# Reactions of Ruthenium Acetylide Complexes with Isothiocyanate 

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Treatment of $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC} \equiv \mathrm{CPh}\left(2 ; \mathrm{Cp}=\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)$ with $\mathrm{PhN}=\mathrm{C}=\mathrm{S}$ at room temperature affords the $[2+2]$ cycloaddition product $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}-$ $(=\mathrm{NPh}) \mathrm{S}(3 \mathrm{a})$, containing a four-membered ring, and the neutral vinylidene phosphonate complex $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(=\mathrm{O})(\mathrm{OMe})_{2}\right] \mathrm{Ru}=\mathrm{C}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(\mathrm{SH})=\mathrm{NPh}(4 \mathbf{a})$ in a 9:1 ratio. F ormation of $4 \mathbf{a}$ results from an Arbuzov-like dealkylation reaction possibly after addition of $\mathrm{PhN}=\mathrm{C}=\mathrm{S}$. The same reaction at $40^{\circ} \mathrm{C}$ affords a higher yield of $\mathbf{4 a}$ and $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathrm{C}$ -


#### Abstract

$(\mathrm{Ph}) \mathrm{C}(=\mathrm{S}) \mathrm{N}(\mathrm{R}) \mathrm{C}(=\mathrm{NR}) \mathrm{S}(\mathbf{5 a} ; \mathrm{R}=\mathrm{Ph})$ which results from addition of a second isothiocyanate to the four-membered ring of $\mathbf{3 a}$. The reaction of $\mathbf{2}$ with $\mathrm{PhCH}_{2} \mathrm{~N}=\mathrm{C}=\mathrm{S}$ at room temperature directly affords the six-membered-ring product $\mathbf{5 b}\left(\mathrm{R}=\mathrm{CH}_{2} \mathrm{Ph}\right)$. Trimerization of phenyl isothiocyanate is catalyzed by $\mathrm{Cp}(\mathrm{dppe}) \mathrm{RuC} \equiv \mathrm{CPh}\left(\mathbf{1}^{\prime}\right.$; dppe $=\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{CH}_{2} \mathrm{PPh}_{2}$ ) in refluxing $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. 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 $\mathbf{1}^{\prime}$ and $(\operatorname{PhNCS})_{3}(\mathbf{8})$. The structures of $\mathbf{3 a}, \mathbf{4 a , 5 b}$, and the cocrystallization product of $\mathbf{1}^{\prime}$ and $\mathbf{8}$ have been determined by singlecrystal X-ray diffraction analysis.


## Introduction

Metal acetylide complexes have been the focus of recent study due to their application in organometallic ${ }^{1}$ and materials ${ }^{2}$ chemistry. The acetylideligand 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. ${ }^{3} \mathrm{Cy}$ cloadditions of organic substrates such as $\mathrm{CS}_{2},{ }^{4}$ $(\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CF}_{3}\right)_{2}$, and $(\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}(\mathrm{CN})_{2}{ }^{5}$ to the acetylide ligand in various metal complexes have been reported. Nickel(0) complexes promote the cydlocoupling of alkynes with isocyanates. ${ }^{6}$ This reaction may proceed through

[^0]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 heterocydic ligands. With $\mathrm{Cp}(\mathrm{dppe}) \mathrm{RuC} \equiv \mathrm{CPh},[2$ +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 $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{RuC} \equiv \mathrm{CPh}(\mathbf{1})^{7}$ with $\mathrm{P}(\mathrm{OMe})_{3}$ in n -decane at reflux temperature affords a racemic mixture of Cp $\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC} \equiv \mathrm{CPh}(\mathbf{2})$ in high yield. ${ }^{8}$ Complex $\mathbf{2}$ is soluble in polar solvents such as $\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{CHCl}_{3}$, acetone, and THF. In the ${ }^{31 P}$ NMR spectrum, two doublet resonances at $\delta 158.3$ and 56.6 are assigned to the phosphite and phosphine ligands, respectively. Complex $\mathbf{2}$ could also be prepared in lower yield from

[^1]
treatment of $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{RuCl}$ with $\mathrm{P}(\mathrm{OMe})_{3}$ followed by the reaction with $\mathrm{HC} \equiv \mathrm{CPh}$. Treatment of $\mathbf{1}$ with dppe affords $\mathrm{Cp}(\mathrm{dppe}) \mathrm{RuC} \equiv \mathrm{CPh}\left(\mathbf{I}^{\prime}\right)$ in high yield.
[2+2] Cycloaddition and Arbuzov-like Dealkylation. Treatment of 2 with a 10 -fold excess of $\mathrm{PhN}=\mathrm{C}=\mathrm{S}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at room temperature for 3 days affords the yellow [ $2+2$ ] cycloaddition product Cp $\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{NPh}) \mathrm{S}$ (3a) and the neutral red-orange phosphonate vinylidene complex Cp $\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(=\mathrm{O})(\mathrm{OMe})_{2}\right] \mathrm{Ru}=\mathrm{C}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(\mathrm{SH})=\mathrm{NPh}(4 \mathrm{a})$ 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 $\mathrm{C} \equiv \mathrm{C}$ triple bond with the $\mathrm{C}=\mathrm{S}$ double bond. This neutral complex is stable in air but, in $\mathrm{CHCl}_{3}$ solution, decomposes to give 2. The ${ }^{31}$ P NMR spectrum has two doublet resonances at $\delta 56.2$ and 151.7 with J p-p $=68.8 \mathrm{~Hz}$, which are assigned to the $\mathrm{PPh}_{3}$ and the $\mathrm{P}(\mathrm{OMe})_{3}$ ligands, respectively. The air-stable complex 4a is formed by an Arbuzov-like deal kylation reaction of the phosphite ligand. ${ }^{9}$ The two OMe groups in $\mathbf{4 a}$ are diastereotopic and occur in the ${ }^{1} \mathrm{H}$ NMR spectrum at $\delta 3.18$ and 3.03 with $\mathrm{J}-\mathrm{H}=11.5 \mathrm{~Hz}$. The ${ }^{31} \mathrm{P}$ NMR spectrum of 4 a has resonances at $\delta 48.0$ and 93.4, the latter due to the phosphonate.
Interestingly, if the reaction is carried out at $40^{\circ} \mathrm{C}$ in the presence of excess $\mathrm{PhN}=\mathrm{C}=\mathrm{S}$, the yield of $\mathbf{4 a}$ increases and the new product $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right]-$
RuC $=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{S}) \mathrm{N}(\mathrm{Ph}) \mathrm{C}(=\mathrm{NPh}) \mathrm{S}(5 \mathrm{a})$ could be isolated in moderate yield. Complex $\mathbf{5 a}$ was also prepared directly from the reaction of 3 a with excess PhNCS at $40^{\circ} \mathrm{C}$. In 5a two 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 MeNCS to a cobaltacyclopentadiene complex, possibly through $\mathrm{C}=\mathrm{N}$ bond insertion into a $\mathrm{Co}-\mathrm{C}$ bond followed
by reductive elimination. ${ }^{10}$ Other organic compounds with similar heterocyclic ring structures have been reported. ${ }^{11}$ By treatment of complex 2 with excess $\mathrm{PhCH}_{2} \mathrm{~N}=\mathrm{C}=\mathrm{S}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at room temperature, the analogous red-orange complex $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right]-$
$\mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{S}) \mathrm{N}\left(\mathrm{CH}_{2} \mathrm{Ph}\right) \mathrm{C}\left(=\mathrm{NCH}_{2} \mathrm{Ph}\right) \mathrm{S}(5 \mathbf{b})$ was directly obtained. Spectroscopic data for $\mathbf{5 b}$ are consistent with this formulation and are comparable with those for 5a. This reaction also yields the corresponding phosphonate complex 4b. For $\mathrm{PhCH}_{2} \mathrm{~N}=\mathrm{C}=\mathrm{S}$, the analogous four-membered-ring compound $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)$ $\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}\left(=\mathrm{NCH}_{2} \mathrm{Ph}\right) \mathrm{S}$ (3b), a precursor of $5 \mathbf{5}$, is obtained at $5^{\circ} \mathrm{C}$ but transforms, in the presence of $\mathrm{PhCH}_{2} \mathrm{NCS}$, to $\mathbf{5 b}$ over 20 min at room temperature.

Isolation of the phosphonate complex indicates that the $\mathrm{C} \alpha-\mathrm{S}$ bond is labile. Thus, $\mathbf{3}$ may easily form the zwitterionic vinylidene complex A (Scheme 1). Structure $\mathbf{A}$ 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 $1.388(10) \AA$ typical of a $\mathrm{C}=\mathrm{C}$ double bond. The bond distances for C1-S and C9-S (1.868(7) and 1.823(8) Å) are typical of C-S single bonds. ${ }^{12}$ The

[^2]Table 1. Crystal and Intensity Collection Data for $\mathbf{C p}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathbf{C}(\mathrm{Ph}) \mathrm{C}(\mathrm{S})=\mathrm{NPh}(\mathbf{3 a})$,
 and $\mathbf{C p}($ dppe $) \mathrm{RuC} \equiv \mathbf{C P h} \cdot(\mathbf{P h N C S})_{3}$

| mol formula | $\mathrm{C}_{41} \mathrm{H}_{38} \mathrm{NO}_{3} \mathrm{P}_{2} \mathrm{SRuCl}_{3}$ (3a) | $\mathrm{C}_{41} \mathrm{H}_{39} \mathrm{NO}_{3} \mathrm{P}_{2} \mathrm{SRu}$ (4a) | $\mathrm{C}_{52} \mathrm{H}_{53} \mathrm{~N}_{2} \mathrm{O}_{3.5} \mathrm{P}_{2} \mathrm{~S}_{2} \mathrm{Ru}$ (5b) | $\mathrm{C}_{60} \mathrm{H}_{49} \mathrm{~N}_{3} \mathrm{SRu}$ |
| :---: | :---: | :---: | :---: | :---: |
| space group | P1 | P1 | P21/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 |
| $V, \AA^{3}$ | 1040.6(13) | 1858.5(10) | 4666.5(24) | 10 568(4) |
| Z | 2 | 2 | 4 | 8 |
| cryst dimens, mm radiation | $0.20 \times 0.20 \times 0.30$ | $\begin{aligned} 0.25 \times 0.25 & \times 0.30 \\ & \text { MoK } \alpha, \lambda= \end{aligned}$ | $\begin{aligned} & 0.50 \times 0.40 \times 0.20 \\ & .7107 \AA \end{aligned}$ | $0.20 \times 0.20 \times 0.30$ |
| $2 \theta$ range, deg | 2-45 | 2-45 | 2-45 | 2-60 |
| scan type |  | $\theta-2$ |  |  |
| total no. of rflns | 5303 | 4848 | 6069 | 8099 |
| no. of unique reflns, I > $2 \sigma(\mathrm{l})$ | 3077 | 2958 | 3685 | 4983 |
| R | 0.042 | 0.041 | 0.051 | 0.054 |
| $\mathrm{R}_{\mathrm{w}}$ | 0.040 | 0.042 | 0.047 | 0.052 |



Figure 1. ORTE P drawing (50\% thermal ellipsoids) of 3a. Three phenyl groups on the triphenylphosphineligand and all hydrogen atoms are eliminated for clarity.

| (deg) of $\mathbf{C p}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathbf{C}(\mathrm{Ph}) \mathbf{C}(=\mathrm{NPh}) \mathbf{S}$ (3a) |  |  |  |
| :---: | :---: | :---: | :---: |
| Ru-P1 | $2.2263(23)$ | $\mathrm{N}-\mathrm{C} 9$ | 1.271(10) |
| Ru-P2 | $2.3095(21)$ | $\mathrm{N}-\mathrm{C} 10$ | 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) |
| $\mathrm{Ru}-\mathrm{C} 1-\mathrm{C} 2$ | 138.0(5) | $\mathrm{N}-\mathrm{C} 9-\mathrm{C} 2$ | 131.3(7) |

$\mathrm{C} 9=\mathrm{N}$ bond distance of $1.271(10) \AA$ confirms an imino group. The dihedral angle between the phenyl plane (C10-C15) on the imino group and the plane ( $\mathrm{S}, \mathrm{C} 1$, C2, C9) formed by the four-membered ring is $37.8(3)^{\circ}$. The two ruthenium-phosphorus bonds in 3a are Ru$\mathrm{P} 1=2.226(2) \AA$ and $\mathrm{Ru}-\mathrm{P} 2=2.310(2) \AA$, 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. ${ }^{13}$ The structural features of the 2-imino-2H-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 $\mathrm{C} \equiv \mathrm{C}$ bond of an iron acetylide with $\mathrm{CS}_{2}$, yielding 2 H -thiete-2-thione ( $\beta$-dithiolactone), has been reported. ${ }^{4}$ A similar process has been proposed for the first stage of the reaction of alkynes with $\mathrm{CS}_{2} .^{4}$ The reaction of phosphenium complexes with isocyanates leading to [2 + 2] addition via the $\mathrm{N}=\mathrm{C}$ bond to give four-membered phosphametallacycles has been reported. ${ }^{14}$ 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 $\mathrm{C}=\mathrm{C}$ bond of the vinylidene to give unusual cyclic $\mathrm{C}_{4}$ bridging has also been reported. ${ }^{15}$

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) $=2.303(2) \AA$ and $\mathrm{Ru}-\mathrm{P} 2=$ $2.323(2) \AA$ ) are now comparable. The rutheniumcarbon bond has a formal bond order of 2 , consistent with a short Ru-C1 bond (1.798(6) Å). The carboncarbon double bond of the vinylideneligand is 1.337(9) $\AA$, typical for a $C\left(s p^{2}\right)-C(s p)$ allene bond. ${ }^{16}$ The ruthe-nium-vinylidene linkage is very nearly linear (Ru-C1$\left.\mathrm{C} 2=175.2(5)^{\circ}\right)$. The $\mathrm{N}-\mathrm{C} 9$ and $\mathrm{S}-\mathrm{C} 9$ bond lengths of 1.344(8) and 1.641(6) $\AA$, respectively, both display partial double-bond character, indicative of several resonance contributions.

The molecular structure of $\mathbf{5 b}$ was determined by an X-ray diffraction study; an ORTEP drawing which emphasizes the heterocydic 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 $2.239(3) \AA$ is shorter than

[^3]

Figure 2. ORTEP drawing ( $50 \%$ thermal ellipsoids) of $\mathbf{4 a}$. Three phenyl groups on the triphenyl phosphineligand and all hydrogen atoms are eliminated for clarity.


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

| Ru-P1 | 2.3027(20) | $\mathrm{N}-\mathrm{C} 9$ | 1.344(8) |
| :---: | :---: | :---: | :---: |
| Ru-P2 | $2.3234(20)$ | $\mathrm{N}-\mathrm{Cl} 10$ | 1.417 (8) |
| Ru-C1 | 1.799(6) | C1-C2 | 1.336 (8) |
| P1-01 | 1.582(4) | C2-C3 | 1.503(9) |
| P1-02 | 1.617(5) | C2-C9 | 1.478(8) |
| P1-03 | 1.491(4) | C9-S | 1.641(6) |
| P1-Ru-P2 | 92.95(7) | P1-02-C17 | 120.0(4) |
| P1-Ru-C1 | 91.13(19) | $\mathrm{C} 9-\mathrm{N}-\mathrm{C} 10$ | 129.2(5) |
| P2-Ru-C1 | 90.57(21) | $\mathrm{Ru}-\mathrm{C} 1-\mathrm{C} 2$ | 175.2(5) |
| Ru-P1-O1 | 107.81(19) | C1-C2-C3 | 116.8(5) |
| Ru-P1-02 | 110.00(19) | C1-C2-C9 | 124.2(6) |
| Ru-P1-03 | 119.06(19) | C3-C2-C9 | 119.0(5) |
| O1-P1-02 | 96.8(3) | $\mathrm{N}-\mathrm{C} 9-\mathrm{C} 2$ | 114.0(5) |
| O1-P1-03 | 112.8(3) | $\mathrm{N}-\mathrm{C} 9-\mathrm{S}$ | 125.4(5) |
| O2-P1-O3 | 108.0(3) | C2-C9-S | 120.5(5) |
| P1-O1-C16 | 122.8(5) |  |  |

that of $\mathrm{Ru}-\mathrm{P} 2$ (phosphine) (2.341(3) $\AA$ ). The Ru-C1 bond length of 2.105(7) $\AA$ is typical of a Ru-C single bond, and the C1-C2 bond length of $1.356(10) \AA$ is typical of a double bond. The carbon-sulfur double bond in $\mathbf{5 b}$ is $1.635(8) \AA$, which is comparable to that in ethylene trithiocarbonate (1.652(2) Å). ${ }^{17}$ The two $\mathrm{C}\left(\mathrm{sp}^{2}\right)-\mathrm{S}$ single bonds ( $\mathrm{C} 1-\mathrm{S} 2=1.749$ (8) and C17-S2

Table 4. Selected Bond Distances ( $\AA$ ) and Angles (deg) of $\mathbf{C p}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right]$ -

| Ru-P1 | 2.2389(24) | N 1-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 | $1.356(10)$ |
| P1-01 | 1.594(6) | C2-C3 | $1.514(10)$ |
| P1-02 | $1.596(6)$ | C2-C9 | $1.477(10)$ |
| P1-03 | 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) | $\mathrm{Ru}-\mathrm{C} 1-\mathrm{S} 2$ | 106.2(4) |
| C1-S2-C17 | 108.6(4) | $\mathrm{Ru}-\mathrm{C} 1-\mathrm{C} 2$ | 135.6(6) |
| Ru-P1-01 | 116.75(24) | S2-C1-C2 | 117.5(6) |
| Ru-P1-02 | 121.81(24) | C1-C2-C3 | 120.4(7) |
| Ru-P1-O3 | 108.70(24) | C1-C2-C9 | 128.0(7) |
| O1-P1-02 | 97.6(3) | C3-C2-C9 | 111.5(6) |
| O1-P1-03 | 106.8(3) | S1-C9-N1 | 120.0(6) |
| O2-P1-03 | 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 | $114.2(6)$ |
| $\mathrm{Ru}-\mathrm{P} 2-\mathrm{C} 40$ | 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) |
| P1-02-C26 | 121.9(6) | C46-C47-C48 | 106.8(7) |
| P1-03-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) |

$=1.750(8) \AA$ ) in the six-membered ring are short enough to reflect some double-bond character. ${ }^{18}$ The heterocyclic six-membered ring is essentially planar.
Reactions of $\mathbf{2}$ with Isocyanate. Treatment of $\mathbf{2}$ with PhNCO at $-20^{\circ} \mathrm{C}$ for 7 days afforded the two products $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{NPh}) \mathrm{O}(\mathbf{6})$ and $\quad \mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{O}) \mathrm{N}(\mathrm{Ph}) \mathrm{C}-$ ( $=\mathrm{NPh}$ ) $\mathrm{O}\left(\mathbf{7}\right.$ ) in a 1:1 ratio, as indicated by ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR spectra. These products are unstable at room temperature and were only characterized by spectroscopic methods. In the ${ }^{31}$ P NMR spectrum of the crude mixture, the two doublet resonances at $\delta 155.3$ and 56.9 with J p-p $=66.9 \mathrm{~Hz}$ are assigned to the $\mathrm{P}(\mathrm{OMe})_{3}$ and $\mathrm{PPh}_{3}$ ligands of 6 and another set of ${ }^{31} \mathrm{P}$ resonances at $\delta 151.7$ and 55.0 with J p-p $=69.1 \mathrm{~Hz}$ 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 $\mathbf{3}$ and $\mathbf{5}$, it is plausible to conclude that $\mathbf{3}$ and $\mathbf{6}$ have similar structures, as do complexes 5 and 7. The dealkylation phosphonate product was not observed at $-20^{\circ} \mathrm{C}$. However, when the reaction was carried out at room temperature, more than three phosphonate complexes were observed by the ${ }^{31}$ P NMR spectra. Separation of these complexes by chromatography caused decomposition, and no further characterization was attempted.

[^4](18) Waters, J. M.; I bers, J. A. Inorg. Chem. 1977, 12, 3273.

Scheme 2


8



Trimerization of Isothiocyanate. Our efforts to prepare the dppe analogues of $\mathbf{3}$ and 5 by reacting Cp(dppe)RuC $\equiv \mathrm{CPh}\left(\mathbf{1}^{\prime}\right)$ with PhNCS led to isolation of a cocrystallization product of $\mathbf{1}^{\prime}$ and 1,3,5-triphenyl-1,3,5-triazinane-2,4,6-trithione (PhNCS) ${ }_{3}(8),{ }^{19}$ a trimerization product of isothiocyanate. In the reaction, the [2 +2 ] cycloaddition product $\mathrm{Cp}(\mathrm{dppe}) \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{NPh})-$ $\mathrm{S}^{7}(9 \mathrm{a})$ and $\mathrm{Cp}($ dppe $) \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{S}) \mathrm{N}(\mathrm{Ph}) \mathrm{C}(=\mathrm{NPh}) \mathrm{S}$ (10a) were also isol ated and identified. The reaction of $\mathbf{1}^{\prime}$ with a 10 -fold excess of PhNCS at room temperature for 3 days afforded the orange-yellow complex 9 a 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 ${ }^{31} \mathrm{P}$ NMR spectroscopy. At the beginning of the reaction, the ${ }^{31} \mathrm{P}$ resonance of $\mathbf{1}^{\prime}$ appeared at $\delta 86.0$; within 3 days the resonance attributed to 9a appeared at $\delta 94.1$, and after 4 more days the resonance of 10a appeared at $\delta$ 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 $40^{\circ} \mathrm{C}$ for 2 days, a mixture composed of the major organometallic product 11, which showed a resonance at $\delta 79.4$ in the ${ }^{31} \mathrm{P}$ NMR spectrum, and 8 were obtained. Compounds 11 and 8 were separated by column chromatography. Complex $\mathbf{1 1}$ is dark brown and stable in air. Attempts to obtain single crystals of 11 by recrystallization led to the yellow cocrystallization product of $\mathbf{1}$ ' and $\mathbf{8}$. The mass spectrum of $\mathbf{1 1}$ displays only the parent peaks attributed to $\mathbf{1}^{\prime}$. However, the ${ }^{31} \mathrm{P}$ NMR resonance of $\mathbf{1 1}(\delta 79.6)$ is different from those of $\mathbf{1}^{\prime}$ and 10a. On the basis of these data, we believe that $\mathbf{1 1}$ is a precursor of the trimerization product. The ${ }^{31}$ P NMR chemical shift of $\mathbf{1 1}$ falls in the region for that

[^5]

Figure 4. ORTEP drawing ( $50 \%$ thermal ellipsoids) of the cocrystallization product of $\mathbf{1}^{\prime}$ and $\mathbf{8}$. 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 $\mathbf{1 1}$ is depicted in Scheme 2. The formation of $\mathbf{1 1}$ may be initiated by opening of the six-membered ring of 10a to give the zwitterionic vinylidene complex $\mathbf{C}$, 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 $\mathbf{1}^{\prime}$ and releases the six-membered trimerization product 8. It is less likely that the N atom will attack the $\mathrm{C} \alpha$ atom because of the lower stability of an eightmembered ring.

The crystal structure of the cocrystallization product of $\mathbf{1}^{\prime}$ and $\mathbf{8}$ 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

Table 5. Selected Bond Distances ( $\AA$ ) and Angles (deg) of Cp(dppe)RuCCPh•(PhNCS) 3

| 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) $\AA$, respectively. The $\mathrm{Ru}-\mathrm{C} 3$ bond length of $1.89(2) \AA$ is typical for a Ru$\mathrm{C}(\mathrm{sp})$ single bond, and the C3-C4 bond length of 1.186(2) $\AA$ 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) A.. The heterocydic six-membered ring is essentially planar (the distances of all constituent atoms to the plane are within the 0.029(10) and $-0.038(22) \AA$ range), with a slight double-bond character for all $\mathrm{C}-\mathrm{N}$ bonds.

The reaction of $\mathbf{1}^{\prime}$ with $\mathrm{PhCH}_{2} \mathrm{NCS}$ at room temperature afforded $\mathrm{Cp}($ dppe $) \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{S}) \mathrm{N}\left(\mathrm{CH}_{2} \mathrm{Ph}\right) \mathrm{C}$ $\left(=\mathrm{NCH}_{2} \mathrm{Ph}\right) \mathrm{S}(\mathbf{1 0 b})$ in moderate yield. At $5{ }^{\circ} \mathrm{C}$, the product was $\mathrm{Cp}($ dppe $) \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}\left(=\mathrm{NCH}_{2} \mathrm{Ph}\right) \mathrm{S}(9 b)$, which resulted from [2+2] cycloaddition of $\mathrm{PhCH}_{2} \mathrm{NCS}$ 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 $\mathbf{1}^{\prime}$ with PhNCO was carried out at $5{ }^{\circ} \mathrm{C}$, 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 $\mathbf{1 2}$ is stable at $5^{\circ} \mathrm{C}$ but decomposes at room temperature. The ${ }^{31} \mathrm{P}$ NMR resonance of 12 appears at $\delta 96.4$, and a weak resonance at $\delta 98.2$, 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, trimerization of phenyl isocyanate occurs in the presence of $\mathbf{1}^{\prime}$, giving $(\text { PhNCO })_{3} .{ }^{20}$ After 2 days, a ${ }^{31}$ P NMR resonance at $\delta$ 76.0 indi cates a major organometallic product, presum-

[^6]ably a vinylidene complex with a trimer unit bound to the acetylideligand. The acetylide complex is a catalyst in this reaction. Without this catalyst, the thermolysis of phenyl isocyanate in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ yields diphenylurea, (PhNH) ${ }_{2} \mathrm{CO}$.

Various metal-promoted coupling modes of isothiocyanates have been studied using a dirhenium complex ${ }^{21}$ and a dirhodium complex. ${ }^{22}$ In our system, transformation of isothiocyanates uses a metal-coordinated acetylide ligand. However, as can been seen in Schemes 1 and 2, the other ligands, such as dppe and a combination of $\mathrm{P}(\mathrm{OMe})_{3}$ and $\mathrm{PPh}_{3}$, play a crucial role in differentiating the conversion of $\mathbf{1 0}$ 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 heterocydic six-membered ring. For the cationic vinylidene complex with a $\mathrm{P}(\mathrm{OMe})_{3}$ ligand, an Arbuzovlike dealkylation of $\mathrm{P}(\mathrm{OMe})_{3}$ 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. $\mathrm{CH}_{3} \mathrm{CN}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ were distilled from $\mathrm{CaH}_{2}$ and diethyl ether and THF from $\mathrm{Na} / \mathrm{ketyl}$. 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 $\delta$ with residual protons in the solvent as an internal standard $\left(\mathrm{CDCl}_{3}, \delta 7.24 ; \mathrm{CD}_{3} \mathrm{CN}, \delta 1.93 ; \mathrm{C}_{2} \mathrm{D}_{6}\right.$ CO, $\delta$ 2.04). FAB mass spectra were recorded on a J EOL SX102A spectrometer and are reported in $\mathrm{m} / \mathrm{z}$ units. Complexes $\mathrm{Cp}(\mathrm{dppe}) \mathrm{RuC} \equiv \mathrm{CPh}\left(\mathbf{1}^{\prime}\right)$ and $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{RuC} \equiv \mathrm{CPh}^{23}$ 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 $\left.\mathbf{C p}\left(\mathrm{PPh}_{3}\right)[\mathbf{P ( O M e})_{3}\right] R u C \equiv \mathbf{C P h}$ (2). In a Schlenk flask charged with $\mathrm{P}(\mathrm{OMe})_{3}(7.70 \mathrm{~mL}, 63.30 \mathrm{mmol})$ and $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{RuC} \equiv \mathrm{CPh}(\mathbf{1} ; 10.00 \mathrm{~g}, 12.66 \mathrm{mmol})$, 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 precipitateformed. After filtration, the precipitate was washed with $2 \times 20 \mathrm{~mL}$ of pentane to give the product $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)-$ $\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC} \equiv \mathrm{CPh}(2 ; 7.60 \mathrm{~g}, 11.64 \mathrm{mmol}, 92 \%$ yield). Spectroscopic data for $\mathbf{2}$ are as follows. ${ }^{1} \mathrm{H}$ NMR: 7.69-6.86 (m, $20 \mathrm{H}, \mathrm{Ph}$ ); 4.64 ( $\mathrm{s}, 5 \mathrm{H}, \mathrm{Cp}$ ); 3.37 (d, J p-н $=11.6 \mathrm{~Hz}, 9 \mathrm{H}$, P(OMe) $)_{3}$. ${ }^{31} \mathrm{P}$ NMR: 158.3 (d, J p-p $\left.=64.5 \mathrm{~Hz}, \mathrm{P}(\mathrm{OMe})_{3}\right) ; 56.6$ (d, J p-p $=64.5 \mathrm{~Hz}, \mathrm{PPh}_{3}$ ). ${ }^{13} \mathrm{C}$ NMR: 139.2-122.9 (Ph); 130.3 ( $\mathrm{C}_{\alpha}$ ); $112.6\left(\mathrm{C}_{\beta}\right) ; 84.2(\mathrm{Cp}) ; 51.9$ ( $\mathrm{P}(\mathrm{OMe})_{3}$ ). Mass: $654.0\left(\mathrm{M}^{+}\right)$, $553.1\left(\mathrm{M}^{+}-\mathrm{C}_{2} \mathrm{Ph}\right) ; 428.9\left(\mathrm{M}^{+}-\mathrm{C}_{2} \mathrm{Ph}, \mathrm{P}(\mathrm{OMe})_{3}\right)$. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{34} \mathrm{O}_{3} \mathrm{P}_{2} \mathrm{Ru}: \mathrm{C}, 62.47 ; \mathrm{H}, 5.24$. Found: C, $62.68 ; \mathrm{H}, 5.32$.

[^7]Reaction of $\mathbf{2}$ with PhNCS. To a Schlenk flask charged with $2(0.50 \mathrm{~g}, 0.76 \mathrm{mmol})$ was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$, and PhNCS ( $0.92 \mathrm{~mL}, 7.66 \mathrm{mmol}$ ) 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 sol vent 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 orangeyellow 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 -
$\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right] \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(=\mathrm{NPh}) S(\mathbf{3 a})$. The yield of $\mathbf{3 a}$ after recrystallization from hexane/ $\mathrm{CH}_{2} \mathrm{Cl}_{2}(1: 1)$ is $0.38 \mathrm{~g}(63 \%$ yield). After a similar workup procedure, the brown band gave the orange-red phosphonate complex $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(=\mathrm{O})(\mathrm{OMe})_{2}\right]$ $\mathrm{Ru}=\mathrm{C}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(\mathrm{SH})=\mathrm{NPh}$ (4a; $0.030 \mathrm{~g}, 5 \%$ yield). Spectroscopic data for 3a are as follows. ${ }^{1} \mathrm{H}$ NMR: 7.29-7.00 ( $\mathrm{m}, 20$ H, Ph); 4.75 (s, 5H, Cp); 3.37 (d, J p-H $\left.=11.0 \mathrm{~Hz}, 9 \mathrm{H}, \mathrm{P}(\mathrm{OMe})_{3}\right)$. ${ }^{31}$ P NMR: $151.7\left(\mathrm{~d}, \mathrm{~J}\right.$ p-p $\left.=68.9 \mathrm{~Hz}, \mathrm{P}(\mathrm{OMe})_{3}\right) ; 56.2\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{p}-\mathrm{p}}=\right.$ $68.9 \mathrm{~Hz}, \mathrm{PPh}_{3}$ ). ${ }^{13} \mathrm{C}$ NMR: $134.1-122.7$ ( $\mathrm{Ph}, \mathrm{C}_{\beta}, \mathrm{C}_{\gamma}$ ); $84.8(\mathrm{Cp})$; 52.3 (d, J c-p $\left.=7.5 \mathrm{~Hz}, \mathrm{P}(\mathrm{OMe})_{3}\right)$. Mass: $790.2\left(\mathrm{M}^{+}\right), 553.1$ ( $\mathrm{M}^{+}-\mathrm{C}_{2} \mathrm{Ph}$ ); $429.1\left(\mathrm{M}^{+}-\mathrm{C}_{2} \mathrm{Ph}, \mathrm{P}(\mathrm{OMe})_{3}\right)$. Anal. Calcd for $\mathrm{C}_{41} \mathrm{H}_{39} \mathrm{NO}_{3} \mathrm{P}_{2} \mathrm{SRu}: \mathrm{C}, 62.42 ; \mathrm{H}, 4.98 ; \mathrm{N}, 1.78$. Found: C, 61.99; H, 5.12; N, 1.73. Spectroscopic data for 4a are as follows. ${ }^{1} \mathrm{H}$ NMR: 7.70-6.70 (m, $20 \mathrm{H}, \mathrm{Ph}$ ); 5.26 (s, 5H, Cp); 3.18 (d, J p-н $=11.5 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OMe}) ; 3.03(\mathrm{~d}, \mathrm{~J} \mathrm{p}-\mathrm{H}=11.5 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OMe}) .{ }^{13} \mathrm{C}$ NMR: $345.2\left(\mathrm{t}, \mathrm{J} \mathrm{c}-\mathrm{p}=17.1 \mathrm{~Hz}, \mathrm{C}_{\alpha}\right) ; 137.9-123.4\left(\mathrm{Ph}, \mathrm{C}_{\beta}, \mathrm{C}_{\gamma}\right)$; $93.0(\mathrm{Cp}) ; 52.2(\mathrm{~d}, \mathrm{~J}$ c-p $=8.6 \mathrm{~Hz}, \mathrm{OMe}) ; 51.8(\mathrm{~d}, \mathrm{~J}$ c-p $=8.4$ $\mathrm{Hz}, \mathrm{OMe})$. ${ }^{31} \mathrm{p}$ NMR: 95.3 (d, J p-p $\left.=45.9 \mathrm{~Hz}, \mathrm{P}(\mathrm{OMe})_{2}\right) ; 48.0$ (d, J p-p $=45.9 \mathrm{~Hz}, \mathrm{PPh}_{3}$ ). Mass: $776.0\left(\mathrm{M}^{+}\right), 744.0\left(\mathrm{M}^{+}-\mathrm{S}\right)$; $539.0\left(\mathrm{M}^{+}-\mathrm{C}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(\mathrm{SH}) \mathrm{C}=\mathrm{NPh}\right)$. Anal. Calcd for $\mathrm{C}_{40} \mathrm{H}_{37} \mathrm{NO}_{3} \mathrm{P}_{2} \mathrm{SRu}: \mathrm{C}, 62.00 ; \mathrm{H}, 4.81 ; \mathrm{N}, 1.81$. Found: $\mathrm{C}, 61.74$; H, 5.01; N, 1.70. The ${ }^{31}$ P NMR spectrum of the crude product (after 3 days of reaction time) displayed the resonances attributed to 3 a and $\mathbf{4 a}$ in a 9:1 ratio.

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

Reaction of $\mathbf{2}$ with $\mathbf{P h C H}_{\mathbf{2}} \mathbf{N C S}$. In a Schlenk flask charged with $2(0.50 \mathrm{~g}, 0.76 \mathrm{mmol}), \mathrm{PhCH}_{2} \mathrm{NCS}(1.01 \mathrm{~mL}, 766$ mmol ) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$ 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 $2 \times 15 \mathrm{~mL}$ of hexane to give the solid product $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(\mathrm{OMe})_{3}\right]$ -
$\mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(\mathrm{S}) \mathrm{N}\left(\mathrm{CH}_{2} \mathrm{Ph}\right) \mathrm{C}\left(=\mathrm{NCH}_{2} \mathrm{Ph}\right) \mathrm{S}(5 \mathbf{b} ; 0.42 \mathrm{~g}, 58 \%$ yield). The orange band, after the same treatment, gave the orange phosphonate complex $\mathrm{Cp}\left(\mathrm{PPh}_{3}\right)\left[\mathrm{P}(=\mathrm{O})(\mathrm{OMe})_{2}\right]$ $\mathrm{Ru}=\mathrm{C}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(\mathrm{SH})=\mathrm{NCH}_{2} \mathrm{Ph}(4 \mathbf{b} ; 0.06 \mathrm{~g}, 10 \%$ yield). Spectroscopic data for $\mathbf{5 b}$ are as follows. ${ }^{1} \mathrm{H}$ NMR: 7.35-6.99 (m, $30 \mathrm{H}, \mathrm{Ph}$ ); 6.19 (d, J н-н $=12.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Ph}$ ); 6.02 (d, J н-н
$=12.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Ph}$ ); $4.34(\mathrm{~s}, 5 \mathrm{H}, \mathrm{Cp}) ; 3.92\left(\mathrm{~d}, \mathrm{~J}_{\text {н-н }}=16.9\right.$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Ph}$ ); 3.84 (d, J $\mathrm{J}_{-\mathrm{H}}=16.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Ph}$ ); 3.35 $\left(\mathrm{d}, \mathrm{J}_{\mathrm{p}-\mathrm{H}}=10.9 \mathrm{~Hz}, 9 \mathrm{H}, \mathrm{P}(\mathrm{OMe})_{3}\right) .{ }^{31} \mathrm{P}$ NMR: $148.6(\mathrm{~d}, \mathrm{~J} \mathrm{p}-\mathrm{p}=$ $\left.73.3 \mathrm{~Hz}, \mathrm{P}(\mathrm{OMe})_{3}\right) ; 57.9$ (d, J p-p $=73.3 \mathrm{~Hz}, \mathrm{PPh}_{3}$ ). ${ }^{13} \mathrm{C}$ NMR: 134.1-122.7 (Ph, C ${ }_{\beta}, \mathrm{C}_{\gamma}$ ); $84.8(\mathrm{Cp}) ; 52.3(\mathrm{~d}, \mathrm{~J}$ c-p $=7.5 \mathrm{~Hz}$, $\left.\mathrm{P}(\mathrm{OMe})_{3}\right)$. Mass: $790.2\left(\mathrm{M}^{+}\right)$, $553.1\left(\mathrm{M}^{+}\right.$- organic ligand); 429.1 ( $\mathrm{M}^{+}$- organic ligand, $\mathrm{P}(\mathrm{OMe})_{3}$ ). Anal. Calcd for $\mathrm{C}_{50} \mathrm{H}_{48} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{P}_{2} \mathrm{~S}_{2} \mathrm{Ru}: \mathrm{C}, 63.08 ; \mathrm{H}, 5.08 ; \mathrm{N}, 2.94$. Found: C, 62.95; H, 5.04; N, 3.12. Spectroscopic data for $\mathbf{4 b}$ are as follows. ${ }^{1} \mathrm{H}$ NMR: 10.86 (s, 1H, SH ); 7.63-6.67 (m, $20 \mathrm{H}, \mathrm{Ph}$ ); 5.19 (s, 5H, Cp); 3.07 (d, J p-H $=11.2 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OMe}$ ); 2.97 (d, $\left.\mathrm{J}_{\mathrm{P}-\mathrm{H}}=11.5 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OMe}\right) ; 2.44\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=7.3 \mathrm{~Hz}, 1 \mathrm{H},-\mathrm{NCH}_{2^{-}}\right.$ Ph); 2.39 (d, J ${ }_{\mathrm{H}-\mathrm{H}}=7.3 \mathrm{~Hz}, 1 \mathrm{H},-\mathrm{NCH}_{2} \mathrm{Ph}$ ). ${ }^{13} \mathrm{C}$ NMR: 343.5 (t, J c-p = $17.0 \mathrm{~Hz}, \mathrm{C}_{\alpha}$ ); 142.4-126.8 (Ph, C ${ }_{\beta}, \mathrm{C}_{\gamma}$ ); 92.9 (Cp); 50.5 (d, J c-p $=9.4 \mathrm{~Hz}, \mathrm{OMe}) ; 50.1$ (d, J c-p $=8.4 \mathrm{~Hz}, \mathrm{OMe}$ ). ${ }^{31} \mathrm{P}$ NMR: $95.2\left(\mathrm{~d}, \mathrm{~J} \mathrm{p}-\mathrm{p}=45.8 \mathrm{~Hz}, \mathrm{P}(\mathrm{OMe})_{2}\right) ; 49.3(\mathrm{~d}, \mathrm{~J} \mathrm{p}-\mathrm{p}=$ $45.8 \mathrm{~Hz}, \mathrm{PPh}_{3}$ ). Mass: $790.0\left(\mathrm{M}^{+}\right), 758.0\left(\mathrm{M}^{+}-\mathrm{S}\right), 539.0\left(\mathrm{M}^{+}\right.$ - organicligand); 428.9 ( $\mathrm{M}^{+}$- organic ligand, $\left.\mathrm{P}(\mathrm{OMe})_{3}\right)$. Anal. Calcd for $\mathrm{C}_{41} \mathrm{H}_{39} \mathrm{NO}_{3} \mathrm{P}_{2} \mathrm{SRu}: \mathrm{C}, 62.42 ; \mathrm{H}, 4.98 ; \mathrm{N}, 1.78$. Found: C, 62.57; H, 4.64; N, 1.95.

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

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

Reaction of $\mathbf{C p}($ dppe $)$ RuC $\equiv \mathbf{C P h}\left(1^{\prime}\right)$ with PhNCS. In a Schlenk flask charged with $\mathbf{1}^{\prime}(0.30 \mathrm{~g}, 0.46 \mathrm{mmol})$, PhNCS ( $0.55 \mathrm{~mL}, 4.59 \mathrm{mmol}$ ) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$ were added; the mixture was stirred at room temperature for 4 days and the col or of the solution changed from bright yellow to brown. The solvent was removed under vacuum and the residue was washed with $2 \times 30 \mathrm{~mL}$ 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 $\mathrm{g}, 72 \%$ yield). Spectroscopic data for 9 a are as follows. ${ }^{1} \mathrm{H}$ NMR: 7.80-6.30 (m, $30 \mathrm{H}, \mathrm{Ph}$ ); 4.50 ( $\mathrm{s}, 5 \mathrm{H}, \mathrm{Cp}$ ); 2.60-2.47 ( $\mathrm{m}, 4 \mathrm{H}, \mathrm{PCH}_{2}$ ). ${ }^{13} \mathrm{C}$ NMR: $133.7-122.6\left(\mathrm{Ph}, \mathrm{C}_{\beta}, \mathrm{C}_{\gamma}\right) ; 84.6(\mathrm{Cp})$;
$29.3\left(\mathrm{t}, \mathrm{J}_{\mathrm{c}-\mathrm{p}}=21.5 \mathrm{~Hz}, \mathrm{CH}_{2}\right)$. ${ }^{31} \mathrm{P} \mathrm{NMR}$ : $93.9\left(\mathrm{PPh}_{2}\right)$. FAB mass: $801.0\left(\mathrm{M}^{+}\right), 565.0\left(\mathrm{M}^{+}\right.$- organic ligand). Anal. Calcd for $\mathrm{C}_{46} \mathrm{H}_{39} \mathrm{NP}_{2} \mathrm{SRu}$ : 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 $\mathrm{Cp}($ dppe)RuC=C-
(Ph)C(S)N (Ph)C(=NPh)S (10a; $0.28 \mathrm{~g}, 65 \%$ yield) was isolated. Spectroscopic data for 10a are as follows. ${ }^{1} \mathrm{H}$ NMR: 7.756.94 (m, $35 \mathrm{H}, \mathrm{Ph}$ ); 3.68 (s, 5H, Cp); 2.65-2.30 (m, 4 H, PCH 2 ). ${ }^{13} \mathrm{C}$ NMR: 151.0-121.5 (Ph, $\mathrm{C}_{\beta}, \mathrm{C}_{\gamma}$ ); 85.1 (Cp); 30.7 (t, J c-p $=$ $22.0 \mathrm{~Hz}, \mathrm{CH}_{2}$ ). ${ }^{31} \mathrm{P}$ NMR: $99.3\left(\mathrm{PPh}_{2}\right)$. Mass: $936.0\left(\mathrm{M}^{+}+\right.$ 1), 565.0 ( $\mathrm{M}^{+}$- organic ligand). Anal. Calcd for $\mathrm{C}_{53} \mathrm{H}_{44} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{~S}_{2^{-}}$ Ru: C, 68.00; H, 4.74; N, 2.99. Found: C, 67.79; H, 5.01; N, 2.85.

Reaction of $\mathbf{1}^{\prime}(0.30 \mathrm{~g}, 0.46 \mathrm{mmol})$ with $\mathrm{PhCH}_{2} \mathrm{NCS}(0.61$ $\mathrm{mL}, 4.58 \mathrm{mmol}$ ) was carried out in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$ 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)-
$\mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}(\mathrm{S}) \mathrm{N}\left(\mathrm{CH}_{2} \mathrm{Ph}\right) \mathrm{C}\left(=\mathrm{NCH}_{2} \mathrm{Ph}\right) \mathrm{S}(\mathbf{1 0 b} ; 0.27 \mathrm{~g}, 62 \%$ yield). Spectroscopic data for 10b are as follows. ${ }^{1} \mathrm{H}$ NMR: 7.62-6.75 (m, $35 \mathrm{H}, \mathrm{Ph}$ ); 5.96 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Ph}$ ); 3.56 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CH}_{2^{-}}$ Ph); 3.84 (s, 5H, Cp); 2.90-2.58 (m, $4 \mathrm{H}, \mathrm{PCH}_{2}$ ). ${ }^{13} \mathrm{C}$ NMR: 184.8, 151.4, 143.3-125.6 (Ph, $\mathrm{C}_{\beta}, \mathrm{C}_{\gamma}$ ); $84.8(\mathrm{Cp}) ; 52.4,51.6$ (2 $\left.\times \mathrm{CH}_{2} \mathrm{Ph}\right) ; 30.0\left(\mathrm{~J} \mathrm{c-p}=22.2 \mathrm{~Hz}, \mathrm{CH}_{2}\right) .{ }^{31} \mathrm{P} \mathrm{NMR}: 88.4(\mathrm{~s}$, $\mathrm{PPh}_{2}$ ). Mass: $965.1\left(\mathrm{M}^{+}+1\right), 565.0\left(\mathrm{M}^{+}-\right.$organic ligand). Anal. Calcd for $\mathrm{C}_{55} \mathrm{H}_{48} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{~S}_{2} \mathrm{Ru}$ : C, 68.52; $\mathrm{H}, 5.01 ; \mathrm{N}, 2.91$. Found: C, 68.75; H, 4.84; N, 3.18. If the same reaction is carried out at $5{ }^{\circ} \mathrm{C}$ for 5 days, the two products Cp (dppe)-
$\mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}\left(=\mathrm{NCH}_{2} \mathrm{Ph}\right) \mathrm{S}(\mathbf{9 b})$ and 10b in a $1: 4$ ratio are observed in the NMR spectrum. $\mathbf{9 b}$ is unstable and is converted to 10b in about 2 h at room temperature. Spectroscopic data for 9b are as follows. ${ }^{1} \mathrm{H}$ NMR: 7.69-6.85 (m, 30 H, Ph); 4.43 (s, 2H, CH2 Ph); 3.91 (s, 5H, Cp); 2.90-2.60 (m, 4 $\mathrm{H}, \mathrm{PCH}_{2}$ ). ${ }^{31} \mathrm{P}$ NMR: 94.5 (s, $\mathrm{PPh}_{2}$ ). Mass: 816.1 ( $\mathrm{M}^{+}+1$ ), $565.0\left(\mathrm{M}^{+}-\right.$organic ligand).

Trimerization of PhNCS on $\mathbf{C p}($ dppe)RuC $\equiv \mathbf{C P h}$. A Schlenk flask was charged with $\mathbf{1}^{\prime}(0.07 \mathrm{~g}, 0.11 \mathrm{mmol})$, and the atmosphere was replaced with nitrogen; then PhNCS ( 0.55 $\mathrm{mL}, 4.59 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$ were introduced and the mixture was heated to reflux. The ${ }^{31} \mathrm{P}$ 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 $2 \times 30 \mathrm{~mL}$ of hexane to give a brown-black product. After filtration, the solid was further washed with 20 mL of pentane, giving the product $(\mathrm{PhNCS})_{3}(8 ; 0.26 \mathrm{~g}, 72 \%$ yield). Spectroscopic data are consistent with those in the literature. ${ }^{14}$

Trimerization of PhNCO on Cp(dppe)RuC $\equiv \mathbf{C P h}$. A Schlenk flask was charged with $\mathbf{1}^{\prime}(0.10 \mathrm{~g}, 0.15 \mathrm{mmol})$, and the atmosphere was replaced with nitrogen; then PhNCO (1.00 $\mathrm{mL}, 1.50 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$ were introduced and the mixture was stored at $5{ }^{\circ} \mathrm{C}$ 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 el uted 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 $\mathrm{Cp}($ dppe $) \mathrm{RuC}=\mathrm{C}(\mathrm{Ph}) \mathrm{C}-$

[^8]$\mathrm{C}_{2} \mathrm{Ph}$ ). Anal. Calcd for $\mathrm{C}_{53} \mathrm{H}_{44} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{P}_{2} \mathrm{Ru}: \mathrm{C}, 70.42 ; \mathrm{H}, 4.91$; N, 3.10. Found: C, 70.63; H, 4.78; N, 3.34.

A Schlenk flask was charged with $\mathbf{1}^{\prime}(0.20 \mathrm{~g}, 0.31 \mathrm{mmol})$, and the atmosphere was repl aced with nitrogen; then PhNCO ( $1.00 \mathrm{~mL}, 9.21 \mathrm{mmol}$ ) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$ 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 col or 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 thestarting 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; $0.45 \mathrm{~g}, 41 \%$ yield). Spectroscopic data for $8 \mathbf{a}$ are consistent with those in the literature. ${ }^{14}$

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 $0.20 \times 0.20 \times 0.30 \mathrm{~mm}^{3}$ 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 $7^{\circ} \mathrm{min}^{-1}$.
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. Crystallgraphic computations were carried out on a Microvax III computer using the NRCC structure determination package. ${ }^{24}$ Merging of equivalent and duplicate reflections gave a total of 5303 unique measured data, from which 3077 were considered observed (I > 2.0 $0(\mathrm{I})$ ). 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 leastsquares program was $w\left(\left|F_{d}\right|-\mid F_{c}\right)^{2}$. The analytical forms of the scattering factor tables for the neutral atoms were used. ${ }^{25}$ 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 $\mathrm{R}=0.042$ and $\mathrm{R}_{\mathrm{w}}=$ 0.040 . The procedures for $\mathbf{4 a}, \mathbf{5 b}$, and the cocrystallization product of $\mathbf{1}$ ' and $\mathbf{8}$ 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 $\mathbf{4 b}, 5 \mathbf{b}$, and the cocrystallization product of $\mathbf{1}^{\prime}$ and $\mathbf{8}$, respectively. Final values of all refined atomic positional parameters (with esd's) and tables of thermal parameters are given in the Supporting Information.

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Supporting Information Available: Details of the structural determination for complexes $\mathbf{3 a} \mathbf{a} \mathbf{4 a}$, and $\mathbf{5 b}$ and the cocrystallization product of $\mathbf{1}^{\prime}$ and $\mathbf{8}$, 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.

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