

Reactions of Ruthenium Acetylide Complexes with EtO₂CNCS: Alkylation of the Thione with Dichloromethane

Chao-Wan Chang,[†] Ying-Chih Lin,^{*,‡} Gene-Hsiang Lee,[‡] and Yu Wang[‡]

National University Preparatory School for Overseas Chinese Students, Linkou, Taipei Hsien 244, Taiwan, Republic of China, and Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, Republic of China

Received May 8, 2003

Treatment of the ruthenium acetylide complexes [M]C≡CPh (**1a**, [M] = [Ru] = Cp(Ph₂-PCH₂CH₂PPh₂)Ru; **1b**, [M] = [Ru'] = Cp(PPh₃)[P(OMe)₃]Ru) with 1.1 equiv of EtO₂CN=C=S results in [2 + 2] cycloadditions yielding the four-membered-ring 2-iminothiete products **2a,b**, respectively. Isomerization of complex **2a** results in formation of **3a** containing the six-membered-ring oxazinethione ligand. Alkylation of complex **3a** by CH₂Cl₂ takes place at the thione sulfur to give **4a**, which loses ethyl chloride, yielding the new six-membered-ring [1,3]-oxazin-2-one complex **5a**. Further alkylation of **3a** by the chloromethyl group of **5a** affords the dinuclear complex **6a** with two oxazin-2-one ligands bridged by a methylene group. Structures of **2b**, **3a**, **5a** and **6a** have been determined by single-crystal X-ray diffraction analysis.

Introduction

The synthesis and reactivity of metal acetylide complexes have been the focus of several recent works, due to their applications in organometallic¹ and material² chemistry. The coordinated acetylide ligand is reactive toward electrophiles, undergoing either alkylation or protonation at C_β to give stable vinylidene complexes. Cycloadditions of metal acetylide with isocyanates take place in several Ni(0) complexes.³ The other common reaction observed for the acetylide is the [2 + 2] cycloadditions of the triple bond with unsaturated organic substrates.⁴ Cycloadditions of organic substrates such as CS₂,⁵ (NC)₂C=C(CF₃)₂, (NC)₂C=C(CN)₂,⁶ and Ph₂C=C=O⁷ to the acetylide ligand in various metal complexes have been reported.

In investigating chemical properties of acetylide complexes of ruthenium, we previously reported reactions of isocyanate and isothiocyanate with two such ruthenium complexes.⁸ The cycloaddition reaction of an isothiocyanate molecule with the ruthenium acetylide formed an unstable four-membered-ring 2-iminothiete complex. During purification, gradual loss of the isothiocyanate portion occurred in solution, giving back the acetylide complex. In the presence of excess isothiocyanates, expansion of the 2-iminothiete rings by coupling of the second isothiocyanate molecule generated complexes with a six-membered-ring 2-imino-1,3-thiazine-4-thione ligand. In this paper we report reactions of ruthenium acetylide complexes with EtO₂CNCS, a more reactive isothiocyanate. As expected, in the initial stage, cycloaddition of the C=S bond of EtO₂CNCS to the acetylide ligand gives the anticipated complex with the four-membered thiete ring containing an imino ester group. However, for the product with a dppe ligand, isomerization of this thiete ring generates a six-membered oxazine ring with a thione group, at which alkylation by CH₂Cl₂ take place readily. Herein we report the synthesis and characterization of these thiete and oxazine complexes. An unusual alkylation of the thione group by using CH₂Cl₂ is also described.

Results and Discussion

Reactions of Ruthenium Acetylide Complexes with EtO₂CNCS. Treatment of [Ru]C≡CPh (**1a**, [Ru] = Cp(dppe)Ru) with 1.1 equiv of EtO₂CN=C=S in CHCl₃ at room temperature results in a color change of the solution from yellow to orange in 10 min. The reaction is complete in 1 h and affords the orange

[†] National University Preparatory School for Overseas Chinese Students.

[‡] National Taiwan University.

(1) (a) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (b) Hegedus, L. S. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: New York, 1994; p 383. (c) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem.* **1996**, *35*, 414. (d) Ting, P. C.; Lin, Y. C.; Lee, G. H.; Cheng, M. C.; Wang, Y. J. *Am. Chem. Soc.* **1996**, *118*, 6433.

(2) (a) Myers, L. K.; Langhoff, C.; Thompson, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 7560. (b) Kaharu, T.; Matsubara, H.; Takahashi, S. *J. Mater. Chem.* **1992**, *2*, 43. (c) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J. P. *Organometallics* **1996**, *15*, 1530. (d) Wu, I. Y.; Lin, J. T.; Luo, J.; Sun, S. S.; Lee, C. S.; Lin, K. J.; Tsai, C.; Hsu, C. C.; Lin, J. L. *Organometallics* **1997**, *16*, 2038.

(3) Hoberg, H.; Oster, B. W. *J. Organomet. Chem.* **1983**, *252*, 359.

(4) Bruce, M. I.; Hambley, T. W.; Leddell, M. J.; Snow, M. R.; Swincer, A. G.; Tiekink, R. T. *Organometallics* **1990**, *9*, 96.

(5) (a) Selegue, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 119. (b) Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1985**, *4*, 2062. (c) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972.

(6) (a) Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1979**, *166*, C13. (b) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 501. (c) Barrette, A. G. M.; Carpenter, N. E.; Mortier, J.; Sabat, M. *Organometallics* **1990**, *9*, 151.

(7) Hong, P.; Sonogashira, K.; Hagihara, N. *J. Organomet. Chem.* **1981**, *219*, 363.

(8) Chang, C. W.; Lin, Y. C.; Lee, G. H.; Huang, S. L.; Wang, Y. *Organometallics* **1998**, *17*, 2534.

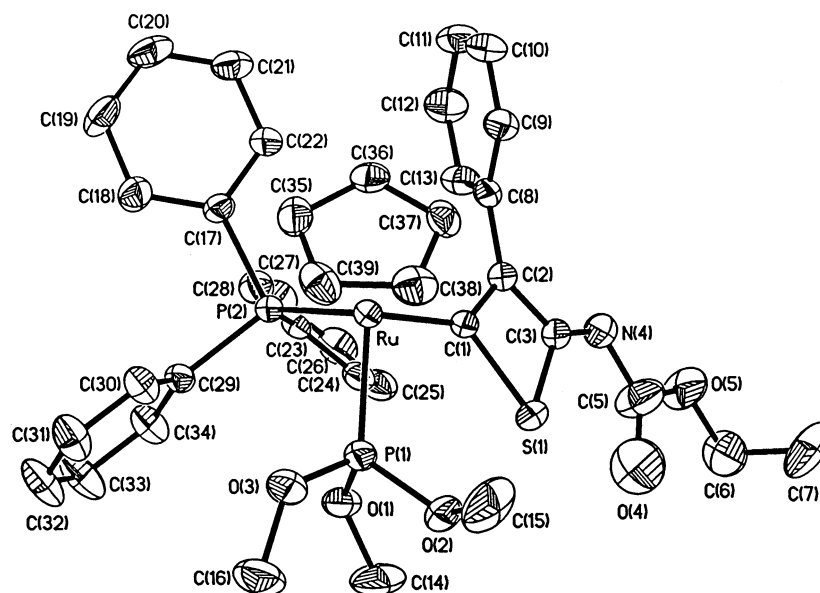


Figure 1. ORTEP drawing of **2b**. Thermal ellipsoids are drawn at the 50% probability level.

2-iminothiete product $[\text{Ru}]\text{C}=\text{C}(\text{Ph})\text{C}(\text{=NCO}_2\text{Et})\text{S}$ (**2a**) in 92% isolated yield. We reported earlier⁸ that the optimized conditions for the reaction of **1a** with PhNCS, yielding a similar product, required a 10-fold excess of PhNCS and a long reaction time (3 days). However, the reaction of **1a** with EtO_2CNCS needs only a slight excess of isothiocyanate and is much faster. A [2 + 2] cycloaddition of the $\text{C}\equiv\text{C}$ triple bond of **1a** to the $\text{C}=\text{S}$ double bond of EtO_2CNCS satisfactorily accounts for the formation of **2a**. The ^{31}P NMR spectrum of **2a** displays a broad singlet resonance at δ 96.72 assigned to the dppe ligand. The FAB mass spectrum displays a parent peak at m/z 798.2 ($\text{M}^+ + 1$), consistent with the formula of **2a**. Cycloaddition of a $\text{C}\equiv\text{C}$ bond of iron acetylide to CS_2 was found to yield 2*H*-thiete-2-thione (β -dithiolactone).⁵ A similar process has been proposed in the first stage of the reaction of alkyne with CS_2 , giving a 2*H*-thiete-2-thione intermediate which was characterized spectroscopically.⁵ Reaction of phosphonium complexes with isocyanates via a [2 + 2] addition of the $\text{N}=\text{C}$ bond to give the four-membered phosphametallacycles has also been reported.⁹

Similarly, treatment of the complex $[\text{Ru}']\text{C}\equiv\text{CPh}$ (**1b**, $[\text{Ru}'] = \text{Cp}(\text{PPh}_3)[\text{P}(\text{OMe})_3]\text{Ru}$) with 1.1 equiv of EtO_2CNCS in CH_2Cl_2 at room temperature results in formation of the thiete product $[\text{Ru}']\text{C}=\text{C}(\text{Ph})\text{C}(\text{=NCO}_2\text{Et})\text{S}$ (**2b**) in 83% yield. In the ^{31}P NMR spectrum, two doublet resonances at δ 152.72 and 56.92 with $J_{\text{P-P}} = 67.1$ Hz are assigned to the $\text{P}(\text{OMe})_3$ and PPh_3 ligands, respectively. The parent peak in the FAB mass spectrum is consistent with the formula. Complex **2b** was recrystallized from a mixture of CH_2Cl_2 and hexane (1:3) at 5 °C, and the molecular structure was determined by 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 listed in Table 2. The coordination sphere of the ruthenium atom contains a η^5 -cyclopentadienyl ring, two phosphorus atoms of phos-

phite and phosphine ligands, and the carbon atom (C1) of the organic ligand. The four-membered ring formed by [2 + 2] cycloaddition is essentially planar, with a C1–C2 distance of 1.373(7) Å, typical of a C–C double bond. The bond distances for C1–S1 and C3–S1 (1.879(4) and 1.800(6) Å, respectively) are both typical of C–S single bonds.^{8,10} The C3=N4 bond distance of 1.277(6) Å confirms the presence of an imino group. The two ruthenium–phosphorus bonds in **2b** are Ru–P1 = 2.2312(13) Å and Ru–P2 = 2.3276(13) Å, with the shorter distance belonging to the phosphite ligand. The S1–C1–C2, C1–C2–C3, and C2–C3–S1 bond angles of 92.8(3), 100.8(4), and 94.1(4)°, respectively, are much smaller than an sp^2 hybridization bond angle, and the C1–S1–C3 bond angle of 72.0(2)° is smaller than a typical bond angle for a four-membered ring. 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 some 1,2-dithio-3-imines.¹¹ 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 groups, are similar to those in **2b**.

Isomerization of 2a. From the reaction of **1a** with 1.1 equiv of EtO_2CNCS for 1 day in CHCl_3 , a mixture containing **2a** and **3a** in a 1:3 ratio was isolated. Single crystals of **3a** suitable for X-ray diffraction analysis are obtained by recrystallization of the mixture from CHCl_3 /*n*-pentane (1:3). Pure complex **2a** in CHCl_3 also undergoes isomerization to yield a mixture of **2a** and **3a** in a similar ratio. ^{31}P NMR resonances of complexes **2a** and **3a** are almost identical (at δ 96.72 and 96.03), but two ethyl groups are distinguishable in their ^1H NMR spectra. Resonances of the ethyl group of **3a** appear at δ 3.79 and 0.88 with $J_{\text{H-H}} = 7.05$ Hz. The FAB mass spectrum of **3a** displays a parent peak and fragmentation peaks comparable to that of **2a**. The structure of **3a** has been determined by single crystal X-ray diffrac-

(10) Frank, G. W.; Degen, P. J. *Acta Crystallogr., Sect. B* **1973**, B29, 1815.

(11) Goerdeler, J.; Yunis, M.; Puff, H.; Roloff, A. *Chem. Ber.* **1986**, 119, 162.

(9) Malisch, W.; Hahner, C.; Grün, J.; Reising, J.; Goddard, R.; Krüger, C. *Inorg. Chim. Acta* **1996**, 244, 147.

Table 1. Crystal and Intensity Collection Data for Compounds **2b**, **3a**, **5a**, and **6a**

	2b	3a ·CHCl ₃ ^c	5a ·CH ₃ COCH ₃ ^c	6a ·CH ₃ OH ^c
formula	C ₃₈ H ₃₉ NO ₅ P ₂ RuS	C ₄₄ H ₄₀ Cl ₃ NO ₅ P ₂ RuS	C ₄₅ H ₄₂ ClNO ₅ P ₂ RuS	C ₈₄ H ₇₄ N ₂ O ₅ P ₄ Ru ₂ S ₂
fw	784.77	916.19	875.32	1581.59
temp, K	295(2)	150(1)	295(2)	295(2)
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	10.8554(2)	14.1727(5)	12.2203(1)	14.82850(10)
<i>b</i> , Å	12.1181(2)	15.6797(5)	18.8528(2)	16.0216(2)
<i>c</i> , Å	14.3910(1)	18.5534(6)	18.4824(1)	16.63470(10)
α , deg	88.109(1)	94.6404(10)	90	98.2560(10)
β , deg	79.027(1)	98.1618(8)	103.031(1)	107.4950(10)
γ , deg	82.301(1)	90.4884(8)	90	91.1730(10)
<i>V</i> , Å ³	1841.67(5)	4067.0(2)	4148.45(6)	3721.65(6)
<i>Z</i>	2	4	4	2
<i>d</i> (calcd), Mg/m ³	1.415	1.496	1.401	1.411
abs coeff, mm ⁻¹	0.612	0.752	0.610	0.602
<i>F</i> (000)	808	1872	1800	1624
no. of rflns collected	20 610	54 419	28 120	40 442
no. of indep rflns	7509 (<i>R</i> _{int} = 0.0611)	18671 (<i>R</i> _{int} = 0.0614)	8481 (<i>R</i> _{int} = 0.0315)	13105 (<i>R</i> _{int} = 0.0634)
GOF ^a on <i>F</i> ²	1.028	1.113	1.088	1.014
<i>R</i> (<i>I</i> > 2σ(<i>I</i>)) ^b	<i>R</i> 1 = 0.0582 w <i>R</i> 2 = 0.1229	<i>R</i> 1 = 0.0636 w <i>R</i> 2 = 0.1294	<i>R</i> 1 = 0.0427 w <i>R</i> 2 = 0.1141	<i>R</i> 1 = 0.0406 w <i>R</i> 2 = 0.0809
<i>R</i> (all data)	<i>R</i> 1 = 0.0988 w <i>R</i> 2 = 0.1415	<i>R</i> 1 = 0.0859 w <i>R</i> 2 = 0.1404	<i>R</i> 1 = 0.0535 w <i>R</i> 2 = 0.1221	<i>R</i> 1 = 0.0754 w <i>R</i> 2 = 0.0915
peak, hole, e Å ⁻³	1.056, -0.819	0.945, -0.751	1.066, -0.593	0.591, -0.400

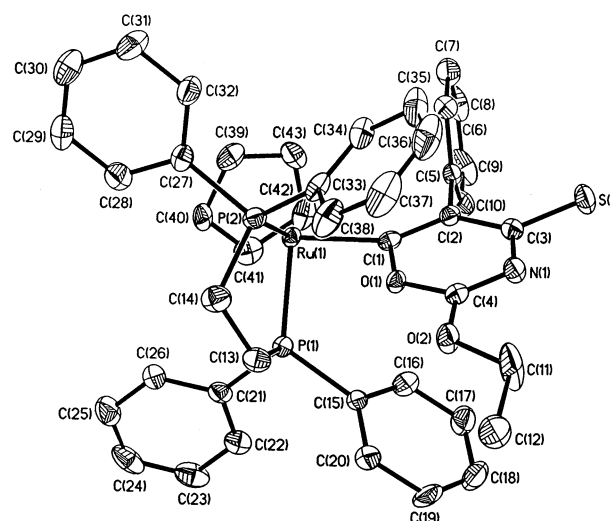
^a GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where *n* and *p* denote the number of data and parameters. ^b *R*1 = $(\sum||F_o| - |F_c||)/\sum|F_o|$ and w*R*2 = $[\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [F_o^2 + 2F_c^2]/3$. ^c The solvent was found to incorporate with the crystals.

Table 2. Selected Bond Distances (Å) and Angles (deg) of

Cp(PPh₃)[P(OMe)₃]RuC=C(Ph)C(=NCO₂Et)S (2b)			
Ru-P(1)	2.2312(13)	Ru-P(2)	2.3276(13)
Ru-C(1)	2.012(5)	S(1)-C(1)	1.879(4)
S(1)-C(3)	1.800(6)	O(4)-C(5)	1.271(9)
O(5)-C(5)	1.158(10)	O(5)-C(6)	1.463(8)
C(1)-C(2)	1.373(7)	C(2)-C(3)	1.433(6)
C(3)-N(4)	1.277(6)	N(4)-C(5)	1.407(8)
C(6)-C(7)	1.473(9)		
P(1)-Ru-P(2)	92.37(5)	Ru-C(1)-C(2)	138.2(3)
C(1)-Ru-P(1)	90.17(13)	C(3)-S(1)-C(1)	72.0(2)
C(5)-O(5)-C(6)	122.0(10)	C(2)-C(1)-S(1)	92.8(3)
Ru-C(1)-S(1)	129.0(3)	C(1)-C(2)-C(3)	100.8(4)
C(2)-C(3)-S(1)	94.1(4)	C(3)-N(4)-C(5)	120.1(6)
O(4)-C(5)-O(5)	118.8(8)	O(4)-C(5)-N(4)	123.3(7)
O(5)-C(5)-N(4)	116.8(8)		

tion analysis. An ORTEP drawing is shown in Figure 2. Selected bond distances and angles are listed in Table 3. Two independent molecules, which are essentially very similar, are observed in the unit cell of the crystal, along with two solvated chloroform molecules. The six-membered oxazinethione ring is basically planar, with a C1-C2 distance of 1.387(6) Å, typical of a C-C double bond. The bond distance for C3-S1 (1.684(4) Å) is typical of a C=S double bond. The C4=N1 bond distance of 1.279(5) Å differs from the neighboring C3-N1 distance of 1.388(5) Å, indicating localization of double bonds in the six-membered ring.

The isomerization could involve opening of the four-membered 2-iminothiete ring to form zwitterionic vinylidene with the anionic charge delocalized between the sulfur atom and the oxygen atom of the carbonyl group (see Scheme 1). A more electronegative oxygen atom makes **3a**, with the six-membered oxazine ring containing a thione group, the predominant species after ring closure. Even though EtO₂CNCS is known to undergo nucleophilic attack at the isothiocyanate C atom,¹² the fact that no **3a** is observed in the early stage of the reaction of **1a** with EtO₂CNCS indicates that

**Figure 2.** ORTEP drawing of **3a**·CHCl₃. Thermal ellipsoids are drawn at the 50% probability level. Chloroform molecules are omitted for clarity.

formation of **2a** may involve a fast concerted [2 + 2] cycloaddition, not via the zwitterionic vinylidene intermediate. Transformation between **2a** and **3a** is a slow step. It takes 1 day to establish the equilibrium of **2a** and **3a** in a 1:3 ratio.

Alkylation Reaction at the Thione Sulfur of the Oxazine Complex. The reaction of complex **2a** with CH₂Cl₂ for 4 days gave the six-membered oxazine

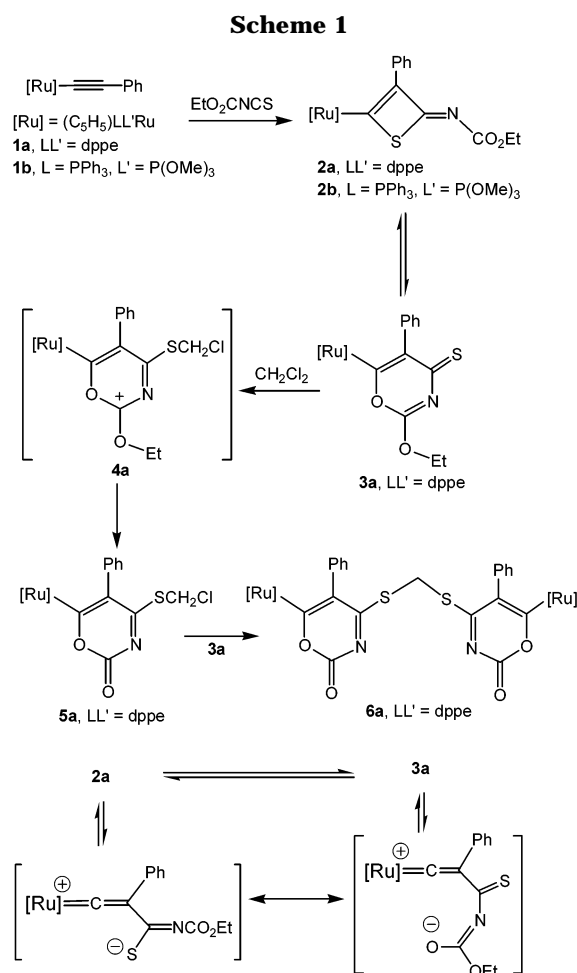
complex [Ru]C=C(Ph)C(SCH₂Cl)NC(=O)O (**5a**) in 87% isolated yield. The reaction of **3a** with CH₂Cl₂ takes 3 days to give **5a** in high yield. Also direct reaction of **1a** with a 5-fold excess of EtO₂CNCS in CH₂Cl₂ at room

- (12) (a) Kurzer, F.; Secker, J. L. *J. Heterocycl. Chem.* **1989**, *26*, 355. (b) Molina, P.; Alajarin, M.; Lopez-Lazaro, A. *Tetrahedron* **1991**, *47*, 6747. (c) Molina, P.; Alajarin, M.; Arques, A.; Benzel, R. *J. Chem. Soc., Perkin Trans. 1* **1982**, 351. (d) Garmaise, D. L.; Schwartz, R.; McKay, A. F. *J. Am. Chem. Soc.* **1958**, *80*, 3332.

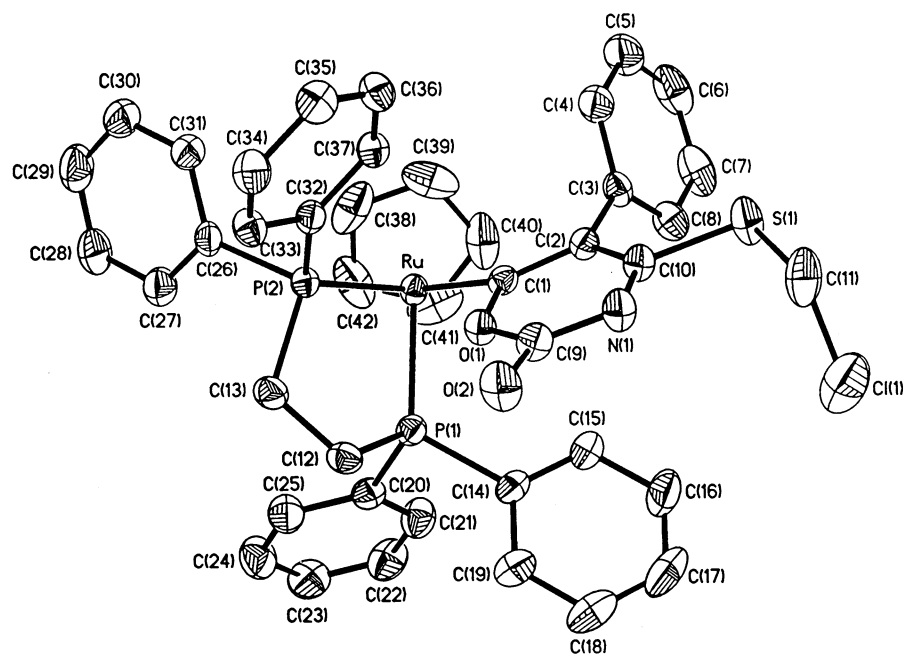
Table 3. Selected Bond Distances (Å) and Angles (deg) of $\text{Cp}(\text{dppe})\text{RuC}=\text{C}(\text{Ph})\text{C}(\text{S})\text{N}=\text{C}(\text{OEt})\text{O}$ (**3a**)

Ru(1)–P(1)	2.2756(11)	Ru(1)–C(1)	2.047(4)
Ru(1)–P(2)	2.2619(12)	S(1)–C(3)	1.684(4)
O(1)–C(1)	1.420(5)	O(1)–C(4)	1.323(5)
O(2)–C(4)	1.323(5)	O(2)–C(11)	1.443(6)
N(1)–C(4)	1.279(5)	N(1)–C(3)	1.388(5)
C(1)–C(2)	1.387(6)	C(2)–C(3)	1.436(6)
C(1)–Ru(1)–P(1)	87.69(12)	C(1)–Ru(1)–P(2)	89.36(12)
P(1)–Ru(1)–P(2)	84.59(4)	C(4)–O(1)–C(1)	122.1(3)
C(4)–O(2)–C(11)	116.3(4)	C(4)–N(1)–C(3)	115.8(4)
C(2)–C(1)–Ru(1)	136.5(3)	C(2)–C(1)–O(1)	112.9(3)
O(1)–C(1)–Ru(1)	110.6(3)	C(1)–C(2)–C(3)	121.7(4)
N(1)–C(3)–C(2)	120.1(4)	N(1)–C(3)–S(1)	116.5(3)
C(2)–C(3)–S(1)	123.4(3)	N(1)–C(4)–O(1)	127.4(4)
N(1)–C(4)–O(2)	124.7(4)	O(1)–C(4)–O(2)	107.9(4)

temperature for 7 days afforded **5a** with lower overall yield. The reaction carried out in CHCl_3 yielded no alkylation product. Characterization of **5a** by spectroscopic methods and by structure determination indicates that an unusual alkylation by CH_2Cl_2 takes place at the thione sulfur atom. Resonances at δ 4.86 and 43.1 in the ^1H and ^{13}C NMR spectra, respectively, of **5a** are assigned to the chloromethyl group on the sulfur atom. The reaction also yielded volatile ethyl chloride, observed by the ^1H NMR spectrum of the reaction mixture. Complex **5a** was recrystallized from a mixture of acetone and hexane (1:3) at 5 °C, and the molecular structure was determined by single-crystal X-ray diffraction analysis; an ORTEP drawing of **5a** is shown in Figure 3, and selected bond distances and angles are listed in Table 4. The bond distance of Ru–C(1) (2.040(3) Å) is typical of a Ru–C single bond. The C(1)–C(2), N(1)–C(9), and N(1)–C(10) bond lengths of 1.399(4), 1.355(5), and 1.324(4) Å, respectively, all displaying partial double-bond character, are indicative of several resonance contributions. The bond distance of O(2)–C(9) is 1.214(4) Å, comparable to an idealized C=O double bond. The bond distances of O(1)–C(9) (1.385(4) Å) and



O(1)–C(1) (1.398(4) Å) are both typical of a C–O single bond. The heterocyclic six-membered oxazine ring is essentially planar. The bond angle S(1)–C(11)–Cl(1) of the thiochloromethyl group is 114.4(3)°, close to that expected for $\text{C}(\text{sp}^3)$ hybridization. The bond distances

**Figure 3.** ORTEP drawing of **5a**· CH_3COCH_3 . Thermal ellipsoids are drawn at the 50% probability level. Acetone molecules are omitted for clarity.

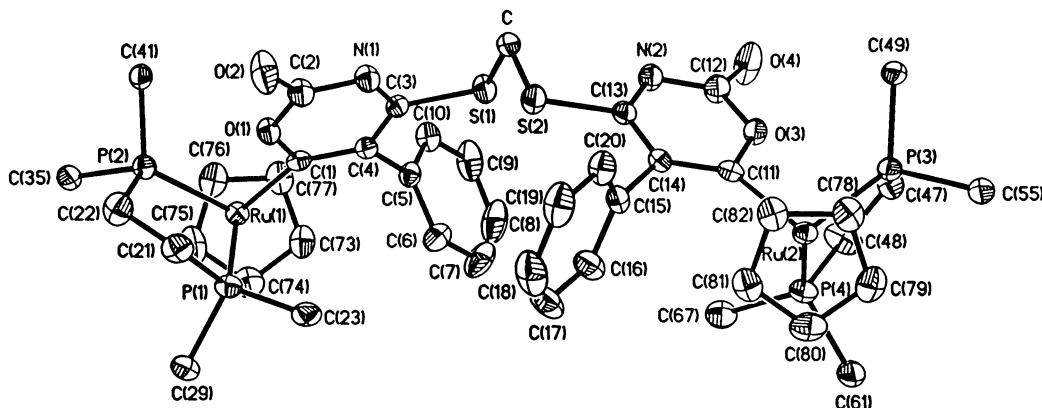


Figure 4. ORTEP drawing of **6a**·CH₃OH. Thermal ellipsoids are drawn at the 50% probability level. Methanol molecules are omitted for clarity. For the phenyl groups on dppe, only the ipso carbons are shown.

Table 4. Selected Bond Distances (Å) and Angles (deg) of Cp(dppe)RuC≡C(Ph)C(SCH₂Cl)NC(=O)O (5a)

Ru–P(1)	2.2694(9)	Ru–C(1)	2.040(3)
Ru–P(2)	2.2774(87)	S(1)–C(10)	1.783(4)
S(1)–C(11)	1.781(5)	Cl(1)–C(11)	1.764(6)
O(1)–C(9)	1.385(4)	O(2)–C(9)	1.214(4)
O(1)–C(1)	1.398(4)	N(1)–C(9)	1.355(5)
N(1)–C(10)	1.324(4)	C(1)–C(2)	1.399(4)
C(2)–C(10)	1.408(5)		
C(1)–Ru–P(1)	86.20(9)	C(1)–Ru–P(2)	90.45(9)
P(1)–Ru–P(2)	84.24(3)	C(9)–O(1)–C(1)	126.2(3)
C(10)–N(1)–C(9)	116.1(3)	C(2)–C(1)–O(1)	113.0(3)
C(2)–C(1)–Ru	133.9(2)	O(1)–C(1)–Ru	112.9(2)
C(1)–C(2)–C(10)	118.1(3)	C(1)–C(2)–C(3)	123.1(3)
C(10)–C(2)–C(3)	118.8(3)	O(2)–C(9)–O(1)	115.6(3)
O(2)–C(9)–N(1)	125.2(3)	N(1)–C(9)–O(1)	119.1(3)
N(1)–C(10)–C(2)	127.1(3)	N(1)–C(10)–S(1)	116.8(3)
C(2)–C(10)–S(1)	116.2(2)	Cl(1)–C(11)–S(1)	114.4(3)

S(1)–C(11) and C(11)–Cl(1) of 1.781(5) and 1.764(6) Å, respectively, are in the range of normal C–S and C–Cl single bonds.

Alkylation of the six-membered thiazine thione ring is known¹³ to take place at the thione sulfur atom. It is therefore not surprising to see the formation of **5a** from **3a** or from **2a** in CH₂Cl₂. Formation of **5a** from **2a** could be induced¹⁴ initially by isomerization of **2a** to **3a** followed by nucleophilic attack of the thione sulfur at CH₂Cl₂ (Scheme 1). This unusual alkylation at the sulfur atom stimulates us to investigate this reaction in detail. The reaction of **2a** with CH₂Cl₂ reveals some interesting insight into the process. When the reaction is monitored by ³¹P NMR spectroscopy, an additional intermediate is observed. Within 1 day, the ³¹P resonance at δ 96.72 of **2a** diminished while a resonance at δ 96.03 attributed to **3a** appeared. This was followed by the emergence of a new resonance at δ 92.7 assignable to the intermediate **4a**. After two more days, the ³¹P resonance attributed to the final product **5a** ap-

peared at δ 98.65. The intermediate **4a** could possibly be a cationic alkylation product before loss of EtCl (see Scheme 1). Formation of **5a** is thus considered to proceed via a stepwise process.

Formation of **5a** from **2a** is concentration dependent; namely, **5a** is the only product (87% yield) at the concentration of 5 mM of **2a** in CH₂Cl₂, but at higher concentration (25 mM), in addition to **5a** (ca. 50% yield),

the new product [Ru]C≡C(Ph)C(S–)NC(=O)O]₂CH₂ (**6a**) formed in 33% yield. Complex **6a**, insoluble in acetone, is readily separated from **5a** by washing the mixture with acetone. The NMR spectra of complexes **5a** and **6a** are very similar. The FAB mass spectrum of **6a** displays a parent peak at *m/z* 1551.0. Complex **6a** is a stable yellow compound, soluble in polar solvents such as CH₂Cl₂ and CHCl₃, moderately soluble in acetone, acetonitrile, and methanol, and insoluble in diethyl ether and hexane. Formation of **6a** could occur by a nucleophilic attack of the thione sulfur atom of **3a** at the chloromethyl group of **5a**, followed by elimination of EtCl. Recently Grapperhaus et al. reported a similar reaction that CH₂Cl₂ alkylated a trithiolato–ruthenium complex to yield a methylene-bridged thioether core.¹⁵

Recrystallization of **6a** by slow evaporation of a CH₂Cl₂/MeOH solution at room temperature affords yellow crystals. The structure of **6a** has been determined by single-crystal X-ray diffraction analysis. An ORTEP drawing is shown in Figure 4, and selected bond distances and angles are listed in Table 5. The bond distances of both Ru(1)–C(1) (2.041(3) Å) and Ru(2)–C(11) (2.041(3) Å) are typical of a Ru–C single bond. The C(1)–C(4) and C(11)–C(14) bond lengths of 1.396(4) and 1.395(4) Å indicate double bonds. The C(3)–N(1), C(13)–N(2), C(2)–N(1), and C(12)–N(2) bond lengths of 1.330(4), 1.328(4), 1.343(4), and 1.357(4) Å, respectively, all display partial double-bond character. The bond distance of C(2)–O(2) is 1.221(4) Å, comparable to an idealized C–O double bond. Both heterocyclic six-membered-ring ligands are essentially coplanar. The methylene-bridged bond angle S(2)–C–S(1) (114.77(18)°) is close to S(2)–C(11)–Cl(1) in **5a**. The bond distances of S(1)–C and S(2)–C (1.799(3) and 1.795(3) Å, respectively) are in the range of a normal C–S single bond. Ligand-based reactivity of metal-coordinated thiolates has been known in the literature, and alkylation,

(13) (a) Chang, C. W.; Lin, Y. C.; Lee, G. H.; Huang, S. L.; Wang, Y. *J. Organomet. Chem.* **2002**, *660*, 127. (b) Schatz, J.; Sauer, J. *Tetrahedron Lett.* **1994**, *35*, 4767. (c) Kakioka, Y.; Uebori, S.; Tsuno, M.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *J. Org. Chem.* **1996**, *61*, 372.

(14) (a) Mukerjee, A. K.; Ashare, R. *Chem. Rev.* **1991**, *91*, 1. (b) Adams, R. D.; Huang, M. *Chem. Ber.* **1996**, *129*, 485. (c) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993**, *12*, 3812. (d) Adams, R. D.; Huang, M. *Organometallics* **1996**, *15*, 2125. (e) Cowie, M.; Dwight, S. K. *J. Organomet. Chem.* **1980**, *198*, C20. (f) Werner, H. *Coord. Chem. Rev.* **1982**, *43*, 165.

(15) (a) Grapperhaus, C. A.; Poturovic, S.; Mashuta, M. S. *Inorg. Chem.* **2002**, *41*, 4309.

Table 5. Selected Bond Distances (Å) and Angles (deg) of [Cp(dppe)RuC≡C(Ph)C(S–)N(=O)O]₂CH₂ (6a)

Ru(1)–C(1)	2.041(3)	Ru(2)–C(11)	2.041(3)
O(1)–C(2)	1.391(4)	O(2)–C(2)	1.221(4)
O(1)–C(1)	1.404(4)	O(3)–C(12)	1.395(4)
O(3)–C(11)	1.399(4)	O(4)–C(12)	1.208(4)
C(1)–C(4)	1.396(4)	C(11)–C(14)	1.395(4)
C(3)–C(4)	1.420(4)	C(13)–C(14)	1.417(4)
N(1)–C(3)	1.330(4)	N(2)–C(13)	1.328(4)
N(1)–C(2)	1.343(4)	N(2)–C(12)	1.357(4)
S(1)–C(3)	1.773(3)	S(2)–C(13)	1.774(3)
S(1)–C	1.799(3)	S(2)–C	1.795(3)
C(2)–O(1)–C(1)	125.5(3)	O(1)–C(1)–Ru(1)	114.4(2)
C(2)–N(1)–C(3)	116.5(3)	S(2)–C–S(1)	114.77(18)
N(1)–C(2)–O(1)	119.8(3)	N(1)–C(3)–S(1)	117.7(2)
C(1)–C(4)–C(3)	118.4(3)	N(1)–C(3)–C(4)	126.3(3)
C(3)–S(1)–C	101.94(16)	C(4)–C(3)–S(1)	116.0(2)

metalation, oxygenation, and adduct formation have all been recognized.¹⁶ The strength of the coordinated thiolate's nucleophilicity was established by the fact that even weak electrophiles, such as CH₂Cl₂, are prone to attack. In the past, alkylation of the *trans*-dithiolato-ruthenium complex [Ru(PPh₃)₂dttd] by CH₂Cl₂, yielding the chloromethyl thioether complexes [Ru(X)(PPh₃)₂dttd-CH₂Cl], where X is azide or cyanide, has been reported.¹⁷ Alkylation across *cis* thiolates, yielding a methylene-bridged dithioether Ru complex, has been reported lately.¹⁵ Similar additions of CH₂Br₂ across adjacent sulfido sulfurs have been previously reported.¹⁸

Concluding Remarks. Reactions of two ruthenium acetylide complexes with EtO₂CNCS have yielded a series of addition products. Cycloaddition of the C=S bond of EtO₂CNCS with the acetylide ligand gives the four-membered-ring 2-iminothiete product. Opening of the 2-iminothiete ring causes slow isomerization of complex **2a** to **3a**, which undergoes alkylation by CH₂-Cl₂ at the thione sulfur atom to yield the new six-membered-ring oxazine complex **5a**. Alkylation of complex **3a** by the chloromethyl group of **5a** followed by loss of EtCl affords the binuclear complex **6a** with two heterocyclic six-membered-ring ligands bridged by a methylene group.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH₂Cl₂ was distilled from CaH₂ and diethyl ether and THF from sodium benzophenone 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 at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvents as an initial

standard (CDCl₃, δ 7.24; acetone-*d*₆, δ 2.04). The complexes [M]C≡CPh (**1a**, [M] = [Ru] = Cp(dppe)Ru; **1b**, [M] = [Ru'] = Cp(PPh₃)[P(OMe)₃]Ru) were prepared by following the methods reported in the literature.^{19,8} FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

Synthesis of [Ru]C≡C(Ph)C(=NCO₂Et)S (2a**).** In a Schlenk flask charged with **1a** (300.1 mg, 0.451 mmol) was added CHCl₃ (20 mL), and then EtO₂CNCS (56.0 μL, 0.473 mmol) was injected by a microsyringe. The resulting solution was stirred at room temperature for 1 h, and the color changed from bright yellow to orange. The solvent was reduced to 1 mL under vacuum, and 30 mL of *n*-pentane was added to cause precipitation of an orange powder. After filtration, the precipitate was washed with 10 mL of *n*-pentane and dried under vacuum to give the product **2a** (331.2 mg, 0.416 mmol, 92% yield). Spectroscopic data of **2a** are as follows. ¹H NMR (CDCl₃): δ 7.79–6.69 (m, 25H, Ph), 4.60 (s, 5H, Cp), 4.07 (q, 2H, CH₂, *J*_{H–H} = 7.10 Hz), 2.60, 2.15 (m, 2H, PCH₂), 1.19 (t, 3H, CH₃, *J*_{H–H} = 7.10 Hz). ³¹P NMR (CDCl₃): δ 96.72. ¹³C NMR (CDCl₃): δ 162.0 (CO), 143.4 (SCN), 136.4–126.1 (m, Ph, C_α and C_β), 87.9 (Cp), 61.3 (OCH₂), 30.4 (t, PCH₂, *J*_{C–P} = 22.4 Hz), 14.0 (CH₃). MS (FAB, *m/z*): 798.2 (M⁺ + 1), 666.2 (M⁺ – EtO₂CNCS), 565.5 (M⁺ – EtO₂CNCS – C≡CPh). Anal. Calcd for C₄₃H₃₉O₂NSP₂Ru: C, 64.81; H, 4.93; N, 1.76. Found: C, 65.12; H, 5.09; N, 1.63.

Synthesis of [Ru']C≡C(Ph)C(=NCO₂Et)S (2b**).** In a Schlenk flask charged with **1a** (200.1 mg, 0.306 mmol) was added CHCl₃ (20 mL), and EtO₂CNCS (39.6 μL, 0.336 mmol) was injected by a microsyringe. The resulting solution was stirred at room temperature for 1 h, and the color changed from bright yellow to orange. The solvent was reduced to 1 mL under vacuum, and 20 mL of hexane was added to cause precipitation of an orange powder. After filtration, the precipitate was washed with 10 mL of hexane and then dried under vacuum to give the product **2b** (199.4 mg, 0.254 mmol, 83% yield). Spectroscopic data of **2b** are as follows. ¹H NMR (acetone-*d*₆): δ 7.85–6.90 (m, 20H, Ph), 4.21 (s, 5H, Cp), 4.13 (q, 2H, CH₂, *J*_{H–H} = 7.14 Hz), 3.42 (d, 9H, P(OMe)₃, *J*_{H–P} = 11.12 Hz), 1.16 (t, 3H, CH₃, *J*_{H–H} = 7.14 Hz). ³¹P NMR (CDCl₃): δ 152.72, 56.92 (2d, *J*_{P–P} = 67.13 Hz). ¹³C NMR (CDCl₃): δ 167.4, 161.8 (CO and SCN), 138.4–126.5 (m, Ph, C_α and C_β), 86.2 (Cp), 61.6 (OCH₂), 52.8 (d, *J*_{C–P} = 7.5 Hz, P(OMe)₃), 14.7 (CH₃). MS (FAB, *m/z*): 786.1 (M⁺ + 1), 553.1 (M⁺ – EtO₂CNCS – C≡CPh), 429.0 [M⁺ – EtO₂CNCS – C≡CPh – P(OMe)₃]. Anal. Calcd for C₃₈H₃₉O₅NSP₂Ru: C, 58.15; H, 5.01; N, 1.78. Found: C, 58.38; H, 5.24; N, 1.75.

Synthesis of [Ru]C≡C(Ph)C(=S)N=C(OEt)O (3a**).** In a Schlenk flask charged with **1a** (200.3 mg, 0.301 mmol) was added CHCl₃ (20 mL), and then EtO₂CNCS (37.3 μL, 0.316 mmol) was injected by a microsyringe. The resulting solution was stirred at room temperature for 1 day. The solvent was reduced to 1 mL under vacuum, and 30 mL of *n*-pentane was added to cause precipitation of an orange-yellow powder. After filtration, the precipitate was washed with 10 mL of *n*-pentane and dried under vacuum to give a mixture of **2a** and **3a** (211.0 mg, 88% total yield) in a ratio of ca. 1:3. Spectroscopic data of **3a** are as follows. ¹H NMR (CDCl₃): δ 7.79–6.95 (m, 25H, Ph), 3.88 (s, 5H, Cp), 3.79 (q, 2H, CH₂, *J*_{H–H} = 7.05 Hz), 3.10, 2.65 (m, 2H, PCH₂), 0.88 (t, 3H, CH₃, *J*_{H–H} = 7.05 Hz). ³¹P NMR (CDCl₃): δ 96.03. ¹³C NMR (CDCl₃): δ 216.6 (t, C_α, *J*_{C–P} = 13.6 Hz), 194.6 (CS), 155.5 (CO), 143.4, 134.0–126.6 (m, Ph, and C_β), 84.9 (Cp), 64.0 (OCH₂), 29.8 (t, PCH₂, *J*_{C–P} = 22.7

(16) (a) Thompson, M. C.; Busch, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 3651–3656. (b) Constable, E. C. *Metals and Ligand Reactivity: An Introduction to the Organic Chemistry of Metal Complexes*, 2nd ed.; VCH: Weinheim, Germany, 1996. (c) Musie, G.; Reibenspies, J. H.; Darenbourg, M. Y. *Inorg. Chem.* **1998**, *37*, 302. (d) Grapperhaus, C. A.; Darenbourg, M. Y. *Acc. Chem. Res.* **1998**, *31*, 451. (e) Darenbourg, M. Y.; Tuntulani, T.; Reibenspies, J. H. *Inorg. Chem.* **1995**, *34*, 6287. (f) Lyon, E. J.; Musie, G.; Reibenspies, J. H.; Darenbourg, M. Y. *Inorg. Chem.* **1998**, *37*, 6942.

(17) (a) Sellmann, D.; Waerber, M.; Binder, H.; Boese, R. Z. *Naturforsch., B: Chem. Sci.* **1986**, *41b*, 1541. (b) dttd^{2–} = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2–).

(18) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; DuBois, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

(19) Synthesis of acetylide: (a) Bruce, M. I. *Aust. J. Chem.* **1977**, *30*, 1602. (b) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.

Hz), 14.0 (CH₃). MS (FAB, *m/z*): 797.0 (M⁺), 565.0 (M⁺ – EtO₂–CNCS – C≡CPh).

Observation of the Intermediate {[Ru]C≡C(Ph)C–(SCH₂Cl)NC(OEt)O}[Cl] (**4a**). In a Schlenk flask charged with a mixture of **2a** and **3a** in a ratio of ca. 1:3 was added CH₂Cl₂ (20 mL). The reaction was monitored by ³¹P NMR spectroscopy. The resulting solution was stirred at room temperature for hours, and the additional intermediate {[Ru]C≡C(Ph)C(SCH₂Cl)NC(OEt)O}[Cl] (**4a**) was observed. We failed to isolate **4a**. Spectroscopic data of **4a** are as follows. ¹H NMR (CDCl₃): δ 4.70 (CH₂Cl), 4.12 (s, 5H, Cp), 4.06 (q, 2H, CH₂, *J*_{H–H} = 7.02 Hz), 1.04 (t, 3H, CH₃, *J*_{H–H} = 7.02 Hz). ³¹P NMR (CDCl₃): δ 92.71. MS (*m/z*, Ru, ¹⁰²Cl³⁵): 846.0 (M⁺ – Cl), 593.0 (M⁺ – Cl + CO – organic ligand), 565.0 (M⁺ – Cl – organic ligand).

Synthesis of [Ru]C≡C(Ph)C(SCH₂Cl)NC(=O)O (5a**).** In a Schlenk flask charged with **2a** (200.1 mg, 0.251 mmol) was added CH₂Cl₂ (50 mL). The resulting solution was stirred at room temperature for 4 days, and the color changed from orange-yellow to yellow. The solvent was removed under vacuum, and the yellow precipitate was washed with 2 × 10 mL of hexane and dried under vacuum to give the product **5a** (178.7 mg, 0.219 mmol, 87% yield). Spectroscopic data of **5a** are as follows. ¹H NMR (CDCl₃): δ 7.70–7.12 (m, 25H, Ph), 4.86 (s, 2H, CH₂), 3.95 (s, 5H, Cp), 3.42, 2.54 (m, 4H, PCH₂–CH₂P). ³¹P NMR (CDCl₃): δ 98.65. ¹³C NMR (CDCl₃): δ 233.6 (t, C_α, *J*_{C–P} = 14.5 Hz), 152.1 (CO), 139.5 (NCS), 133.2–128.1 (m, Ph and C_β), 84.4 (Cp), 43.1 (CH₂), 29.7 (t, PCH₂, *J*_{C–P} = 22.4 Hz). MS (FAB, *m/z*): 818.1 (M⁺ + 1), 593.1 (M⁺ + CO – organic ligand), 565.1 (M⁺ – organic ligand). Anal. Calcd for C₄₂H₃₆O₂NSClP₂Ru: C, 61.72; H, 4.44; N, 1.71. Found: C, 62.07; H, 4.72; N, 1.63.

Synthesis of [Ru]C≡C(Ph)C(S–)NC(=O)O]₂CH₂ (6a**).** In a Schlenk flask charged with **2a** (200.1 mg, 0.251 mmol) was added CH₂Cl₂ (10 mL). The resulting solution was stirred at room temperature for 4 days to give a mixture of **5a** and **6a** in a ratio of ca. 3:2. Complexes **5a** and **6a** were separated by their different solubilities in acetone. Thus, after the solvent was removed under vacuum, 30 mL of cold acetone was added. Complex **6a** precipitated out from the acetone solution. After filtration, the yellow precipitate was washed with 2 × 5 mL of cold acetone and then dried under vacuum to give the

product **6a** (64.2 mg, 0.042 mmol, 33% yield). Spectroscopic data of **6a** are as follows. ¹H NMR (CDCl₃): δ 7.63–7.02 (m, 50H, Ph), 4.20 (s, 2H, CH₂), 3.93 (s, 10H, Cp), 3.43, 2.55 (m, 4H, PCH₂). ³¹P NMR (CDCl₃): δ 98.84. ¹³C NMR (CDCl₃): δ 154.2 (CO), 143.6 (NCS), 133.5–127.6 (m, Ph and C_β), 84.4 (Cp), 30.9 (CH₂), 29.7 (t, PCH₂, *J*_{C–P} = 22.4 Hz). MS (FAB, *m/z*): 1551.0 (M⁺ + 1), 593.0 (M⁺ + CO – organic ligand), 565.1 (M⁺ – organic ligand). Anal. Calcd for C₈₃H₇₀O₄N₂S₂P₄Ru₂: C, 64.33; H, 4.55; N, 1.81. Found: C, 64.11; H, 4.78; N, 1.68.

X-ray Analysis of 2b, 3a, 5a, and 6a. Single crystals suitable for X-ray diffraction studies were grown as mentioned above. The chosen single crystal was glued to a glass fiber and mounted on a SMART CCD diffractometer. The data were collected with use of 3 kW sealed-tube molybdenum Kα radiation (λ = 0.7107 Å). The exposure time was 5 s per frame.²⁰ The intensity was intergrated, and absorption corrections were applied by using SADABS.²¹ Data were processed and refined by the SHELXTL²² program. Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times those for the atoms to which the hydrogen is attached and 1.5 times those for the methyl hydrogens. Crystal data for **2b**, **3a**, **5a**, and **6a** are listed in Table 1. 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.

Supporting Information Available: Details about the X-ray crystal structures, including diagrams and tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **2b**, **3a**, **5a**, and **6a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM030341W

(20) X-ray: SAINT (Siemens Area Detector Intergration) program; Siemens Analytical X-ray: Madison, WI, 1995.

(21) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(22) SHELXTL: Structure Analysis Program, version 5.04; Siemens Industrial Automation, Inc., Madison, WI, 1995.