

# Reactions of Ruthenium Acetylide Complexes with Isothiocyanate

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Received December 2, 1997

Treatment of  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}\equiv\text{CPh}$  (**2**;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) with  $\text{PhN}=\text{C}=\text{S}$  at room temperature affords the  $[2 + 2]$  cycloaddition product  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{=NPh})\text{S}$  (**3a**), containing a four-membered ring, and the neutral vinylidene phosphonate complex  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{=O})(\text{OMe})_2]\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{C}(\text{SH})=\text{NPh}$  (**4a**) in a 9:1 ratio. Formation of **4a** results from an Arbuzov-like dealkylation reaction possibly after addition of  $\text{PhN}=\text{C}=\text{S}$ . The same reaction at 40 °C affords a higher yield of **4a** and  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{=S})\text{N}(\text{R})\text{C}(\text{=NR})\text{S}$  (**5a**;  $\text{R} = \text{Ph}$ ) which results from addition of a second isothiocyanate to the four-membered ring of **3a**. The reaction of **2** with  $\text{PhCH}_2\text{N}=\text{C}=\text{S}$  at room temperature directly affords the six-membered-ring product **5b** ( $\text{R} = \text{CH}_2\text{Ph}$ ). Trimerization of phenyl isothiocyanate is catalyzed by  $\text{Cp}(\text{dppe})\text{RuC}\equiv\text{CPh}$  (**1'**;  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) in refluxing  $\text{CH}_2\text{Cl}_2$ . This catalytic reaction proceeds through a pathway in which the first two steps are the same as those observed in the reaction of **2a**. An attempt to purify the precursor of the trimerization product gave the cocrystallization of **1'** and  $(\text{PhNCS})_3$  (**8**). The structures of **3a**, **4a**, **5b**, and the cocrystallization product of **1'** and **8** have been determined by single-crystal X-ray diffraction analysis.

## Introduction

Metal acetylide complexes have been the focus of recent study due to their application in organometallic<sup>1</sup> and materials<sup>2</sup> chemistry. The acetylide ligand is quite reactive toward electrophiles, undergoing either alkylation or protonation at the  $\beta$ -carbon to give stable vinylidene complexes. Another common reaction observed for this ligand is the  $[2 + 2]$  cycloaddition of the triple bond with unsaturated organic substrates.<sup>3</sup> Cycloadditions of organic substrates such as  $\text{CS}_2$ ,<sup>4</sup>  $(\text{NC})_2\text{C}=\text{C}(\text{CF}_3)_2$ , and  $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$ <sup>5</sup> to the acetylide ligand in various metal complexes have been reported. Nickel(0) complexes promote the cyclocoupling of alkynes with isocyanates.<sup>6</sup> This reaction may proceed through

a metallacycle in which one alkyne and one isocyanate have been coupled. Herein we report that the reaction of isocyanate and isothiocyanate with two ruthenium acetylide complexes results in sequential additions of the organic substrate to the acetylide ligand to produce novel heterocyclic ligands. With  $\text{Cp}(\text{dppe})\text{RuC}\equiv\text{CPh}$ ,  $[2 + 2]$  cycloaddition is the first step and is followed by further addition of two isothiocyanate molecules to give a trimerization product. When a trimethyl phosphite ligand is present, the cycloaddition is accompanied by an Arbuzov-like dealkylation reaction to give a useful side product from which the mechanism of the trimerization reaction could be delineated. Structural characterization of several relevant complexes is reported herein.

## Results and Discussion

**Synthesis of Acetylide Complexes.** Treatment of  $\text{Cp}(\text{PPh}_3)_2\text{RuC}\equiv\text{CPh}$  (**1**)<sup>7</sup> with  $\text{P}(\text{OMe})_3$  in *n*-decane at reflux temperature affords a racemic mixture of  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}\equiv\text{CPh}$  (**2**) in high yield.<sup>8</sup> Complex **2** is soluble in polar solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , acetone, and THF. In the <sup>31</sup>P NMR spectrum, two doublet resonances at  $\delta$  158.3 and 56.6 are assigned to the phosphite and phosphine ligands, respectively. Complex **2** could also be prepared in lower yield from

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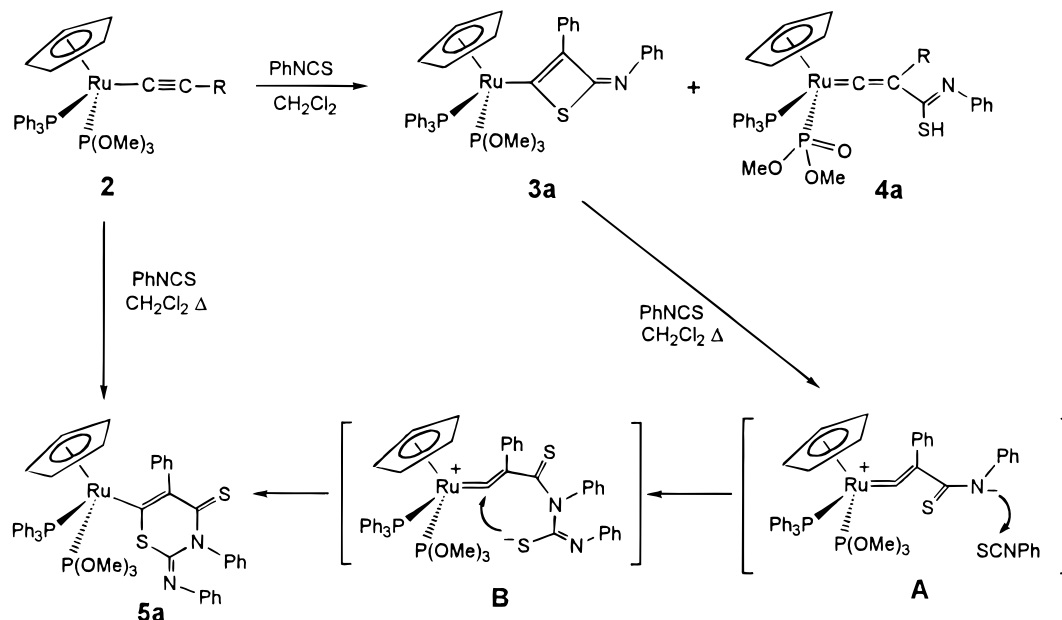
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Scheme 1



treatment of  $\text{Cp}(\text{PPh}_3)_2\text{RuCl}$  with  $\text{P}(\text{OMe})_3$  followed by the reaction with  $\text{HC}\equiv\text{CPh}$ . Treatment of **1** with dppe affords  $\text{Cp}(\text{dppe})\text{RuC}\equiv\text{CPh}$  (**1'**) in high yield.

**[2 + 2] Cycloaddition and Arbuzov-like Dealkylation.** Treatment of **2** with a 10-fold excess of  $\text{PhN}=\text{C}=\text{S}$  in  $\text{CH}_2\text{Cl}_2$  at room temperature for 3 days affords the yellow [2 + 2] cycloaddition product  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{=NPh})\text{S}$  (**3a**) and the neutral red-orange phosphonate vinylidene complex  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{=O})(\text{OMe})_2]\text{Ru}=\text{C}(\text{Ph})\text{C}(\text{SH})\text{NPh}$  (**4a**) in a 9:1 ratio (75% total yield). The two complexes can be separated by column chromatography. Complex **3a** is derived from a [2 + 2] cycloaddition of the  $\text{C}\equiv\text{C}$  triple bond with the  $\text{C}=\text{S}$  double bond. This neutral complex is stable in air but, in  $\text{CHCl}_3$  solution, decomposes to give **2**. The  $^{31}\text{P}$  NMR spectrum has two doublet resonances at  $\delta$  56.2 and 151.7 with  $J_{\text{P-P}} = 68.8$  Hz, which are assigned to the  $\text{PPh}_3$  and the  $\text{P}(\text{OMe})_3$  ligands, respectively. The air-stable complex **4a** is formed by an Arbuzov-like dealkylation reaction of the phosphite ligand.<sup>9</sup> The two OMe groups in **4a** are diastereotopic and occur in the  $^1\text{H}$  NMR spectrum at  $\delta$  3.18 and 3.03 with  $J_{\text{P-H}} = 11.5$  Hz. The  $^{31}\text{P}$  NMR spectrum of **4a** has resonances at  $\delta$  48.0 and 93.4, the latter due to the phosphonate.

Interestingly, if the reaction is carried out at 40 °C in the presence of excess  $\text{PhN}=\text{C}=\text{S}$ , the yield of **4a** increases and the new product  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{=S})\text{N}(\text{Ph})\text{C}(\text{=NPh})\text{S}$  (**5a**) could be isolated in moderate yield. Complex **5a** was also prepared directly from the reaction of **3a** with excess  $\text{PhNCS}$  at 40 °C. In **5a** two  $\text{PhNCS}$  molecules and the acetylide ligand are incorporated to form a six-membered ring. In analogy to this, we note that the heterocyclic compound 2-thiopyridone can be prepared by the addition of  $\text{MeNCS}$  to a cobaltacyclopentadiene complex, possibly through  $\text{C}=\text{N}$  bond insertion into a  $\text{Co}-\text{C}$  bond followed

by reductive elimination.<sup>10</sup> Other organic compounds with similar heterocyclic ring structures have been reported.<sup>11</sup> By treatment of complex **2** with excess  $\text{PhCH}_2\text{N}=\text{C}=\text{S}$  in  $\text{CH}_2\text{Cl}_2$  at room temperature, the analogous red-orange complex  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{=S})\text{N}(\text{CH}_2\text{Ph})\text{C}(\text{=NCH}_2\text{Ph})\text{S}$  (**5b**) was directly obtained. Spectroscopic data for **5b** are consistent with this formulation and are comparable with those for **5a**. This reaction also yields the corresponding phosphonate complex **4b**. For  $\text{PhCH}_2\text{N}=\text{C}=\text{S}$ , the analogous four-membered-ring compound  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{=NCH}_2\text{Ph})\text{S}$  (**3b**), a precursor of **5b**, is obtained at 5 °C but transforms, in the presence of  $\text{PhCH}_2\text{NCS}$ , to **5b** over 20 min at room temperature.

Isolation of the phosphonate complex indicates that the  $\text{C}\alpha-\text{S}$  bond is labile. Thus, **3** may easily form the zwitterionic vinylidene complex **A** (Scheme 1). Structure **A** has a negative charge localized on the N atom, which may attack the carbon atom of a second isothiocyanate to give **B**. Subsequent ring closure gives the six-membered-ring complex **5**.

**Structure Determination.** Complex **3a** was characterized by a single-crystal X-ray diffraction analysis; an ORTEP drawing is shown in Figure 1. Crystal and intensity collection data are given in Table 1, and selected bond distances and angles are given in Table 2. The central coordination sphere of the ruthenium atom contains an  $\eta^5$ -cyclopentadienyl ring, the phosphorus atoms of phosphite and phosphine ligands, and the carbon atom (C1) of the organic ligand. The four atoms of the four-membered ring formed by the [2 + 2] cycloaddition are essentially planar with the C1–C2 distance of 1.388(10) Å typical of a  $\text{C}=\text{C}$  double bond. The bond distances for C1–S and C9–S (1.868(7) and 1.823(8) Å) are typical of  $\text{C}-\text{S}$  single bonds.<sup>12</sup> The

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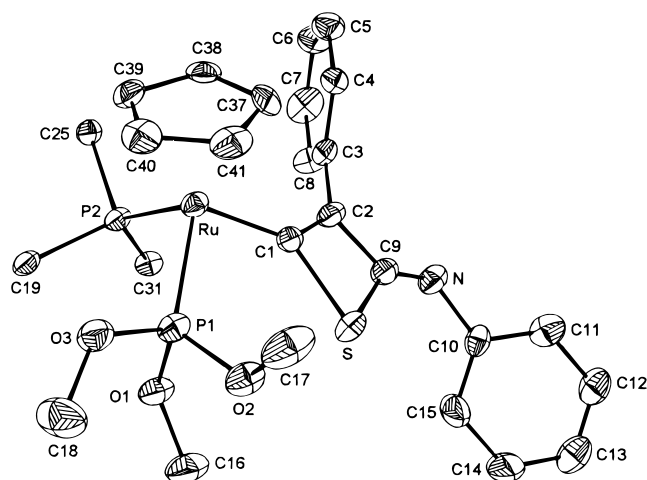
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**Table 1.** Crystal and Intensity Collection Data for  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{S})=\text{NPh}$  (**3a**),  $\text{Cp}(\text{PPh}_3)[\text{P}(=\text{O})(\text{OMe})_2]\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{C}(\text{SH})=\text{NPh}$  (**4a**),  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{S})\text{NPhC}(\text{NPh})\text{S}$  (**5b**), and  $\text{Cp}(\text{dppe})\text{RuC}\equiv\text{CPh}(\text{PhNCS})_3$ 

mol formula	$\text{C}_{41}\text{H}_{38}\text{NO}_3\text{P}_2\text{SRuCl}_3$ ( <b>3a</b> )	$\text{C}_{41}\text{H}_{39}\text{NO}_3\text{P}_2\text{SRu}$ ( <b>4a</b> )	$\text{C}_{52}\text{H}_{53}\text{N}_2\text{O}_{3.5}\text{P}_2\text{S}_2\text{Ru}$ ( <b>5b</b> )	$\text{C}_{60}\text{H}_{49}\text{N}_3\text{SRu}$
space group	$P1$	$P1$	$P2_1/c$	$Cc$
$a$ , Å	10.316(3)	10.970(3)	18.798(8)	18.904(5)
$b$ , Å	11.237(6)	12.064(5)	13.714(3)	15.951(2)
$c$ , Å	18.010(4)	14.595(3)	19.934(4)	35.173(8)
$\alpha$ , deg	100.64(3)	90.39(4)	90.00	90.00
$\beta$ , deg	94.02(2)	101.59(2)	114.76(4)	94.82(2)
$\gamma$ , deg	93.59(3)	100.51(4)	90.00	90.00
$V$ , Å <sup>3</sup>	1040.6(13)	1858.5(10)	4666.5(24)	10 568(4)
$Z$	2	2	4	8
cryst dims, mm	$0.20 \times 0.20 \times 0.30$	$0.25 \times 0.25 \times 0.30$	$0.50 \times 0.40 \times 0.20$	$0.20 \times 0.20 \times 0.30$
radiation		Mo K $\alpha$ , $\lambda = 0.7107$ Å		
$2\theta$ range, deg	2–45	2–45	2–45	2–60
scan type			$\theta-2\theta$	
total no. of rflns	5303	4848	6069	8099
no. of unique reflns, $I > 2\sigma(I)$	3077	2958	3685	4983
$R$	0.042	0.041	0.051	0.054
$R_w$	0.040	0.042	0.047	0.052

**Figure 1.** ORTEP drawing (50% thermal ellipsoids) of **3a**. Three phenyl groups on the triphenylphosphine ligand and all hydrogen atoms are eliminated for clarity.**Table 2.** Selected Bond Distances (Å) and Angles (deg) of  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{S})=\text{NPh}$  (**3a**)

Ru–P1	2.2263(23)	N–C9	1.271(10)
Ru–P2	2.3095(21)	N–C10	1.418(9)
Ru–C1	2.025(7)	C1–C2	1.388(11)
S–C1	1.868(7)	C2–C3	1.459(10)
S–C9	1.823(8)	C2–C9	1.439(10)
P1–Ru–P2	93.94(8)	S–C1–C2	92.9(5)
P1–Ru–C1	90.50(21)	C1–C2–C3	132.3(6)
P2–Ru–C1	94.81(20)	C1–C2–C9	101.3(6)
C1–S–C9	72.6(3)	C3–C2–C9	126.4(7)
C9–N–C10	122.2(6)	S–C9–N	135.5(6)
Ru–C1–S	129.1(4)	S–C9–C2	93.1(5)
Ru–C1–C2	138.0(5)	N–C9–C2	131.3(7)

C9=N bond distance of 1.271(10) Å confirms an imino group. The dihedral angle between the phenyl plane (C10–C15) on the imino group and the plane (S, C1, C2, C9) formed by the four-membered ring is 37.8(3)°. The two ruthenium–phosphorus bonds in **3a** are Ru–P1 = 2.226(2) Å and Ru–P2 = 2.310(2) Å, with the shorter distance belonging to the phosphite ligand. Organic compounds containing similar four-membered rings with an imino group have been observed as stable products from the phosphine-induced elimination of a sulfur atom from 1,2-dithio 3-imines.<sup>13</sup> The structural features of the 2-imino-2*H*-thiete portion, including the

dihedral angle between the planes of the four-membered ring and the phenyl substituent in the imino group, are similar to that in **3a**. The [2 + 2] cycloaddition of a C≡C bond of an iron acetylide with CS<sub>2</sub>, yielding 2*H*-thiete-2-thione (β-dithiolactone), has been reported.<sup>4</sup> A similar process has been proposed for the first stage of the reaction of alkynes with CS<sub>2</sub>.<sup>4</sup> The reaction of phosphonium complexes with isocyanates leading to [2 + 2] addition via the N=C bond to give four-membered phosphametallacycles has been reported.<sup>14</sup> Interestingly, such a reaction does not take place with the bis-(triphenylphosphine) analogue of **2**. The reaction of vinylidene complexes with metal acetylide leading to [2 + 2] addition via the terminal C=C bond of the vinylidene to give unusual cyclic C<sub>4</sub> bridging has also been reported.<sup>15</sup>

The molecular structure of **4a** was determined by an X-ray diffraction study; an ORTEP drawing is shown in Figure 2. Crystal and intensity collection data are given in Table 1, and selected bond distances and angles are given in Table 3. With the formation of the phosphonate ligand, the two ruthenium–phosphorus bonds (Ru–P1(phosphite) = 2.303(2) Å and Ru–P2 = 2.323(2) Å) are now comparable. The ruthenium–carbon bond has a formal bond order of 2, consistent with a short Ru–C1 bond (1.798(6) Å). The carbon–carbon double bond of the vinylidene ligand is 1.337(9) Å, typical for a C(sp<sup>2</sup>)-C(sp) allene bond.<sup>16</sup> The ruthenium–vinylidene linkage is very nearly linear (Ru–C1–C2 = 175.2(5)°). The N–C9 and S–C9 bond lengths of 1.344(8) and 1.641(6) Å, respectively, both display partial double-bond character, indicative of several resonance contributions.

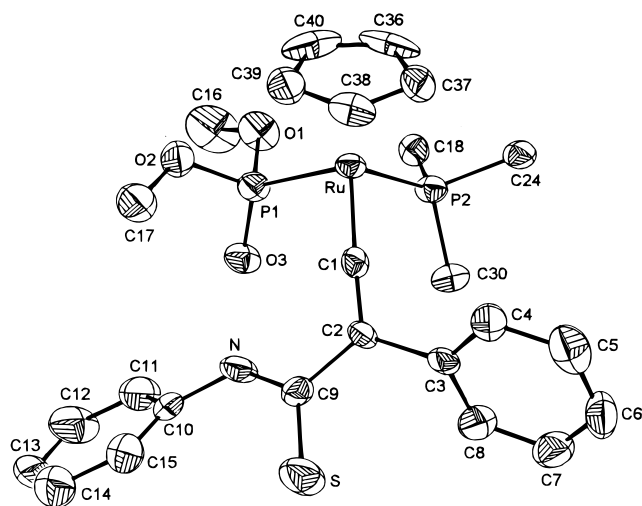
The molecular structure of **5b** was determined by an X-ray diffraction study; an ORTEP drawing which emphasizes the heterocyclic six-membered ring is shown in Figure 3. Crystal and intensity collection data are given in Table 1, and selected bond distances and angles are given in Table 4. As observed in **3a**, the Ru–P1-(phosphite) bond length of 2.239(3) Å is shorter than

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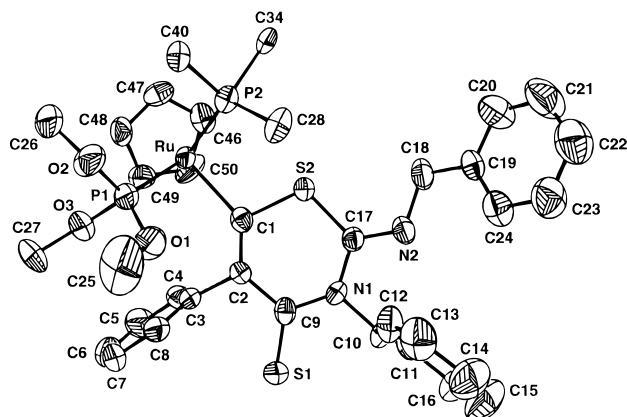
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**Figure 2.** ORTEP drawing (50% thermal ellipsoids) of **4a**. Three phenyl groups on the triphenylphosphine ligand and all hydrogen atoms are eliminated for clarity.



**Figure 3.** ORTEP drawing (50% thermal ellipsoids) of **5b**. Three phenyl groups on the triphenylphosphine ligand and all hydrogen atoms are eliminated for clarity.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) of  $\text{Cp}(\text{PPh}_3)[\text{P}(=\text{O})(\text{OMe})_2]\text{Ru}=\text{C}(\text{Ph})\text{C}(\text{SH})=\text{NPh}$  (**4a**)

Ru-P1	2.3027(20)	N-C9	1.344(8)
Ru-P2	2.3234(20)	N-C10	1.417(8)
Ru-C1	1.799(6)	C1-C2	1.336(8)
P1-O1	1.582(4)	C2-C3	1.503(9)
P1-O2	1.617(5)	C2-C9	1.478(8)
P1-O3	1.491(4)	C9-S	1.641(6)
P1-Ru-P2	92.95(7)	P1-O2-C17	120.0(4)
P1-Ru-C1	91.13(19)	C9-N-C10	129.2(5)
P2-Ru-C1	90.57(21)	Ru-C1-C2	175.2(5)
Ru-P1-O1	107.81(19)	C1-C2-C3	116.8(5)
Ru-P1-O2	110.00(19)	C1-C2-C9	124.2(6)
Ru-P1-O3	119.06(19)	C3-C2-C9	119.0(5)
O1-P1-O2	96.8(3)	N-C9-C2	114.0(5)
O1-P1-O3	112.8(3)	N-C9-S	125.4(5)
O2-P1-O3	108.0(3)	C2-C9-S	120.5(5)
P1-O1-C16	122.8(5)		

that of Ru-P2(phosphine) (2.341(3) Å). The Ru-C1 bond length of 2.105(7) Å is typical of a Ru-C single bond, and the C1-C2 bond length of 1.356(10) Å is typical of a double bond. The carbon-sulfur double bond in **5b** is 1.635(8) Å, which is comparable to that in ethylene trithiocarbonate (1.652(2) Å).<sup>17</sup> The two C(sp<sup>2</sup>)-S single bonds (C1-S2 = 1.749(8) and C17-S2

**Table 4.** Selected Bond Distances (Å) and Angles (deg) of  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{Ru}=\text{C}(\text{Ph})\text{C}(=\text{S})\text{N}(\text{CH}_2\text{Ph})\text{C}(=\text{NCH}_2\text{Ph})\text{S}$  (**5b**)

Ru-P1	2.2389(24)	N1-C9	1.410(10)
Ru-P2	2.341(3)	N1-C10	1.487(9)
Ru-C	2.105(7)	N1-C17	1.399(9)
S1-C9	1.635(8)	N2-C17	1.272(10)
S2-C1	1.749(8)	N2-C18	1.456(10)
S2-C17	1.750(8)	C1-C2	1.356(10)
P1-O1	1.594(6)	C2-C3	1.514(10)
P1-O2	1.596(6)	C2-C9	1.477(10)
P1-O3	1.595(6)	C10-C11	1.510(12)
P2-C28	1.863(8)	C18-C19	1.498(11)
P2-C34	1.864(8)	C46-C47	1.443(12)
P2-C40	1.825(8)	C46-C50	1.415(12)
O1-C25	1.430(11)	C47-C48	1.384(12)
O2-C26	1.409(11)	C48-C49	1.397(11)
O3-C27	1.446(11)	C49-C50	1.357(12)
P1-Ru-P2	94.61(9)	C10-N1-C17	113.9(6)
P1-Ru-C1	94.84(21)	C17-N2-C18	118.8(6)
P2-Ru-C1	96.78(21)	Ru-C1-S2	106.2(4)
C1-S2-C17	108.6(4)	Ru-C1-C2	135.6(6)
Ru-P1-O1	116.75(24)	S2-C1-C2	117.5(6)
Ru-P1-O2	121.81(24)	C1-C2-C3	120.4(7)
Ru-P1-O3	108.70(24)	C1-C2-C9	128.0(7)
O1-P1-O2	97.6(3)	C3-C2-C9	111.5(6)
O1-P1-O3	106.8(3)	S1-C9-N1	120.0(6)
O2-P1-O3	103.6(3)	S1-C9-C2	121.1(6)
Ru-P2-C28	122.0(3)	N1-C9-C2	118.9(6)
Ru-P2-C34	117.1(3)	N1-C10-C11	114.2(6)
Ru-P2-C40	115.7(3)	S2-C17-N1	118.1(5)
C28-P2-C34	100.2(4)	S2-C17-N2	124.3(6)
C28-P2-C40	99.7(4)	N1-C17-N2	117.6(6)
C34-P2-C40	98.0(4)	N2-C18-C19	113.3(7)
P1-O1-C25	126.0(6)	C47-C46-C50	106.6(7)
P1-O2-C26	121.9(6)	C46-C47-C48	106.8(7)
P1-O3-C27	125.3(7)	C47-C48-C49	108.6(7)
C9-N1-C10	118.8(6)	C48-C49-C50	109.5(7)
C9-N1-C17	126.9(6)	C46-C50-C49	108.4(7)

= 1.750(8) Å) in the six-membered ring are short enough to reflect some double-bond character.<sup>18</sup> The heterocyclic six-membered ring is essentially planar.

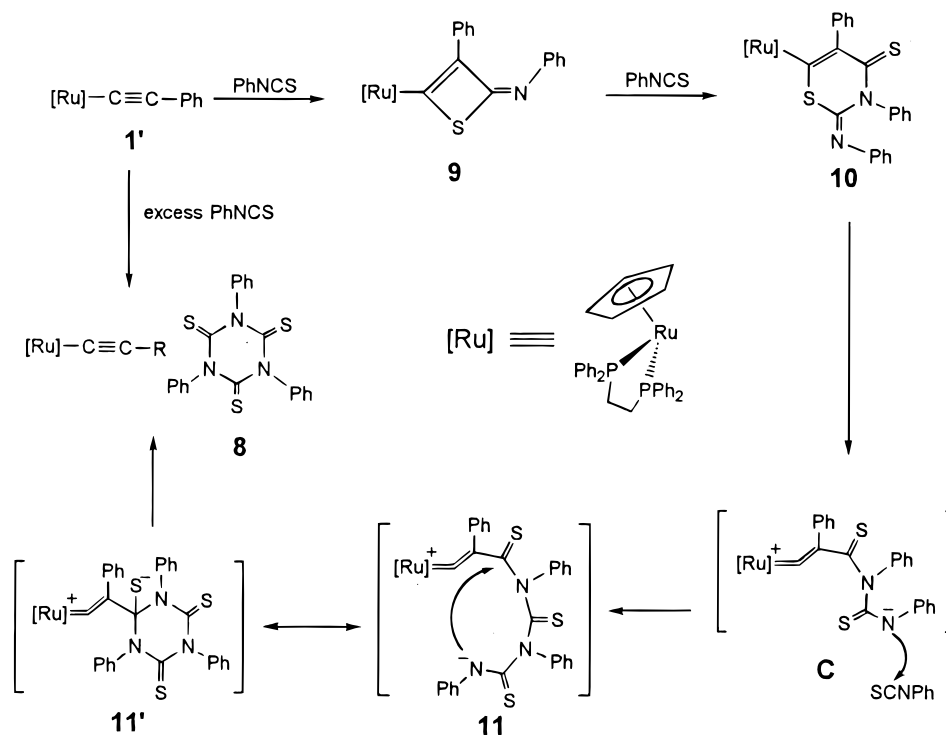
**Reactions of 2 with Isocyanate.** Treatment of **2** with PhNCO at -20 °C for 7 days afforded the two products  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{Ru}=\text{C}(\text{Ph})\text{C}(=\text{NPh})\text{O}$  (**6**)

and  $\text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{Ru}=\text{C}(\text{Ph})\text{C}(=\text{O})\text{N}(\text{Ph})\text{C}(=\text{NPh})\text{O}$  (**7**) in a 1:1 ratio, as indicated by <sup>1</sup>H and <sup>31</sup>P NMR spectra. These products are unstable at room temperature and were only characterized by spectroscopic methods. In the <sup>31</sup>P NMR spectrum of the crude mixture, the two doublet resonances at δ 155.3 and 56.9 with *J*<sub>P-P</sub> = 66.9 Hz are assigned to the P(OMe)<sub>3</sub> and PPh<sub>3</sub> ligands of **6** and another set of <sup>31</sup>P resonances at δ 151.7 and 55.0 with *J*<sub>P-P</sub> = 69.1 Hz are assigned to **7**. The FAB mass spectrum of the crude mixture displayed parent peaks at *m/e* 774.2 and 893.2 for **6** and **7**, respectively. By comparing the spectroscopic data for the two products with those for **3** and **5**, it is plausible to conclude that **3** and **6** have similar structures, as do complexes **5** and **7**. The dealkylation phosphonate product was not observed at -20 °C. However, when the reaction was carried out at room temperature, more than three phosphonate complexes were observed by the <sup>31</sup>P NMR spectra. Separation of these complexes by chromatography caused decomposition, and no further characterization was attempted.

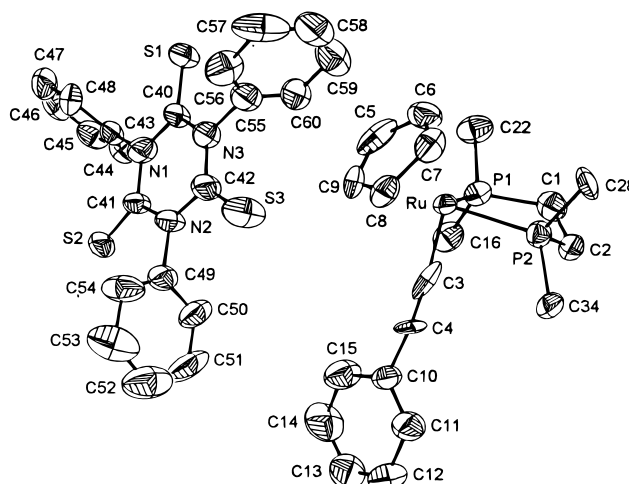
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### Scheme 2



**Trimerization of Isothiocyanate.** Our efforts to prepare the dppe analogues of **3** and **5** by reacting Cp(dppe)RuC≡CPh (**1'**) with PhNCS led to isolation of a cocrystallization product of **1'** and 1,3,5-triphenyl-1,3,5-triazinane-2,4,6-trithione (PhNCS)<sub>3</sub> (**8**),<sup>19</sup> a trimerization product of isothiocyanate. In the reaction, the [2 + 2] cycloaddition product Cp(dppe)RuC=C(Ph)C(=NPh)-S (**9a**) and Cp(dppe)RuC=C(Ph)C(=S)N(Ph)C(=NPh)S (**10a**) were also isolated and identified. The reaction of **1'** with a 10-fold excess of PhNCS at room temperature for 3 days afforded the orange-yellow complex **9a** in 72% yield. When the reaction was carried out for 7 days at room temperature, the brown complex **10a** was isolated in 65% yield. This transformation was monitored by <sup>31</sup>P NMR spectroscopy. At the beginning of the reaction, the <sup>31</sup>P resonance of **1'** appeared at δ 86.0; within 3 days the resonance attributed to **9a** appeared at δ 94.1, and after 4 more days the resonance of **10a** appeared at δ 99.3. With longer reaction time at room temperature, a complex mixture containing several organometallic compounds was obtained. When the reaction was carried out at 40 °C for 2 days, a mixture composed of the major organometallic product **11**, which showed a resonance at δ 79.4 in the <sup>31</sup>P NMR spectrum, and **8** were obtained. Compounds **11** and **8** were separated by column chromatography. Complex **11** is dark brown and stable in air. Attempts to obtain single crystals of **11** by recrystallization led to the yellow cocrystallization product of **1'** and **8**. The mass spectrum of **11** displays only the parent peaks attributed to **1'**. However, the <sup>31</sup>P NMR resonance of **11** (δ 79.6) is different from those of **1'** and **10a**. On the basis of these data, we believe that **11** is a precursor of the trimerization product. The <sup>31</sup>P NMR chemical shift of **11** falls in the region for that



**Figure 4.** ORTEP drawing (50% thermal ellipsoids) of the cocrystallization product of **1'** and **8**. Four phenyl groups on the dppe ligand and all hydrogen atoms are eliminated for clarity.

of a ruthenium vinylidene dppe complex. A possible structure of **11** is depicted in Scheme 2. The formation of **11** may be initiated by opening of the six-membered ring of **10a** to give the zwitterionic vinylidene complex **C**, with the anionic charge localized at the N atom. The nucleophilic attack of this N atom on a free isothiocyanate molecule followed by ring closure regenerates **1'** and releases the six-membered trimerization product **8**. It is less likely that the N atom will attack the C $\alpha$  atom because of the lower stability of an eight-membered ring.

The crystal structure of the cocrystallization product of **1'** and **8** is shown in Figure 4. Crystal and intensity collection data are given in Table 1, and selected bond distances and angles are given in Table 5. The two molecules are packed together with no significant

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**Table 5. Selected Bond Distances (Å) and Angles (deg) of Cp(dppe)RuCCPh·(PhNCS)<sub>3</sub>**

Ru–P1	2.286(5)	N1–C40	1.417(21)
Ru–P2	2.288(5)	N1–C41	1.437(19)
Ru–C3	1.893(18)	N1–C43	1.491(21)
Ru–C5	2.224(17)	N2–C41	1.433(21)
Ru–C6	2.185(16)	N2–C42	1.406(21)
Ru–C7	2.210(15)	N2–C49	1.527(20)
Ru–C8	2.247(17)	N3–C40	1.415(20)
Ru–C9	2.238(16)	N3–C42	1.373(20)
S1–C40	1.644(15)	N3–C55	1.519(23)
S2–C41	1.627(16)	C3–C4	1.183(22)
S3–C42	1.687(19)	C4–C10	1.395(19)
P1–Ru–P2	84.81(17)	Ru–C3–C4	170.9(15)
P1–Ru–C3	88.5(5)	C3–C4–C10	170.5(16)
P2–Ru–C3	88.6(5)	S1–C40–N1	123.7(11)
C40–N1–C41	123.0(13)	S1–C40–N3	119.3(11)
C40–N1–C43	120.3(12)	N1–C40–N3	116.9(12)
C41–N1–C43	116.7(13)	S2–C41–N1	125.7(12)
C41–N2–C42	123.8(12)	S2–C41–N2	119.4(10)
C41–N2–C49	118.0(12)	N1–C41–N2	114.8(13)
C42–N2–C49	117.9(13)	S3–C42–N2	119.3(12)
C40–N3–C42	123.6(13)	S3–C42–N3	122.7(13)
C40–N3–C55	118.3(12)	N2–C42–N3	117.6(15)
C42–N3–C55	117.9(13)		

intermolecular contacts. The two bonds Ru–P1 and Ru–P2 are 2.286(5) and 2.288(5) Å, respectively. The Ru–C3 bond length of 1.89(2) Å is typical for a Ru–C(sp) single bond, and the C3–C4 bond length of 1.186(2) Å is that of a triple bond. In the organic portion, all three carbon–sulfur double bonds are comparable in length: 1.64(2), 1.63(2), and 1.69(2) Å. The heterocyclic six-membered ring is essentially planar (the distances of all constituent atoms to the plane are within the 0.029(10) and –0.038(22) Å range), with a slight double-bond character for all C–N bonds.

The reaction of **1'** with PhCH<sub>2</sub>NCS at room temperature afforded Cp(dppe)RuC=C(Ph)C(=S)N(CH<sub>2</sub>Ph)C(=NCH<sub>2</sub>Ph)S (**10b**) in moderate yield. At 5 °C, the product was Cp(dppe)RuC=C(Ph)C(=NCH<sub>2</sub>Ph)S (**9b**), which resulted from [2 + 2] cycloaddition of PhCH<sub>2</sub>NCS with the acetylide ligand. Like **2**, **1'** can differentiate phenyl isothiocyanate and benzyl isothiocyanate. Interestingly, no trimerization product was observed in this reaction. Decomposition of **10b** under thermal conditions gave a complex mixture from which no isolable product was obtained.

When the reaction of **1'** with PhNCO was carried out at 5 °C, the yellow six-membered-ring complex Cp(dppe)RuC=C(Ph)C(=O)N(Ph)C(=NPh)O (**12**) was isolated in moderate yield. Complex **12** is stable at 5 °C but decomposes at room temperature. The <sup>31</sup>P NMR resonance of **12** appears at δ 96.4, and a weak resonance at δ 98.2, assignable to the precursor of **12**, appears in the initial stage of the reaction and disappears at the end of the reaction. We believe that this species is the [2 + 2] cycloaddition product. In CH<sub>2</sub>Cl<sub>2</sub>, trimerization of phenyl isocyanate occurs in the presence of **1'**, giving (PhNCO)<sub>3</sub>.<sup>20</sup> After 2 days, a <sup>31</sup>P NMR resonance at δ 76.0 indicates a major organometallic product, presum-

ably a vinylidene complex with a trimer unit bound to the acetylide ligand. The acetylide complex is a catalyst in this reaction. Without this catalyst, the thermolysis of phenyl isocyanate in CH<sub>2</sub>Cl<sub>2</sub> yields diphenylurea, (PhNH)<sub>2</sub>CO.

Various metal-promoted coupling modes of isothiocyanates have been studied using a dirhenium complex<sup>21</sup> and a dirhodium complex.<sup>22</sup> In our system, transformation of isothiocyanates uses a metal-coordinated acetylide ligand. However, as can be seen in Schemes 1 and 2, the other ligands, such as dppe and a combination of P(OMe)<sub>3</sub> and PPh<sub>3</sub>, play a crucial role in differentiating the conversion of **10** to **8**.

**Conclusion.** The reactions of ruthenium acetylide complexes with isothiocyanate or isocyanate yielded a series of addition products. Addition of one RNCS molecule to the acetylide ligand via a [2 + 2] cycloaddition gave a four-membered-ring product. Addition of a second RNCS molecule generated a complex with a heterocyclic six-membered ring. For the cationic vinylidene complex with a P(OMe)<sub>3</sub> ligand, an Arbuzov-like dealkylation of P(OMe)<sub>3</sub> resulted in the formation of a neutral vinylidene complex with a phosphonate ligand. Complete characterization of this phosphonate complex assisted in elucidating the mechanism of the sequential addition processes. For the acetylide complex with a bidentate dppe ligand, other than the two addition processes mentioned above, a third addition led to an organic trimerization product and regenerated the acetylide complex.

## Experimental Section

**General Procedures.** All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> were distilled from CaH<sub>2</sub> and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on Bruker AC-200 and AM-300WB FT-NMR spectrometers and are reported in units of δ with residual protons in the solvent as an internal standard (CDCl<sub>3</sub>, δ 7.24; CD<sub>3</sub>CN, δ 1.93; C<sub>2</sub>D<sub>6</sub>-CO, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer and are reported in *m/z* units. Complexes Cp(dppe)RuC≡CPh (**1'**) and Cp(PPh<sub>3</sub>)<sub>2</sub>RuC≡CPh<sup>23</sup> were prepared by following the methods reported in the literature. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

**Preparation of Cp(PPh<sub>3</sub>)<sub>2</sub>[P(OMe)<sub>3</sub>]RuC≡CPh (**2**).** In a Schlenk flask charged with P(OMe)<sub>3</sub> (7.70 mL, 63.30 mmol) and Cp(PPh<sub>3</sub>)<sub>2</sub>RuC≡CPh (**1**; 10.00 g, 12.66 mmol), *n*-decane (80 mL) was added. The resulting solution was heated to reflux for 1 h to give a yellow solution. The solvent was reduced in volume to about 5 mL under vacuum, and a yellow precipitate formed. After filtration, the precipitate was washed with 2 × 20 mL of pentane to give the product Cp(PPh<sub>3</sub>)<sub>2</sub>[P(OMe)<sub>3</sub>]RuC≡CPh (**2**; 7.60 g, 11.64 mmol, 92% yield). Spectroscopic data for **2** are as follows. <sup>1</sup>H NMR: 7.69–6.86 (m, 20 H, Ph); 4.64 (s, 5H, Cp); 3.37 (d, *J*<sub>P–H</sub> = 11.6 Hz, 9 H, P(OMe)<sub>3</sub>). <sup>31</sup>P NMR: 158.3 (d, *J*<sub>P–P</sub> = 64.5 Hz, P(OMe)<sub>3</sub>); 56.6 (d, *J*<sub>P–P</sub> = 64.5 Hz, PPh<sub>3</sub>). <sup>13</sup>C NMR: 139.2–122.9 (Ph); 130.3 (C<sub>α</sub>); 112.6 (C<sub>β</sub>); 84.2 (Cp); 51.9 (P(OMe)<sub>3</sub>). Mass: 654.0 (M<sup>+</sup>), 553.1 (M<sup>+</sup> – C<sub>2</sub>Ph); 428.9 (M<sup>+</sup> – C<sub>2</sub>Ph, P(OMe)<sub>3</sub>). Anal. Calcd for C<sub>34</sub>H<sub>34</sub>O<sub>3</sub>P<sub>2</sub>Ru: C, 62.47; H, 5.24. Found: C, 62.68; H, 5.32.

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**Reaction of 2 with PhNCS.** To a Schlenk flask charged with **2** (0.50 g, 0.76 mmol) was added  $\text{CH}_2\text{Cl}_2$  (20 mL), and PhNCS (0.92 mL, 7.66 mmol) was injected by a syringe. The resulting mixture was stirred at room temperature for 3 days while the color changed from bright yellow to brown. The solvent was removed under vacuum. The residue was redissolved in ether and passed through a silica gel packed column. Hexane eluted the starting material, ether eluted an orange-yellow band, and methanol eluted a brown band. The solvent of the orange-yellow band was removed to give a yellow oil which was washed with hexane to give a yellow powder and further washed with 20 mL of pentane to give the product Cp-

(PPh<sub>3</sub>)[P(OMe)<sub>3</sub>]RuC≡C(Ph)C(=NPh)S (**3a**). The yield of **3a** after recrystallization from hexane/ $\text{CH}_2\text{Cl}_2$  (1:1) is 0.38 g (63% yield). After a similar workup procedure, the brown band gave the orange-red phosphonate complex Cp(PPh<sub>3</sub>)[P(=O)(OMe)<sub>2</sub>]-Ru=C=C(Ph)C(SH)=NPh (**4a**; 0.030 g, 5% yield). Spectroscopic data for **3a** are as follows. <sup>1</sup>H NMR: 7.29–7.00 (m, 20 H, Ph); 4.75 (s, 5H, Cp); 3.37 (d,  $J_{\text{P-H}} = 11.0$  Hz, 9 H, P(OMe)<sub>3</sub>). <sup>31</sup>P NMR: 151.7 (d,  $J_{\text{P-P}} = 68.9$  Hz, P(OMe)<sub>3</sub>); 56.2 (d,  $J_{\text{P-P}} = 68.9$  Hz, PPh<sub>3</sub>). <sup>13</sup>C NMR: 134.1–122.7 (Ph, C<sub>β</sub>, C<sub>γ</sub>); 84.8 (Cp); 52.3 (d,  $J_{\text{C-P}} = 7.5$  Hz, P(OMe)<sub>3</sub>). Mass: 790.2 (M<sup>+</sup>), 553.1 (M<sup>+</sup> – C<sub>2</sub>Ph); 429.1 (M<sup>+</sup> – C<sub>2</sub>Ph, P(OMe)<sub>3</sub>). Anal. Calcd for C<sub>41</sub>H<sub>39</sub>NO<sub>3</sub>P<sub>2</sub>SRu: C, 62.42; H, 4.98; N, 1.78. Found: C, 61.99; H, 5.12; N, 1.73. Spectroscopic data for **4a** are as follows. <sup>1</sup>H NMR: 7.70–6.70 (m, 20 H, Ph); 5.26 (s, 5H, Cp); 3.18 (d,  $J_{\text{P-H}} = 11.5$  Hz, 3 H, OMe); 3.03 (d,  $J_{\text{P-H}} = 11.5$  Hz, 3 H, OMe). <sup>13</sup>C NMR: 345.2 (t,  $J_{\text{C-P}} = 17.1$  Hz, C<sub>α</sub>); 137.9–123.4 (Ph, C<sub>β</sub>, C<sub>γ</sub>); 93.0 (Cp); 52.2 (d,  $J_{\text{C-P}} = 8.6$  Hz, OMe); 51.8 (d,  $J_{\text{C-P}} = 8.4$  Hz, OMe). <sup>31</sup>P NMR: 95.3 (d,  $J_{\text{P-P}} = 45.9$  Hz, P(OMe)<sub>2</sub>); 48.0 (d,  $J_{\text{P-P}} = 45.9$  Hz, PPh<sub>3</sub>). Mass: 776.0 (M<sup>+</sup>), 744.0 (M<sup>+</sup> – S); 539.0 (M<sup>+</sup> – C=C(Ph)C(SH)C=NPh). Anal. Calcd for C<sub>40</sub>H<sub>37</sub>NO<sub>3</sub>P<sub>2</sub>SRu: C, 62.00; H, 4.81; N, 1.81. Found: C, 61.74; H, 5.01; N, 1.70. The <sup>31</sup>P NMR spectrum of the crude product (after 3 days of reaction time) displayed the resonances attributed to **3a** and **4a** in a 9:1 ratio.

The reaction of **2** with PhNCS in refluxing  $\text{CH}_2\text{Cl}_2$  was carried out under nitrogen for 4 days. The workup procedure was similar to that mentioned above. The reaction gave **4a** and Cp(PPh<sub>3</sub>)[P(OMe)<sub>3</sub>]RuC≡C(Ph)C(=S)N(Ph)C(=NPh)S (**5a**) after purification in 40% total yield. The <sup>31</sup>P NMR spectrum of the crude product (after 4 days of reaction time) displayed the resonances attributed to **5a** and **4a** in a 3:2 ratio. Spectroscopic data for **5a** are as follows. <sup>1</sup>H NMR: 7.84–6.52 (m, 30 H, Ph); 4.40 (s, 5H, Cp); 3.06 (d,  $J_{\text{P-H}} = 11.0$  Hz, 9 H, P(OMe)<sub>3</sub>). <sup>31</sup>P NMR: 148.6 (d,  $J_{\text{P-P}} = 72.5$  Hz, P(OMe)<sub>3</sub>); 53.9 (d,  $J_{\text{P-P}} = 72.5$  Hz, PPh<sub>3</sub>). Mass: 925.1 (M<sup>+</sup> + 1), 553.1 (M<sup>+</sup> – C<sub>2</sub>Ph); 429.1 (M<sup>+</sup> – C<sub>2</sub>Ph, P(OMe)<sub>3</sub>). Anal. Calcd for C<sub>48</sub>H<sub>44</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>S<sub>2</sub>Ru: C, 62.39; H, 4.80; N, 3.03. Found: C, 62.52; H, 4.95; N, 3.11. Complex **5a** can also be prepared from the reaction of **3a** with PhNCS in refluxing  $\text{CH}_2\text{Cl}_2$  for 3 days. In the crude mixture, a small amount of **4a** was observed.

**Reaction of 2 with PhCH<sub>2</sub>NCS.** In a Schlenk flask charged with **2** (0.50 g, 0.76 mmol), PhCH<sub>2</sub>NCS (1.01 mL, 766 mmol) and  $\text{CH}_2\text{Cl}_2$  (20 mL) were added and the mixture was stirred at room temperature for 3 days with the color changing from bright yellow to brown. The solvent was removed under vacuum and the residue was subjected to a silica gel packed column chromatograph. Hexane eluted the organic compounds, a 1:1 hexane/ether solution eluted a brown band, and methanol eluted an orange band. The brown band was dried under vacuum and the residue washed with 2 × 15 mL of hexane to give the solid product Cp(PPh<sub>3</sub>)[P(OMe)<sub>3</sub>]-

RuC≡C(Ph)C(S)N(CH<sub>2</sub>Ph)C(=NCH<sub>2</sub>Ph)S (**5b**; 0.42 g, 58% yield). The orange band, after the same treatment, gave the orange phosphonate complex Cp(PPh<sub>3</sub>)[P(=O)(OMe)<sub>2</sub>]-Ru=C=C(Ph)C(SH)=NCH<sub>2</sub>Ph (**4b**; 0.06 g, 10% yield). Spectroscopic data for **5b** are as follows. <sup>1</sup>H NMR: 7.35–6.99 (m, 30 H, Ph); 6.19 (d,  $J_{\text{H-H}} = 12.7$  Hz, 1H, CH<sub>2</sub>Ph); 6.02 (d,  $J_{\text{H-H}}$

= 12.7 Hz, 1H, CH<sub>2</sub>Ph); 4.34 (s, 5H, Cp); 3.92 (d,  $J_{\text{H-H}} = 16.9$  Hz, 1H, CH<sub>2</sub>Ph); 3.84 (d,  $J_{\text{H-H}} = 16.9$  Hz, 1H, CH<sub>2</sub>Ph); 3.35 (d,  $J_{\text{P-H}} = 10.9$  Hz, 9 H, P(OMe)<sub>3</sub>). <sup>31</sup>P NMR: 148.6 (d,  $J_{\text{P-P}} = 73.3$  Hz, P(OMe)<sub>3</sub>); 57.9 (d,  $J_{\text{P-P}} = 73.3$  Hz, PPh<sub>3</sub>). <sup>13</sup>C NMR: 134.1–122.7 (Ph, C<sub>β</sub>, C<sub>γ</sub>); 84.8 (Cp); 52.3 (d,  $J_{\text{C-P}} = 7.5$  Hz, P(OMe)<sub>3</sub>). Mass: 790.2 (M<sup>+</sup>), 553.1 (M<sup>+</sup> – organic ligand); 429.1 (M<sup>+</sup> – organic ligand, P(OMe)<sub>3</sub>). Anal. Calcd for C<sub>50</sub>H<sub>48</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>S<sub>2</sub>Ru: C, 63.08; H, 5.08; N, 2.94. Found: C, 62.95; H, 5.04; N, 3.12. Spectroscopic data for **4b** are as follows. <sup>1</sup>H NMR: 10.86 (s, 1H, SH); 7.63–6.67 (m, 20 H, Ph); 5.19 (s, 5H, Cp); 3.07 (d,  $J_{\text{P-H}} = 11.2$  Hz, 3 H, OMe); 2.97 (d,  $J_{\text{P-H}} = 11.5$  Hz, 3 H, OMe); 2.44 (d,  $J_{\text{H-H}} = 7.3$  Hz, 1H, –NCH<sub>2</sub>–Ph); 2.39 (d,  $J_{\text{H-H}} = 7.3$  Hz, 1H, –NCH<sub>2</sub>Ph). <sup>13</sup>C NMR: 343.5 (t,  $J_{\text{C-P}} = 17.0$  Hz, C<sub>α</sub>); 142.4–126.8 (Ph, C<sub>β</sub>, C<sub>γ</sub>); 92.9 (Cp); 50.5 (d,  $J_{\text{C-P}} = 9.4$  Hz, OMe); 50.1 (d,  $J_{\text{C-P}} = 8.4$  Hz, OMe). <sup>31</sup>P NMR: 95.2 (d,  $J_{\text{P-P}} = 45.8$  Hz, P(OMe)<sub>2</sub>); 49.3 (d,  $J_{\text{P-P}} = 45.8$  Hz, PPh<sub>3</sub>). Mass: 790.0 (M<sup>+</sup>), 758.0 (M<sup>+</sup> – S), 539.0 (M<sup>+</sup> – organic ligand); 428.9 (M<sup>+</sup> – organic ligand, P(OMe)<sub>3</sub>). Anal. Calcd for C<sub>41</sub>H<sub>39</sub>NO<sub>3</sub>P<sub>2</sub>SRu: C, 62.42; H, 4.98; N, 1.78. Found: C, 62.57; H, 4.64; N, 1.95.

The [2 + 2] cycloaddition product Cp(PPh<sub>3</sub>)[P(OMe)<sub>3</sub>]-RuC≡C(Ph)C(=NCH<sub>2</sub>Ph)S (**3b**) could be observed when the same reaction was carried out in CDCl<sub>3</sub> at 5 °C for 5 days and monitored by NMR spectra. Complexes **3b** and **5b** formed simultaneously in a 1:3 ratio at this temperature and at room temperature **3b** transformed to **5b** in ca. 2 h. Spectroscopic data for **3b** are as follows. <sup>1</sup>H NMR: 7.73–6.85 (m, 25 H, Ph); 4.73 (s, 5H, Cp); 4.49, 4.39 (two d,  $J_{\text{H-H}} = 13.6$  Hz, 2H, –NCH<sub>2</sub>); 3.42 (d,  $J_{\text{P-H}} = 11.0$  Hz, 9 H, OMe). <sup>31</sup>P NMR: 151.8 (d,  $J_{\text{P-P}} = 67.8$  Hz, P(OMe)<sub>2</sub>); 56.0 (d,  $J_{\text{P-P}} = 67.8$  Hz, PPh<sub>3</sub>). Mass: 804.1 (M<sup>+</sup> + 1), 553.1 (M<sup>+</sup> – organic ligand); 429.1 (M<sup>+</sup> – organic ligand, P(OMe)<sub>3</sub>).

**Reaction of 2 with PhNCO.** This reaction was monitored by NMR spectroscopy. Complex **2** (0.05 g, 0.08 mmol) and PhNCO (0.10 mL, 0.76 mmol) were dissolved in CDCl<sub>3</sub> (1 mL) in an NMR tube under nitrogen. The resulting mixture was stored at –20 °C for 7 days. The <sup>1</sup>H and <sup>31</sup>P NMR spectra of the mixture indicated formation of the two major products Cp-(PPh<sub>3</sub>)[P(OMe)<sub>3</sub>]RuC≡C(Ph)C(=NPh)O (**6**) and Cp(PPh<sub>3</sub>)-[P(OMe)<sub>3</sub>]RuC≡C(Ph)C(=O)N(Ph)C(=NPh)O (**7**). The total NMR yield of **6** and **7** is estimated to be about 70%, on the basis of the integration of the Cp resonances and the <sup>31</sup>P resonances. Since these two complexes are unstable at room temperature, no attempt was made to isolate the products. The <sup>31</sup>P NMR spectrum of the crude product (after 7 days of reaction time) displayed the resonances attributed to **6** and **7** in a 1:1 ratio. Spectroscopic data for **6** are as follows. <sup>1</sup>H NMR: 8.03–6.84 (m, 25 H, Ph); 4.63 (s, 5H, Cp); 3.62 (d,  $J_{\text{P-H}} = 11.1$  Hz, 9 H, P(OMe)<sub>3</sub>). <sup>31</sup>P NMR: 155.4 (d,  $J_{\text{P-P}} = 66.9$  Hz, P(OMe)<sub>3</sub>); 56.9 (d,  $J_{\text{P-P}} = 66.9$  Hz, PPh<sub>3</sub>). Mass: 774.2 (M<sup>+</sup> + 1), 654.1 (M<sup>+</sup> – C(O)C=NPh); 429.1 (M<sup>+</sup> – C=C(Ph)C(=O)C=NPh, P(OMe)<sub>3</sub>). Spectroscopic data for **7** are as follows. <sup>1</sup>H NMR: 7.85–6.83 (m, 30 H, Ph); 4.43 (s, 5H, Cp); 3.14 (d,  $J_{\text{P-H}} = 11.0$  Hz, 9 H, P(OMe)<sub>3</sub>). <sup>31</sup>P NMR: 151.7 (d,  $J_{\text{P-P}} = 69.1$  Hz, P(OMe)<sub>3</sub>); 54.6 (d,  $J_{\text{P-P}} = 69.1$  Hz, PPh<sub>3</sub>). Mass: 893.2 (M<sup>+</sup> + 1), 654.1 (M<sup>+</sup> – organic ligand + C<sub>2</sub>Ph); 553.1 (M<sup>+</sup> – organic ligand); 429.1 (M<sup>+</sup> – organic ligand, P(OMe)<sub>3</sub>).

**Reaction of Cp(dppe)RuC≡CPh (**1'**) with PhNCS.** In a Schlenk flask charged with **1'** (0.30 g, 0.46 mmol), PhNCS (0.55 mL, 4.59 mmol) and  $\text{CH}_2\text{Cl}_2$  (20 mL) were added; the mixture was stirred at room temperature for 4 days and the color of the solution changed from bright yellow to brown. The solvent was removed under vacuum and the residue was washed with 2 × 30 mL of hexane to give the product. After filtration, the solid was further washed with 20 mL of pentane, giving the product Cp(dppe)RuC≡C(Ph)C(=NPh)S (**9a**; 0.26 g, 72% yield). Spectroscopic data for **9a** are as follows. <sup>1</sup>H NMR: 7.80–6.30 (m, 30 H, Ph); 4.50 (s, 5H, Cp); 2.60–2.47 (m, 4 H, PCH<sub>2</sub>). <sup>13</sup>C NMR: 133.7–122.6 (Ph, C<sub>β</sub>, C<sub>γ</sub>); 84.6 (Cp);

29.3 (t,  $J_{C-P} = 21.5$  Hz,  $CH_2$ ).  $^{31}P$  NMR: 93.9 (PPh<sub>2</sub>). FAB mass: 801.0 ( $M^+$ ), 565.0 ( $M^+$  – organic ligand). Anal. Calcd for  $C_{46}H_{39}NP_2SRu$ : C, 68.98; H, 4.91; N, 1.75. Found: C, 68.99; H, 4.79; N, 1.88. If the same reaction was carried out for 7 days at room temperature, the complex  $Cp(dppe)RuC\equiv C-(Ph)C(S)N(Ph)C(=NPh)S$  (**10a**; 0.28 g, 65% yield) was isolated. Spectroscopic data for **10a** are as follows.  $^1H$  NMR: 7.75–6.94 (m, 35 H, Ph); 3.68 (s, 5H, Cp); 2.65–2.30 (m, 4 H,  $PCH_2$ ).  $^{13}C$  NMR: 151.0–121.5 (Ph,  $C_\beta$ ,  $C_\gamma$ ); 85.1 (Cp); 30.7 (t,  $J_{C-P} = 22.0$  Hz,  $CH_2$ ).  $^{31}P$  NMR: 99.3 (PPh<sub>2</sub>). Mass: 936.0 ( $M^+ + 1$ ), 565.0 ( $M^+$  – organic ligand). Anal. Calcd for  $C_{53}H_{44}N_2P_2S_2Ru$ : C, 68.00; H, 4.74; N, 2.99. Found: C, 67.79; H, 5.01; N, 2.85.

Reaction of **1'** (0.30 g, 0.46 mmol) with  $PhCH_2NCS$  (0.61 mL, 4.58 mmol) was carried out in  $CH_2Cl_2$  (20 mL) at room temperature for 3 days. The solvent was reduced under vacuum to about 1 mL, and the residue was passed through a silica gel packed column. A brown band was eluted with ether, and after removal of ether, the product was washed with  $2 \times 20$  mL of hexane to give the brown-yellow product  $Cp(dppe)-$

$RuC\equiv C(Ph)C(S)N(CH_2Ph)C(=NCH_2Ph)S$  (**10b**; 0.27 g, 62% yield). Spectroscopic data for **10b** are as follows.  $^1H$  NMR: 7.62–6.75 (m, 35 H, Ph); 5.96 (s, 2H,  $CH_2Ph$ ); 3.56 (s, 2H,  $CH_2Ph$ ); 3.84 (s, 5H, Cp); 2.90–2.58 (m, 4 H,  $PCH_2$ ).  $^{13}C$  NMR: 184.8, 151.4, 143.3–125.6 (Ph,  $C_\beta$ ,  $C_\gamma$ ); 84.8 (Cp); 52.4, 51.6 ( $2 \times CH_2Ph$ ); 30.0 ( $J_{C-P} = 22.2$  Hz,  $CH_2$ ).  $^{31}P$  NMR: 88.4 (s, PPh<sub>2</sub>). Mass: 965.1 ( $M^+ + 1$ ), 565.0 ( $M^+$  – organic ligand). Anal. Calcd for  $C_{55}H_{48}N_2P_2S_2Ru$ : C, 68.52; H, 5.01; N, 2.91. Found: C, 68.75; H, 4.84; N, 3.18. If the same reaction is carried out at 5 °C for 5 days, the two products  $Cp(dppe)-$

$RuC\equiv C(Ph)C(=NCH_2Ph)S$  (**9b**) and **10b** in a 1:4 ratio are observed in the NMR spectrum. **9b** is unstable and is converted to **10b** in about 2 h at room temperature. Spectroscopic data for **9b** are as follows.  $^1H$  NMR: 7.69–6.85 (m, 30 H, Ph); 4.43 (s, 2H,  $CH_2Ph$ ); 3.91 (s, 5H, Cp); 2.90–2.60 (m, 4 H,  $PCH_2$ ).  $^{31}P$  NMR: 94.5 (s, PPh<sub>2</sub>). Mass: 816.1 ( $M^+ + 1$ ), 565.0 ( $M^+$  – organic ligand).

**Trimerization of PhNCS on  $Cp(dppe)RuC\equiv CPh$ .** A Schlenk flask was charged with **1'** (0.07 g, 0.11 mmol), and the atmosphere was replaced with nitrogen; then PhNCS (0.55 mL, 4.59 mmol) and  $CH_2Cl_2$  (20 mL) were introduced and the mixture was heated to reflux. The  $^{31}P$  NMR spectrum revealed a complex mixture at the initial stage of the reaction, but after 2 days, only a single product was obtained. The mixture was heated for 4 days, and the color of the solution changed from bright yellow to brown. The solvent was removed under vacuum, and the residue was washed with  $2 \times 30$  mL of hexane to give a brown-black product. After filtration, the solid was further washed with 20 mL of pentane, giving the product  $(PhNCS)_3$  (**8**; 0.26 g, 72% yield). Spectroscopic data are consistent with those in the literature.<sup>14</sup>

**Trimerization of PhNCO on  $Cp(dppe)RuC\equiv CPh$ .** A Schlenk flask was charged with **1'** (0.10 g, 0.15 mmol), and the atmosphere was replaced with nitrogen; then PhNCO (1.00 mL, 1.50 mmol) and  $CH_2Cl_2$  (20 mL) were introduced and the mixture was stored at 5 °C for 2 days. The solvent was removed under vacuum, and the residue was subjected to silica gel packed column chromatography. The organic portion ( $PhNHCONHPh$ ) was eluted with hexane, and the yellow organometallic compound was eluted with ether. Removal of ether solvent followed by addition of hexane gave a yellow precipitate. After filtration, the solid was further washed with 20 mL of pentane, giving the product  $Cp(dppe)RuC\equiv C(Ph)C-$

$(O)N(Ph)C(=NPh)O$  (**12**; 0.10 g, 73% yield). Spectroscopic data for **12** are as follows.  $^1H$  NMR: 8.10–6.90 (m, 30 H, Ph); 3.94 (s, 5H, Cp); 2.45–2.10 (m, 4 H,  $PCH_2$ ).  $^{13}C$  NMR: 153.3, 140.8, 135.0–121.6 (Ph,  $C_\beta$ ,  $C_\gamma$ ); 86.2 (Cp); 29.4 ( $J_{C-P} = 19.5$  Hz,  $CH_2$ ).  $^{31}P$  NMR: 96.4 (PPh<sub>2</sub>). FAB mass: 905.0 ( $M^+$ ), 565.0 ( $M^+$  –

$C_2Ph$ ). Anal. Calcd for  $C_{53}H_{44}N_2O_2P_2Ru$ : C, 70.42; H, 4.91; N, 3.10. Found: C, 70.63; H, 4.78; N, 3.34.

A Schlenk flask was charged with **1'** (0.20 g, 0.31 mmol), and the atmosphere was replaced with nitrogen; then PhNCO (1.00 mL, 9.21 mmol) and  $CH_2Cl_2$  (20 mL) were introduced and the mixture was heated to reflux for 2 days. The  $^{31}P$  NMR spectrum revealed a complex mixture at the initial stage of the reaction, but after 1 day, only a single product was obtained. The mixture was heated for 2 days and the color of the solution changed from bright yellow to brown. The solvent was removed under vacuum, and the residue was subjected to silica gel packed column chromatography. Hexane eluted the starting material, ether eluted the organometallic complex **12**, and methanol eluted the trimer. Removal of methanol under vacuum followed by addition of hexane gave a light yellow precipitate. After filtration, the solid was further washed with 20 mL of pentane, giving the product  $(PhNCO)_3$  (**8a**; 0.45 g, 41% yield). Spectroscopic data for **8a** are consistent with those in the literature.<sup>14</sup>

**X-ray Analysis of 3a.** Single crystals of **3a** suitable for an X-ray diffraction study were grown as mentioned above. A single crystal of dimensions  $0.20 \times 0.20 \times 0.30$  mm<sup>3</sup> was glued to a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centered reflections with  $10.0^\circ < 2\theta < 25^\circ$ . Cell constants and other pertinent data are collected in the Supporting Information. Data were collected using the  $\theta/2\theta$  scan method. The scan angle was determined for each reflection according to the expression  $0.8 + 0.35 \tan \theta$ . The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min<sup>–1</sup>.

The raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz–polarization effects. An empirical correction for absorption based on the azimuthal scan was applied to the data set. Crystallographic computations were carried out on a Microvax III computer using the NRCC structure determination package.<sup>24</sup> Merging of equivalent and duplicate reflections gave a total of 5303 unique measured data, from which 3077 were considered observed ( $I > 2.0\sigma(I)$ ). The structure was first solved by using the heavy-atom method (Patterson synthesis), which revealed the position of the metal, and then refined via standard least-squares and difference Fourier techniques. The quantity minimized by the least-squares program was  $w(|F_o| - |F_c|)^2$ . The analytical forms of the scattering factor tables for the neutral atoms were used.<sup>25</sup> All other non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. Final refinement using full-matrix least squares converged smoothly to values of  $R = 0.042$  and  $R_w = 0.040$ . The procedures for **4a**, **5b**, and the cocrystallization product of **1'** and **8** were similar. The final residuals of the refinement were  $R = 0.041$  and  $R_w = 0.042$ ;  $R = 0.051$  and  $R_w = 0.047$ , and  $R = 0.054$  and  $R_w = 0.052$  for **4b**, **5b**, and the cocrystallization product of **1'** and **8**, respectively. Final values of all refined atomic positional parameters (with esd's) and tables of thermal parameters are given in the Supporting Information.

**Acknowledgment.** We are grateful for support of this work by the National Science Council, Taiwan, Republic of China.

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**Supporting Information Available:** Details of the structural determination for complexes **3a**, **4a**, and **5b** and the cocrystallization product of **1'** and **8**, including tables of crystal data and structure refinement parameters, positional and anisotropic thermal parameters, and bond distances and

angles (32 pages). Ordering information is given on any current masthead page.

OM971056D