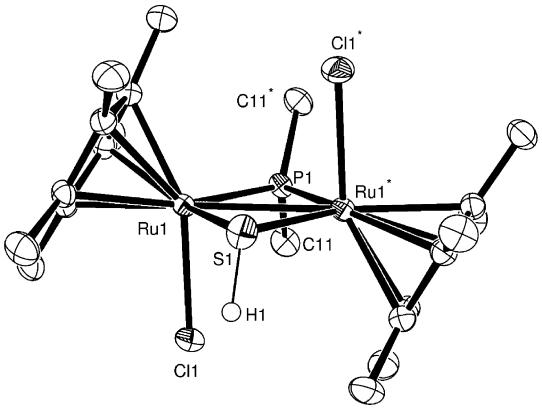
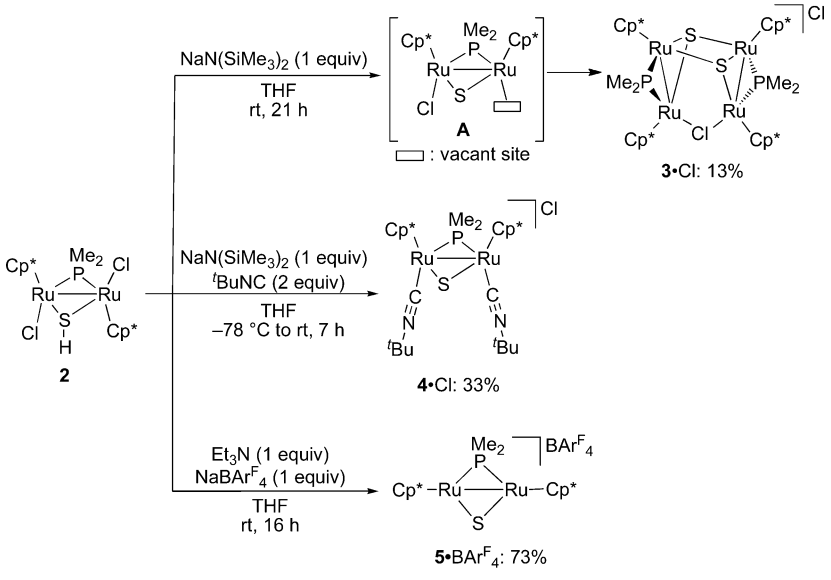



**Figure 1.** ORTEP drawing of **2**. Hydrogen atoms, except for H(1), are omitted for clarity. Selected interatomic distances (Å): Ru(1)−Ru(1)*, 2.8567(3); Ru(1)−Cl(1), 2.4603(6); Ru(1)−S(1), 2.3003(6); Ru(1)−P(1), 2.2924(6); S(1)−H(1), 1.33(5).

Complex **2** is expected to be transformed into the corresponding phosphido- and sulfido-bridged diruthenium complexes via deprotonation of the hydrosulfido ligand. Treatment of **2** with 1 equiv of NaN(SiMe$_3$)$_2$ in THF at room temperature for 21 h gave the unprecedented cationic phosphido- and sulfido-bridged tetraruthenium complex [{Cp*Ru($\mu$-PMe$_2$)-RuCp*}$_2$($\mu_3$-S)$_2$($\mu$-Cl)]Cl (**3**·Cl) in 13% isolated yield (Scheme 2), whose structure was confirmed by an X-ray analysis. An ORTEP drawing of **3** is given in Figure 2. The bond distance between Ru(1) and Ru(2) of Ru$_2$PS cores in **3** (2.8451(8) Å) is slightly shorter than that in **2** but is still in accord with generally known Ru−Ru single-bond distances.[11] On the other hand, the interatomic distances of Ru(1)···Ru(1)* (3.7813(6) Å) and Ru(2)···Ru(2)* (4.2070(5) Å) suggest no interaction between the corresponding ruthenium atoms. The bond distances of Ru−P(1) (2.28 Å, mean) and Ru−S(1) (2.35 Å, mean) within the Ru$_2$PS cores in **3** are comparable to those in [Cp*RuCl($\mu$-PMe$_2$)($\mu$-SR)RuClCp*][8] and **2**, while the sulfido ligands capping three ruthenium atoms coordinate to the other ruthenium atoms in the neighboring Ru$_2$PS core at a slightly longer distance (Ru(1)−S(1)*, 2.4032(16) Å). From the viewpoint of cluster chemistry, construction of complex **3** is quite unique, where the participation of phosphides, sulfides, and chloride in bridging ruthenium atoms furnishes a rare tetraruthenium core. The formation of **3** can be explained reasonably as follows: elimination of hydrogen chloride from **2** should result in the initial formation of the coordinatively unsaturated phosphido- and sulfido-bridged diruthenium complex **A** bearing a Ru$_2$PS core in situ, followed by dimerization of **A** to give the tetraruthenium complex **3**, as described in Scheme 2.

**Scheme 2. Deprotonation of 2 into Phosphido- and Sulfido-Bridged Complexes**





dx.doi.org/10.1021/om3001247 | Organometallics 2012, 31, 3292−3299

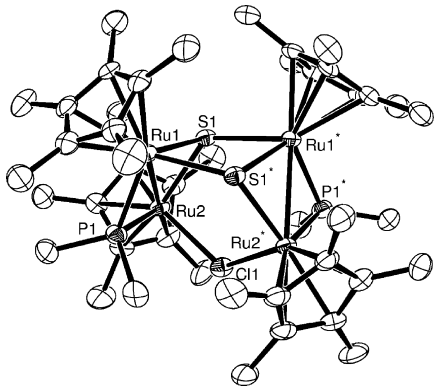



**Figure 2.** ORTEP drawing of the cationic part of **3**·Cl·2$C_4H_8O$. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru(1)−Ru(2), 2.8451(8); Ru(2)−Cl(1), 2.4115(14); Ru(1)−S(1), 2.3611(19); Ru(1)−S(1)*, 2.4032(16); Ru(2)−S(1), 2.3321(18); Ru(1)−P(1), 2.273(2); Ru(2)−P(1), 2.293(2); Ru(1)···Ru(1)*, 3.7813(6); Ru(2)···Ru(2)*, 4.2070(5).

When **2** was reacted with 1 equiv of $NaN(SiMe_3)_2$ in the presence of 2 equiv of *tert*-butyl isocyanide in THF at −78 °C and the solution was warmed slowly to room temperature with further stirring for 7 h, the cationic bis(isonitrile) diruthenium complex [Cp*Ru($CN^tBu$)($\mu$-$PMe_2$)($\mu$-S)Ru($CN^tBu$)Cp*]Cl (**4**·Cl) was obtained in 33% isolated yield (Scheme 2). This result also indicates the formation of a coordinatively unsaturated phosphido- and sulfido-bridged diruthenium complex like **A** in situ, whose vacant sites are subsequently filled by isocyanide. An X-ray crystallographic study has also confirmed the molecular structure of **4**, whose ORTEP drawing is shown in Figure 3. The bond distances of Ru(1)−Ru(2) (2.8703(13) Å), Ru−P(1) (2.28 Å, mean), and Ru−S(1) (2.34 Å, mean), which are close to those in **2**, indicate that the phosphido- and sulfido-bridged complex **4** has also a $Ru_2PS$ core similar to that of the phosphido- and hydrosulfido-bridged complex **2**.

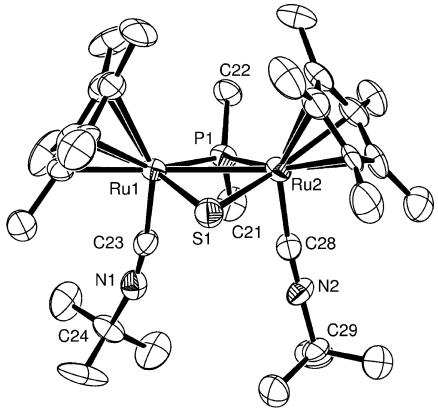



**Figure 3.** ORTEP drawing of the cationic part of **4**·Cl. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru(1)−Ru(2), 2.8703(13); Ru(1)−S(1), 2.345(4); Ru(2)−S(1), 2.331(3); Ru(1)−P(1), 2.287(3); Ru(2)−P(1), 2.277(4).

As expected, a coordinatively unsaturated complex was isolated by the reaction of **2** with a stoichiometric amount of bases. Treatment of **2** with 1 equiv of triethylamine in the presence of 1 equiv of sodium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate ($NaBAr^F_4$) in THF at room temperature for 16 h afforded the coordinatively unsaturated cationic phosphido- and sulfido-bridged diruthenium complex [Cp*Ru($\mu$-$PMe_2$)($\mu$-S)-RuCp*][$BAr^F_4$] (**5**·$BAr^F_4$) in 73% isolated yield (Scheme 2). The detailed structure of **5** was eventually confirmed by an X-ray analysis using a single crystal of **5**·$PF_6$, which was obtained by treatment analogous to that for **2** using $NaPF_6$. An ORTEP drawing of **5** is given in Figure 4. Complex **5** contains one phosphido and one sulfido ligand, and both Cp* rings lie on a horizontal axis, as shown in Figure 4. Corresponding to the decrease in the formal number of $Ru_2$ core electrons from 34 in **2** to 30 in **5**, the interatomic distance between two ruthenium atoms at 2.688(2) Å becomes slightly shorter than those generally known for Ru−Ru single bonds[11] but is rather longer compared to those found in other coordinatively unsaturated diruthenium complexes (2.53−2.66 Å).[12] The bond distances of Ru−P(1) (2.28 Å, mean) in **5** are comparable to those in the phosphido- and sulfido-bridged complexes **2**−**4**, while those of Ru−S(1) (2.20 Å, mean) are fairly shorter than those in complexes **2**−**4**, as the two ruthenium atoms in **5** are connected strongly by the bridging sulfido ligand having delocalized Ru−S−Ru multiple bonding.[13]

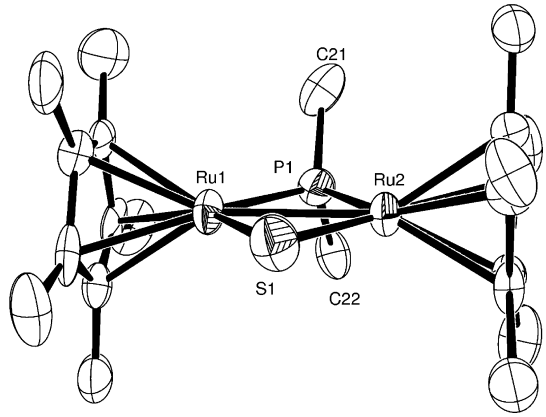
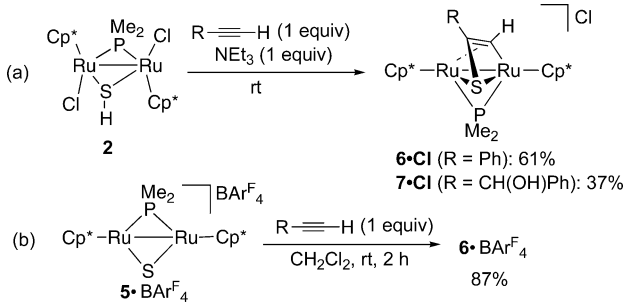



**Figure 4.** ORTEP drawing of the cationic part of **5**·$PF_6$. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru(1)−Ru(2), 2.688(2); Ru(1)−S(1), 2.198(6); Ru(2)−S(1), 2.208(6); Ru(1)−P(1), 2.288(5); Ru(2)−P(1), 2.264(5).

As the formation of unsaturated $Ru_2PS$ species in situ was confirmed by the isolation of **5**, we next investigated reactions with terminal alkynes. Unfortunately, all these diruthenium complexes did not work as catalysts toward the propargylic substitution reactions so far described by our group.[4,6] Stoichiometric reactions of these diruthenium complexes with terminal alkynes revealed that neither the corresponding vinylidene nor alkyne complexes were formed,[14] but insertion of terminal alkynes into the Ru−S bond was found to occur for some diruthenium complexes such as **2** and **5**·$BAr^F_4$. When the reaction of **2** with 1 equiv of phenylacetylene was carried out in the presence of 1 equiv of triethylamine in dichloromethane at room temperature for 15 h, [Cp*Ru{$\mu_3$-SC(Ph)=C(H)}-($\mu$-$PMe_2$)RuCp*]Cl (**6**·Cl) was obtained in 61% isolated yield (Scheme 3a). Separately, we confirmed that reaction of **5**·$BAr^F_4$ with 1 equiv of phenylacetylene under similar conditions also proceeded smoothly to give the corresponding diruthenium complex **6**·$BAr^F_4$ in 87% yield (Scheme 3b). These results indicate that the coordinatively unsaturated cationic complex **5** should be a reactive intermediate in the conversion of **2** into **6**, where the subsequent step is the formation of the

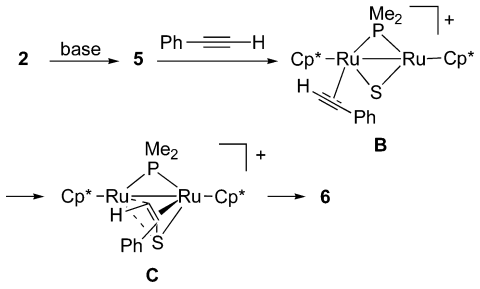

dx.doi.org/10.1021/om3001247 | *Organometallics* 2012, 31, 3292−3299

**Scheme 3. Reaction of 2 and 5·BAr$^F_4$ with Terminal Alkynes**




$\pi$-alkyne complex **B** by the reaction of **5** with the alkyne, followed by an insertion of the alkyne into one Ru−S bond to give **6** (Scheme 4). The regioselective formation of **6** is a result of steric repulsion between the Cp* ring and the substituent on the terminal alkyne.

**Scheme 4. Formation of 6**




The molecular structure of **6** was confirmed by an X-ray analysis of **6**·Cl. As shown by the ORTEP drawing of **6** in Figure 5, the phenylacetylene molecule has been inserted into one of the Ru−S bonds to form a ruthenathiacyclobutene segment (S(1)−Ru(1)−C(1)−C(2)), and the resultant C=C moiety coordinates to the other ruthenium atom in a $\eta^2$ manner at the same time (Ru(2)−C(1), 2.155(3) Å; Ru(2)−C(2), 2.233(3) Å). The two ruthenium atoms also connect to each other by a Ru−Ru single bond at a distance of 2.7254(4) Å. The C(1)−C(2) bond length at 1.393(4) Å is intermediate between the typical C−C single- and double-bond distances[15] and is comparable to those in the $\pi$-bonded alkenethiolato ligands of $[Cp^*Ir\{\mu\text{-}SC(Me)=CHCH_2COMe\}]_2[BF_4]_2$ (1.392(9) Å)[16] and $[(Cp^*Ru)_2(CpTi)_2Pd_2(PPh_3)(\mu_3\text{-}S)_3(\mu_2\text{-}O)\text{-}\{\mu_3\text{-}SC(COOMe)=CCOOMe\}]$ (1.401(9) Å),[17] while the Ru(1)−C(1) and S(1)−C(2) distances at 2.023(4) and 1.772(3) Å, respectively, in **6** are comparable to those for Ru−C and S−C single bonds. The torsion angles of S(1)−Ru(1)−C(1)−C(2) (7.90(11)°) and Ru(1)−S(1)−C(2)−C(3) (−164.21(18)°) indicate that five atoms (Ru(1), C(1), C(2), C(3), and S(1)) are nearly coplanar. Furthermore, the sum of the three bond angles around C(2) associated with three atoms is 359.4°, indicating that the C(2) atom is essentially of sp$^2$ character.

Moreover, the reaction of **2** with 1 equiv of 1-phenyl-2-propyn-1-ol in the presence of triethylamine in THF at room temperature also afforded the corresponding cationic phosphido-bridged diruthenium complex bearing a ruthenathiacyclobutene moiety $[Cp^*Ru\{\mu_3\text{-}SC(CH(OH)Ph)=C(H)\}(\mu\text{-}PMe_2)RuCp^*]Cl$ (**7**·Cl) in 37% isolated yield (Scheme 3a). The molecular structure of **7** was also confirmed by an X-ray study and is found to be similar to that of **6** (Figure 6). In this reaction, no formation of the allenylidene complex was observed.

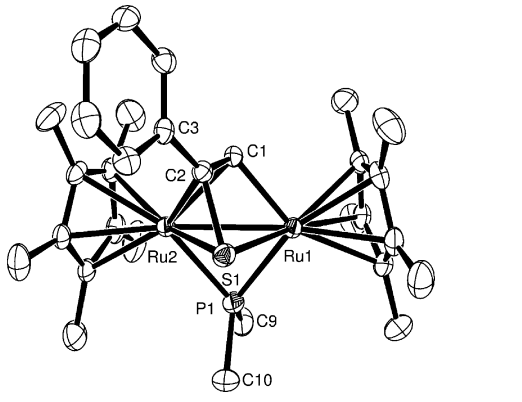



**Figure 5.** ORTEP drawing of the cationic part of **6**·Cl·ClCH$_2$CH$_2$Cl. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru(1)−Ru(2), 2.7254(4); Ru(1)−S(1), 2.4459(8) ; Ru(2)−S(1), 2.4282(8); Ru(1)−P(1), 2.2548(9); Ru(2)−P(1), 2.3401(10); Ru(1)−C(1), 2.023(4); Ru(2)−C(1), 2.155(3); Ru(2)−C(2), 2.233(3); S(1)−C(2), 1.772(3); C(1)−C(2), 1.393(4); C(2)−C(3), 1.481(5). Selected interatomic angles (deg): S(1)−C(2)−C(1), 104.6(3); S(1)−C(2)−C(3), 121.72(19); C(1)−C(2)−C(3), 133.1(3).

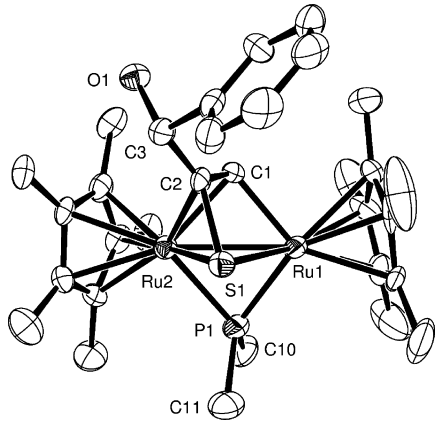



**Figure 6.** ORTEP drawing of the cationic part of **7**·Cl. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru(1)−Ru(2), 2.7230(13); Ru(1)−S(1), 2.455(2); Ru(2)−S(1), 2.424(2); Ru(1)−P(1), 2.247(3); Ru(2)−P(1), 2.3263(19); Ru(1)−C(1), 2.027(7); Ru(2)−C(1), 2.136(7); Ru(2)−C(2), 2.236(7); S(1)−C(2), 1.777(7); C(1)−C(2); 1.408(10), C(2)−C(3), 1.495(10). Selected interatomic angles (deg): S(1)−C(2)−C(1), 105.2(5); S(1)−C(2)−C(3), 121.5(5); C(1)−C(2)−C(3), 132.7(7).

It must be noted that the use of transition-metal complexes for the formation of carbon−sulfur bonds has recently attracted much attention in the organosulfur chemistry, and the insertion of unsaturated compounds such as alkynes into sulfur−sulfur or sulfur−metal bonds has also been developed as a tool for the formation of carbon−sulfur bonds.[18] However, examples of the reaction of a hydrosulfido- or sulfido-bridged diruthenium complex as a sulfur source with alkynes to form carbon−sulfur bonds are still limited in number, and reactions from bis(thiolato)- and bis(sulfido)-bridged diruthenium precursors are reported to undergo insertion of alkynes into metal−sulfur


dx.doi.org/10.1021/om3001247 | Organometallics 2012, 31, 3292−3299

Table 1. Crystallographic Data for 2, 3·Cl·2THF, and 4·Cl

| | 2 | 3·Cl·2$C_4H_8O$ | 4·Cl |
|---|---|---|---|
| chem formula | $C_{22}H_{37}Cl_2PRu_2S$ | $C_{52}H_{88}Cl_2O_2P_2Ru_4S_2$ | $C_{32}H_{54}ClN_2PRu_2S$ |
| formula wt | 637.61 | 1346.52 | 767.42 |
| cryst size, $mm^3$ | 0.35 × 0.25 × 0.15 | 0.40 × 0.20 × 0.20 | 0.20 × 0.15 × 0.05 |
| cryst color, habit | brown, block | dark brown, block | red, platelet |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $C2/c$ (No. 15) | $C2/c$ (No. 15) | $P2_1/n$ (No. 14) |
| $a$, Å | 16.5909(6) | 13.9721(8) | 20.4886(12) |
| $b$, Å | 8.5787(4) | 17.8282(13) | 8.3947(6) |
| $c$, Å | 18.0461(7) | 22.6549(13) | 22.4029(13) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 108.6524(12) | 97.0320(16) | 113.4147(14) |
| $\gamma$, deg | 90 | 90 | 90 |
| $V$, $Å^3$ | 2433.58(16) | 5600.8(6) | 3535.9(4) |
| $Z$ | 4 | 4 | 4 |
| $D_{calcd}$, g $cm^{-3}$ | 1.740 | 1.597 | 1.441 |
| $F(000)$ | 1288 | 2752 | 1584 |
| $\mu_{calcd}$, $cm^{-1}$ | 16.198 | 13.227 | 10.569 |
| transmissn factor range | 0.670−0.784 | 0.606−0.768 | 0.328−0.949 |
| no. of measd rflns | 11 476 | 27 110 | 25 873 |
| no. of unique rflns | 2767 | 6398 | 7751 |
| $R_{int}$ | 0.0266 | 0.0309 | 0.1735 |
| no. of refined params | 204 | 307 | 406 |
| R1 ($I > 2\sigma(I)$)[a] | 0.0175 | 0.0494 | 0.0682 |
| wR2 (all data)[b] | 0.0444 | 0.1522 | 0.2134 |
| max/min residual peaks (e/$Å^3$) | +0.47/−0.37 | +2.04/−1.16 | +7.63/−2.96 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$; $w = 4F_o^2/[pF_o^2 + q\sigma(F_o^2)]$; $p = 0$ (2, 3·Cl·2$C_4H_8O$), 0.001 (4·Cl); $q = 1.072$ (2), 10.4 (3·Cl·2$C_4H_8O$), 0.598 (4·Cl).

bonds so far.[19,20] Now we have succeeded in demonstrating that the monosulfido-bridged diruthenium(III) species also allow the insertion of alkynes into one of the metal−sulfur bonds. The incorporation of the electron-rich phosphido bridging ligand into the electron-poor diruthenium(III) core may presumably contribute to the formation of electron-deficient but slightly stable coordinatively unsaturated diruthenium species and may have brought about the novel reactivity with alkynes.

In summary, a hybrid phosphido- and hydrosulfido-bridged diruthenium(III) complex was newly prepared from a monophosphido-bridged diruthenium complex. The hydrosulfido-bridged diruthenium(III) complex was further converted into the corresponding sulfido-bridged multinuclear ruthenium(III) complexes via deprotonation of the hydrosulfido ligand. The reaction of hydrosulfido-bridged diruthenium(III) complexes with terminal alkynes in the presence of a base gave phosphido-bridged diruthenium(III) complexes bearing ruthenathiacyclobutene moieties. This is a unique example of monosulfido-bridged diruthenium(III) species participating in the insertion of alkynes to Ru−S to form C−S, where the electron-rich phosphido ligand may be also engaged.

## EXPERIMENTAL SECTION

**General Methods.** $^1H$ NMR (270 MHz) and $^{31}P$ NMR (109 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvents. IR spectra were recorded on a JASCO FT/IR 4100 Fourier transform infrared spectrophotometer. Elemental analyses were performed at the Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL Accu TOF JMS-T100LP mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. The monophosphido-bridged diruthenium complex [Cp*RuCl($\mu$-$PMe_2$)($\mu$-Cl)RuClCp*] (**1**) was prepared according to the literature procedures.[7]

**Preparation of 2, a Phosphido- and Hydrosulfido-Bridged Diruthenium(III) Complex.** To a solution of NaSH (50.4 mg, 0.899 mmol) in ethanol (3 mL) was added a solution of [Cp*RuCl($\mu$-$PMe_2$)($\mu$-Cl)RuClCp*] (**1**; 286.5 mg, 0.448 mmol) in ethanol (5 mL), and the mixture was stirred at room temperature for 18 h. The solvent was removed under reduced pressure, and the residue was extracted with toluene (10 mL). The extract was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The obtained residue was recrystallized from toluene−*n*-hexane to give brown block crystals of [Cp*RuCl($\mu$-$PMe_2$)($\mu$-SH)RuClCp*] (**2**; 159.3 mg, 0.250 mmol, 56%). $^1H$ NMR ($C_6D_6$): $\delta$ 1.52 (d, 15H, $J_{P-H}$ = 1.1 Hz), 1.62 (d, 15H, $J_{P-H}$ = 1.1 Hz), 2.03 (d, 3H, $J_{P-H}$ = 11.3 Hz), 2.05 (d, 3H, $J_{P-H}$ = 11.3 Hz), 4.16 (d, 1H, $J_{P-H}$ = 0.8 Hz). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 252.2 (s). IR (KBr, $cm^{-1}$): 2459 (S−H). Anal. Calcd for $C_{22}H_{37}Cl_2PRu_2S$: C, 41.44; H, 5.85. Found: C, 41.50; H, 5.74.

**Preparation of 3·Cl, a Cationic Phosphido- and Sulfido-Bridged Tetraruthenium(III) Complex.** To a solution of **2** (63.7 mg, 0.100 mmol) in THF (1 mL) was added a solution of $NaN(SiMe_3)_2$ (18.2 mg, 0.0993 mmol) in THF (1 mL), and the mixture was stirred at room temperature for 21 h. After the removal of the solvent under reduced pressure, the residue was washed with *n*-hexane and then recrystallized from THF−*n*-hexane to give dark brown block crystals of [{Cp*Ru($\mu$-$PMe_2$)RuCp*}$_2$($\mu_3$-S)$_2$($\mu$-Cl)]-Cl·2$C_4H_8O$ (3·Cl·2$C_4H_8O$), which were further collected and dried in vacuo to give 3·Cl (7.4 mg, 0.0063 mmol, 13%). $^1H$ NMR (THF-$d_8$): $\delta$ 1.19 (d, 6H, $J_{P-H}$ = 11.6 Hz), 1.58 (s, 30H), 1.89 (s, 30H), 2.05 (d, 6H, $J_{P-H}$ = 10.5 Hz). $^{31}P\{^1H\}$ NMR (THF-$d_8$): $\delta$ 210.7 (s). HRMS (ESI-TOF): calcd for $C_{44}H_{72}ClP_2Ru_4S_2$ [3] 1169.03823, found 1169.03604.

**Preparation of 4·Cl, a Cationic Phosphido- and Sulfido-Bridged Bis(isonitrile) Diruthenium(III) Complex.** To a solution of **2** (64.5 mg, 0.101 mmol) and $^t$BuNC (16.9 mg, 0.203 mmol) in THF (5 mL) at −78 °C was added a solution of $NaN(SiMe_3)_2$ (18.5 mg,


dx.doi.org/10.1021/om3001247 | Organometallics 2012, 31, 3292−3299

**Table 2. Crystallographic Data for 5·$PF_6$, 6·Cl·$ClCH_2CH_2Cl$, and 7·Cl**

| | 5·$PF_6$ | 6·Cl·$ClCH_2CH_2Cl$ | 7·Cl |
|---|---|---|---|
| chem formula | $C_{22}H_{36}F_6P_2Ru_2S$ | $C_{32}H_{46}Cl_3PRu_2S$ | $C_{31}H_{44}ClOPRu_2S$ |
| formula wt | 710.66 | 802.25 | 733.31 |
| cryst size, $mm^3$ | 0.10 × 0.10 × 0.05 | 0.36 × 0.34 × 0.05 | 0.10 × 0.05 × 0.01 |
| cryst color, habit | dark brown, platelet | orange, plate | red, chunk |
| cryst syst | triclinic | monoclinic | orthorhombic |
| space group | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $Pna2_1$ (No. 33) |
| $a$, Å | 8.629(2) | 13.4501(5) | 14.0370(7) |
| $b$, Å | 10.694(3) | 14.0500(5) | 19.5485(9) |
| $c$, Å | 14.922(3) | 19.3656(6) | 11.3344(5) |
| $\alpha$, deg | 80.105(5) | 90 | 90 |
| $\beta$, deg | 87.814(6) | 108.9440(8) | 90 |
| $\gamma$, deg | 89.707(7) | 90 | 90 |
| $V$, $Å^3$ | 1355.5(6) | 3461.4(2) | 3110.2(3) |
| $Z$ | 2 | 4 | 4 |
| $D_{calcd}$, g $cm^{-3}$ | 1.741 | 1.539 | 1.566 |
| $F(000)$ | 712 | 1632 | 1496 |
| $\mu_{calcd}$, $cm^{-1}$ | 13.602 | 12.310 | 11.984 |
| transmissn factor range | 0.313–0.934 | 0.675–0.940 | 0.290–0.988 |
| no. of measd rflns | 13016 | 31751 | 25901 |
| no. of unique rflns | 5964 | 7891 | 6892 |
| $R_{int}$ | 0.1471 | 0.0529 | 0.0836 |
| no. of refined params | 327 | 398 | 379 |
| R1 ($I > 2\sigma(I)$)[a] | 0.1079 | 0.0394 | 0.0650 |
| wR2 (all data)[b] | 0.2342 | 0.0705 | 0.1089 |
| max/min residual peaks ($e/Å^3$) | +3.45/−5.33 | +1.01/−1.06 | +3.23/−2.63 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$; $w = 4F_o^2/q\sigma(F_o^2)$; $q$ = 1.407 (5·$PF_6$), 2.93 (6·Cl·$ClCH_2CH_2Cl$), 2.29 (7·Cl).

0.101 mmol) in THF (5 mL). The reaction mixture was warmed to room temperature and stirred for 7 h. After the removal of the solvent under reduced pressure, the residue was washed with *n*-hexane and diethyl ether and was extracted with THF (5 mL). The extract was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from THF–diethyl ether to give red platelet crystals of [Cp*Ru($CN^tBu$)-($\mu$-$PMe_2$)($\mu$-S)Ru($CN^tBu$)Cp*]Cl (4·Cl; 25.4 mg, 0.0331 mmol, 33%). $^1$H NMR (THF-$d_8$): $\delta$ 1.45 (s, 18H), 1.87 (d, 30H, $J_{P-H}$ = 0.81 Hz), 2.30 (d, 3H, $J_{P-H}$ = 11.3 Hz), 2.31 (d, 3H, $J_{P-H}$ = 11.6 Hz). $^{31}P\{^1H\}$ NMR (THF-$d_8$): $\delta$ 196.8 (s). Anal. Calcd for $C_{32}H_{54}ClN_2PRu_2S$: C, 50.08; H, 7.09; N, 3.65. Found: C, 49.93; H, 7.17; N, 3.60.

**Preparation of 5·$BAr^F_4$, a Coordinatively Unsaturated Cationic Phosphido- and Sulfido-Bridged Diruthenium(III) Complex.** To a solution of **2** (64.6 mg, 0.101 mmol) and triethylamine (15 $\mu$L, 0.11 mmol) in THF (10 mL) was added sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($NaBAr^F_4$) (91.2 mg, 0.103 mmol), and the mixture was stirred at room temperature for 16 h. The resultant solution was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from THF–*n*-hexane to give a dark brown crystalline solid of [Cp*Ru($\mu$-$PMe_2$)($\mu$-S)RuCp*][$BAr^F_4$] (5·$BAr^F_4$; 106.1 mg, 0.0743 mmol, 73%). Dark brown platelet crystals of 5·$PF_6$ suitable for an X-ray analysis were obtained by the analogous reaction of **2** with $NaPF_6$. $^1$H NMR (THF-$d_8$): $\delta$ 1.92 (s, 30H), 2.58 (d, 15H, $J_{P-H}$ = 11.3 Hz), 7.58 (br s, 4H), 7.80 (br s, 8H). $^{31}P\{^1H\}$ NMR (THF-$d_8$): $\delta$ 260.9 (s). Anal. Calcd for $C_{54}H_{48}BF_{24}PRu_2S$: C, 45.39; H, 3.39. Found: C, 44.99; H, 3.34.

**Preparation of 6·Cl, a Cationic Phosphido- and Vinylthiolato-Bridged Diruthenium(III) Complex with Phenylacetylene Inserted.** To a solution of **2** (96.1 mg, 0.151 mmol) in dichloromethane (15 mL) were added phenylacetylene (15.6 mg, 0.153 mmol) and triethylamine (15.2 mg, 0.150 mmol), and the mixture was stirred at room temperature for 15 h. The solvent was removed under reduced pressure, and the residue was extracted with toluene (20 mL). The extract was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The obtained residue was recrystallized from 1,2-dichloroethane–diethyl ether to give orange plate crystals of [Cp*Ru($\mu_3$-SCPh=CH)($\mu$-$PMe_2$)RuCp*]Cl·$C_2H_4Cl_2$ (6·Cl·$ClCH_2CH_2Cl$), which were collected and dried in vacuo to give 6·Cl (64.6 mg, 0.0919 mmol, 61%). $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.68 (br d, 30H, $J_{P-H}$ = 1.6 Hz), 2.08 (d, 3H, $J_{P-H}$ = 11.1 Hz), 2.25 (d, 3H, $J_{P-H}$ = 10.8 Hz), 6.99 (br, 1H), 7.47 (br, 3H), 7.90 (br, 1H), 9.45 (s, 1H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 206.8 (s). Anal. Calcd for $C_{30}H_{42}ClPRu_2S$: C, 51.23; H, 6.02. Found: C, 50.75; H, 6.06.

**Preparation of 7·Cl, a Cationic Phosphido- and Vinylthiolato-Bridged Diruthenium(III) Complex with Propargylic Alcohol Inserted.** To a solution of **2** (31.9 mg, 0.0500 mmol) in THF (5 mL) were added 1-phenyl-2-propyn-1-ol (6.6 mg, 0.050 mmol) and triethylamine (5.1 mg, 0.050 mmol), and the mixture was stirred at room temperature for 2 h. The mixture was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The obtained residue was recrystallized from $CH_2Cl_2$–diethyl ether to give red crystals of [Cp*Ru{$\mu_3$-SC(CH-(OH)Ph)=CH}($\mu$-$PMe_2$)RuCp*]Cl (7·Cl·$CH_2Cl_2$; 15.0 mg, 0.018 mmol, 37%). Red chunk crystals of 7·Cl suitable for an X-ray analysis were obtained by further recrystallization from THF–diethyl ether. $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.73 (d, 15H, $J_{P-H}$ = 1.6 Hz), 1.77 (d, 15H, $J_{P-H}$ = 1.4 Hz), 1.97 (d, 3H, $J_{P-H}$ = 10.8 Hz), 2.16 (d, 3H, $J_{P-H}$ = 10.5 Hz), 4.73 (s, 1H), 6.60 (br s, 1H), 7.31 (d, 1H, $J$ = 7.0 Hz), 7.38–7.44 (m, 2H), 7.70 (d, 2H, $J$ = 7.0 Hz), 9.41 (s, 1H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 204.5 (s). Anal. Calcd for $C_{32}H_{46}Cl_3OPRu_2S$: C, 46.97; H, 5.67. Found: C, 46.74; H, 5.72.

**X-ray Diffraction Studies.** Diffraction data for **2**, 3·Cl·$2C_4H_8O$, 4·Cl, 5·$PF_6$, 6·Cl·$ClCH_2CH_2Cl$, and 7·Cl were collected for the $2\theta$ range of 6–55° at −100 °C on a Rigaku R-AXIS RAPID imaging plate area detector with graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.710 75 Å) radiation, with VariMax optics for 6·Cl·$ClCH_2CH_2Cl$ and 7·Cl. Intensity data were corrected for empirical absorptions (ABSCOR) and for Lorentz and polarization effects. The structure solutions and refinements were carried out by using the CrystalStructure package.[21] The positions of non-hydrogen atoms were determined by direct methods (SHELXS-97 for **2**, SIR-92 for 3·Cl·$2C_4H_8O$, SIR-97 for 4·Cl, 6·Cl·$ClCH_2CH_2Cl$, and 7·Cl) or heavy-atom Patterson methods (PATTY for 5·$PF_6$) and subsequent Fourier syntheses (DIRDIFF-99)[22] and were refined on $F_o^2$ using all the unique reflections by full-matrix least squares with anisotropic thermal parameters except for the chlorine, oxygen, and carbon atoms (Cl(3), O(1), O(2), C(23), C(24), C(25)) which comprise the disordered chloride and THF in 3·Cl·$2C_4H_8O$ and two Cp* carbon atoms (C(1) and C(2)) in 5·$PF_6$. The position of the hydrogen atom (H(1)) of the bridging hydrosulfido ligand in **2** was located from the difference Fourier synthesis and was further refined with an atom occupancy of 0.5, where the sulfur atom S(1) is located at a symmetric position. The counteranionic chlorine atom in 3·Cl·$2C_4H_8O$ is heavily disordered and was solved as a mixture of two chlorine atoms (Cl(2) and Cl(3)) with atom occupancies of 0.425 and 0.15 (in a symmetric position), respectively. The oxygen and carbon atoms of the THF molecule in 3·Cl·$2C_4H_8O$ are heavily disordered between two positions and were solved as oxygen atoms (O(1) and O(2)) with atom occupancies of 0.875; thus, the hydrogen atoms of the THF molecule were not located. All other hydrogen atoms were placed at calculated


dx.doi.org/10.1021/om3001247 | *Organometallics* 2012, 31, 3292–3299

positions with fixed isotropic parameters. The goodness of fit indicator $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$ was refined to a value of 1.000 for all the compounds. The Flack parameter was refined to a value of 0.11(5) for **7**·Cl. Anomalous dispersion effects were included in $F_c$, and neutral atom scattering factors and the values for $\Delta f'$ and $\Delta f''$ were taken from ref 23. Details of the crystal and data collection parameters are summarized in Tables 1 and 2.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

CIF files giving crystallographic data for **2**, **3**·Cl·2$C_4H_8O$, **4**·Cl, **5**·Cl, **6**·Cl·$ClCH_2CH_2Cl$, and **7**·Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the Funding Program for Next Generation World-Leading Researchers (GR025) and a Grant-in-Aid for Young Scientists (B) (No. 21750088) from the Ministry of Education, Culture, Sports, Science and Technologyof Japan. T.M. acknowledges the Global COE program for Chemistry Innovation. We thank the Research Hub for Advanced Nano Characterization at The University of Tokyo for X-ray analyses.

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