Ruthenium-Assisted Insertion of Isothiocyanates into the Silicon−Sulfur Bond: A Comparative Study on the Reactivity of the S−Si and S−H Bonds in $CpRu(PPh_3)_2SX$ (X = H, Si^iPr_3) Complexes†

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$CpRu(PPh_3)_2SSi^iPr_3$ (**1**) and $CpRu(PPh_3)_2SH$ (**2**) reacted with phenyl, *p*-tolyl, and 1-naphthyl isothiocyanates, as well as with 1,4-phenylene diisothiocyanate, to give the corresponding κ^2S,S-dithiocarbamato complexes, $CpRu(PPh_3)S_2CNR^1R^2$ (R^1 = Si^iPr_3, R^2 = Ph (**3a**), *p*-Tol (**3b**), 1-Naphth (**3c**); R^1 = H, R^2 = Ph (**3d**), 1-Naphth (**3e**)) and 1,4-$[CpRu(PPh_3)S_2CNR]_2C_6H_4$ (R = Si^iPr_3 (**4a**), H (**4b**)), the result of insertion of the isothiocyanates into the S−Si and S−H bonds, respectively. The reactions of **1** proceed via precoordination of the isothiocyanates to the ruthenium atom, followed by the formation of *N*-silyl κ^2S,S-dithiocarbamates. The reactions of **2**, at least in part, involve direct nucleophilic addition of the S−H bond to the isothiocyanates via κ^1S-dithiocarbamato intermediates. Accordingly, $CpRu(dppe)SSi^iPr_3$, where ligand exchange does not occur, did not react, but CpRu(dppe)SH reacted with phenyl and 1-naphthyl isothiocyanate to give the corresponding κ^1S-dithiocarbamato complexes, CpRu(dppe)SC(S)NHR (R = Ph (**9a**), 1-Naphth (**9b**)), the reaction with 1-naphthyl isothiocyanate being reversible. The crystal structures of **3c** and **4a** have been determined by X-ray diffraction.

Introduction

The reaction of sulfhydryl complexes, M−SH, to give hydrothiosulfito species, M−SS(O)OH, has been suggested as a possible key step in the homogeneously catalyzed Claus reaction[1] and SO_2 hydrogenation.[2] The insertion of SO_2 into the silicon−sulfur bond of ruthenium silanethiolato complexes of the type $CpRuL_2SSi^iPr_3$ to give *O*-silyl thiosulfito complexes, $CpRuL_2SS(O)OSi^iPr_3$, has been reported recently.[3] Thus, the $-SSiR_3$ function in some silanethiolates and the −SH function in some hydrosulfides seemed to have analogous chemistry. Reports on the deprotonation of $Cp_2Ti(SH)_2$[4] and analogous desilation of $[Ru(N)Me_3(SSiMe_3)]^-$,[5] which are believed to take place via common M−S$^-$ type intermediates, support this assumption. However, none of these analogies were confirmed unambiguously, as no products of the type M−SS(O)OH or M−S$^-$ were detected and no *O*-silyl thiosulfito complex was isolated due to their instability. The only direct comparative study, of the reactions of $CpRu(PPh_3)_2SSi^iPr_3$ (**1**) and its hydrosulfido congener $CpRu(PPh_3)_2SH$ (**2**) with SO_2 and PhNSO, gave contrasting results.[3] Complex **1** readily afforded the ligand-substitution product $CpRu(PPh_3)(SO_2)SSi^iPr_3$ and subsequently the insertion product $CpRu(PPh_3)_2SS(O)OSi^iPr_3$. While **2** also reacted with SO_2, no product could be identified. On the other hand, the S−H bond of **2** readily added to PhNSO to give $CpRu(PPh_3)_2SS(O)NHPh$, but the silicon−sulfur bond of **1** remained indifferent (**1** underwent reversible ligand substitution to give $CpRu(PPh_3)(PhNSO)SSi^iPr_3$ in low yield).

The contrasting behavior of the $-SSi^iPr_3$ function of **1** toward SO_2 and PhNSO, as well as the problem of the analogy between silanethiolato and sulfhydryl complexes, prompted us to study the reactions of $CpRu(PPh_3)_2SSi^iPr_3$ and $CpRu(PPh_3)_2SH$ with heterocumulenes. Here we give an account of their reactions with aryl isothiocyanates and report the crystal and molecular structures of $CpRu(PPh_3)S_2CN(Si^iPr_3)Naphth$ (**3c**) and 1,4-$[CpRu(PPh_3)S_2CN(Si^iPr_3)]_2C_6H_4$ (**4a**).

Results

Reaction of $CpRu(PPh_3)_2SSi^iPr_3$ (1) with Aryl Isothiocyanates. $CpRu(PPh_3)_2SSi^iPr_3$ (**1**) reacted readily with equimolar amounts of RNCS (R = Ph, *p*-Tol, 1-Naphth) in THF at room temperature to give the corresponding *N*-silyl κ^2S,S-dithiocarbamato complexes in accordance with eq 1. The new complexes $CpRu(PPh_3)S_2CN(Si^iPr_3)R$ (R = Ph (**3a**), *p*-Tol (**3b**), 1-Naphth

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$$\mathrm{CpRu(PPh_3)_2SSi^iPr_3} + \mathrm{RNCS} \rightarrow \underset{\mathbf{1}}{} \qquad \underset{\mathbf{3a-c}}{\mathrm{CpRu(PPh_3)S_2CN(Si^iPr_3)R}} + \mathrm{PPh_3} \quad (1)$$

(**3c**)) were isolated by crystallization as air and thermally stable, yellow to orange crystals in good yield. When **1** was treated with PhNCS in benzene-d_6, ^{1}H and ^{31}P NMR spectroscopic monitoring indicated quantitative formation of **3a** and free PPh_3 in 1:1 molar ratio upon mixing. However, when this experiment was repeated with $CpRu(dppe)SSi^iPr_3$, the starting materials remained unchanged at room temperature for at least one week.

Complexes **3a**−**c** were characterized by elemental analysis and multinuclear NMR spectroscopy, and the results are in complete agreement with the suggested structures. In particular, the ^{1}H, ^{13}C, and ^{31}P NMR spectra for all three complexes exhibited Cp proton (δ 4.4) and carbon (ca. δ 77), S_2CN carbon (ca. δ 228), ^{i}Pr carbon (ca. δ 14 (CH), 19 (CH_3)), and phosphorus resonances (ca. δ 54) at nearly identical positions, suggesting similar structures and negligible substituent effects. The Cp and PPh_3 resonances agree well with the literature data for $CpRu(PPh_3)S_2CNMe_2$.[6] Integration of the proton spectra indicated the presence of only one PPh_3 ligand in each molecule. Similarly, the S_2CN carbon atoms resonated as a doublet, suggesting P−C coupling with one phosphine only. Curiously, no such carbon resonances were detected for η^5-$C_5R_5RuLS_2CNEt_2$ (R = H, Me; L = P^iPr_2Me, PEt_3) type κ^2S,S-dithiocarbamato complexes, which was attributed to the effect of the quadrupolar ^{14}N nucleus.[7] The ^{1}H NMR spectrum of **3c** exhibited two sets of methyl doublets of equal intensity, which were temperature invariant in the range 20−100 °C, while only one methyl doublet was observed for **3a**,**b**. This difference is probably due to a strong steric interaction between the bulky Si^iPr_3 and naphthyl groups that hinders rotation in the ligand of **3c**.

The crystal structure of **3c** was determined by X-ray diffraction (Figure 1) and verified the presence of the N−Si bond in the dithiocarbamato group. Most of the bond lengths and angles in the $CpRu(PPh_3)S_2CN$ moiety show negligible deviation from those of $CpRu(PPh_3)S_2CNMe_2$ in both of its polymorphic forms.[6,8] The geometry around the nitrogen atom is nearly planar as the N−Si bond subtends an angle of only 9° with the plane defined by the atoms C(33), C(34), and N.

The reaction of 1,4-phenylene diisothiocyanate with 2 equiv of **1** in THF at room temperature gave 1,4-$[CpRu(PPh_3)S_2CN(Si^iPr_3)]_2C_6H_4$ (**4a**) along with 2 equiv of free PPh_3 as shown in eq 2. The ^{31}P NMR spectrum

$$2\ \mathrm{CpRu(PPh_3)_2SSi^iPr_3} + \text{1,4-}(\mathrm{SCN})_2\mathrm{C_6H_4} \rightarrow \underset{\mathbf{1a}}{} \qquad \underset{\mathbf{4a}}{\text{1,4-}[\mathrm{CpRu(PPh_3)S_2CN(Si^iPr_3)}]_2\mathrm{C_6H_4}} + 2\ \mathrm{PPh_3} \quad (2)$$

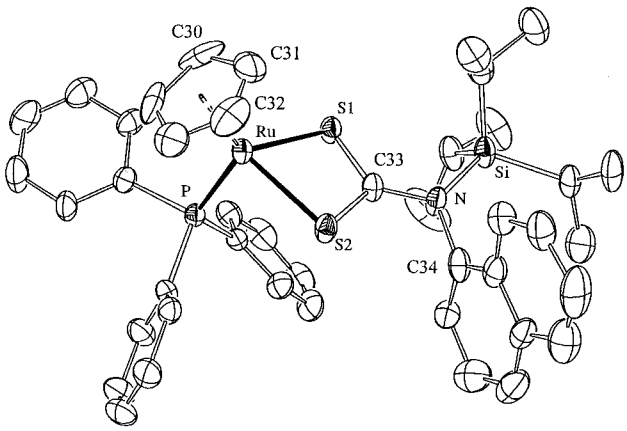

Figure 1. ORTEP drawing of $CpRu(PPh_3)S_2CN(Si^iPr_3)$-Naphth (**3c**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Ru−S(1), 2.387(3); Ru−S(2), 2.394(2); Ru−P, 2.269(2); S(1)−C(33), 1.690(6); S(2)−C(33), 1.708(6); N−C(33), 1.377(7); Si−N, 1.824(5); N−C(34), 1.505(9); S(1)−Ru−S(2), 71.69(8); S(1)−Ru−P, 95.02(9); S(2)−Ru−P, 92.56(9); Ru−S(1)−C(33), 88.8(2); Ru−S(2)−C(33), 88.1(2); S(1)−C(33)−S(2), 111.0(3); S(1)−C(33)−N, 125.8(4); S(2)−C(33)−N, 123.2(5); C(33)−N−Si, 122.5(4); C(33)−N−C(34), 115.9(5); Si−N−C(34), 121.0(4).

of **4a** exhibited a singlet resonance at δ54.7 and one set of ^{i}Pr, Cp, and PPh_3 proton and carbon resonances were observed in its ^{1}H and ^{13}C NMR spectra at expected positions. These spectroscopic features are very similar to those of the mononuclear complexes **3a**,**b** and suggested equivalent $CpRu(PPh_3)S_2CN(Si^iPr_3)$ units in a symmetric molecule.

The crystal structure of **4a** was determined by X-ray diffraction and is shown in Figure 2. The structural analysis unambiguously established that each −NCS function of 1,4-phenylene diisothiocyanate inserted into the S−Si bond of two molecules of **1** to form a phenylene-bridged, dimeric *N*-silyl κ^2S,S-dithiocarbamato structure. Complex **4a** has a center of symmetry, consistent with NMR observations. The bond lengths and angles in the $CpRu(PPh_3)S_2CN(Si^iPr_3)$ moieties are nearly identical with those in **3c**. It is noteworthy that the phenylene ring is eclipsed with one phenyl ring of each PPh_3 ligand and the phenyl planes are parallel to each other. On the macromolecular level, **4a** is packed to form parallel layers separated by hexane molecules. The hexane molecules are crystallographically disordered and do not form a stoichiometric ratio with the complex: 1.4 hexanes were calculated to be present in the unit cell, which agrees well with the value of 1.6 obtained from analytical data.

Reaction of $CpRu(PPh_3)_2SH$ (2) with Aryl Isothiocyanates. $CpRu(PPh_3)_2SH$ (**2**), treated with RNCS (R = Ph, 1-Naphth) in benzene at room temperature, gave ultimately the corresponding κ^2S,S-dithiocarbamato complexes, $CpRu(PPh_3)S_2CNHR$ (R = Ph (**3d**), 1-Naphth (**3e**)), as shown in eq 3. Complex **3e** was

$$\mathrm{CpRu(PPh_3)_2SH} + \mathrm{RNCS} \rightarrow \underset{\mathbf{2}}{} \qquad \underset{\mathbf{3d,e}}{\mathrm{CpRu(PPh_3)S_2CNHR}} + \mathrm{PPh_3} \quad (3)$$

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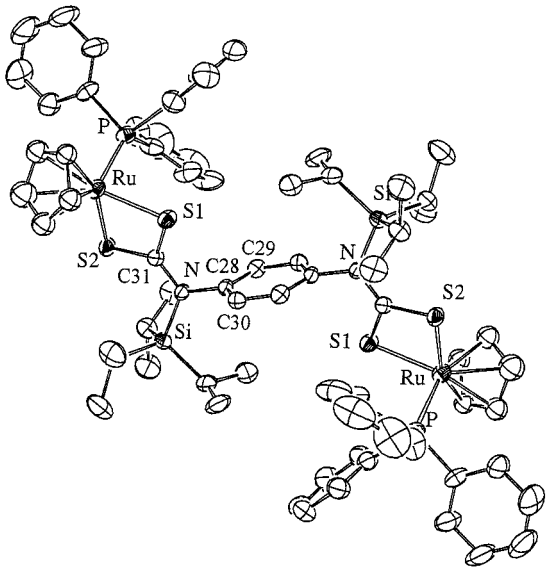


Figure 2. ORTEP drawing of 1,4-[CpRu(PPh$_3$)S$_2$CN(Si-^{i}Pr$_3$)]$_2$C$_6$H$_4$ (**4a**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Ru−S(1), 2.381(2); Ru−P, 2.275(2); S(1)−C(31), 1.700(5); S(2)−C(31), 1.706(5); N−C(31), 1.376(6); Si−N, 1.794(7); N−C(28), 1.445(6); S(1)−Ru−P, 89.64(7); Ru−S(1)−C(31), 89.1(2); Ru−S(2)−C(31), 88.6(2); S(1)−C(31)−N, 124.7(4); S(2)−C(31)−N, 125.2(4); C(31)−N−Si, 124.0(3); C(31)−N−C(28), 113.3(4); Si−N−C(28), 122.2(3).

isolated as air-stable, orange microcrystals, and **3d** was identified in solution. Their ^{1}H and ^{31}P NMR spectra are practically identical with the corresponding resonances for **3a**−**c**, suggesting similar κ^2S,S-dithiocarbamato structures. The S$_2$CN carbon doublet for **3e** was detected at δ 217.4, about 10 ppm upfield from those for **3a**−**c** but close to that for CpRu(PPh$_3$)S$_2$CNMe$_2$.[6] The NH proton resonances for **3d**,**e** were observed at δ 7.43 and 7.82, respectively, as broad singlets.

Monitoring the reactions of **2** by ^{1}H and ^{31}P NMR spectroscopy in benzene-d_6 confirmed the quantitative formation of a 1:1 mixture of **3d**,**e** and free PPh$_3$. In addition, the following observations were made. (1) When the reagents were applied in a stoichiometric ratio, both PhNCS and 1-NaphthNCS reacted at a comparable rate (**2** was consumed in about 1 h). (2) The NH proton resonance and, to a lesser extent, the *ortho* proton resonance(s) of NPh and NNaphth in **3d**,**e** shifted upfield as the reactions progressed. The NH resonance was first observed about 0.25 ppm downfield from its final position, while the *ortho* proton resonances moved only about 0.05 ppm upfield for both complexes. Once the reactions were complete, these resonances did not show any significant change in the temperature range between 20 and 70 °C. (3) In the reaction of PhNCS with **2** a second, transient species was detected in addition to **3d**, which ultimately transformed into **3d**. This minor species was tentatively identified as the κ^1S-dithiocarbamate CpRu(PPh$_3$)$_2$SC(S)NHPh (**5**) on the basis of its phosphorus (δ 42.2), Cp proton (δ 4.78), and NH proton (δ 9.21) resonances. Unlike the NH proton resonance for **3d**, that for **5** did not change its position during the reaction, ruling out a κ^1−κ^2 equilibrium. The naphthyl analogue, CpRu(PPh$_3$)$_2$SC(S)NHNaphth, was not detected.

The reaction of 1,4-phenylene diisothiocyanate with 2 equiv of **2** ultimately gave the anticipated dinuclear κ^2S,S-dithiocarbamato complex 1,4-[CpRu(PPh$_3$)S$_2$CNH]$_2$-C$_6$H$_4$ (**4b**) in accordance with eq 4 as orange microcrystals. Consistent with its symmetrical structure and the κ^2S,S-coordination mode of dithiocarbamato functions a singlet phosphorus resonance was observed at δ 54.1.

$$2\ \underset{\mathbf{2}}{\text{CpRu(PPh}_3)_2\text{SH}} + \text{1,4-(SCN)}_2\text{C}_6\text{H}_4 \rightarrow \underset{\mathbf{4b}}{\text{1,4-[CpRu(PPh}_3)\text{S}_2\text{CNH]}_2\text{C}_6\text{H}_4} + 2\ \text{PPh}_3 \quad (4)$$

When this reaction was performed in benzene-d_6 and monitored by ^{1}H and ^{31}P NMR spectroscopy, a complex reaction sequence was detected because the −NCS groups of 1,4-phenylene diisothiocyanate react at different reaction rates. When it was applied in a 3-fold excess, **2** was immediately consumed and a mono-κ^1S-dithiocarbamato intermediate, 4-[CpRu(PPh$_3$)$_2$SC(S)-NH]C$_6$H$_4$NCS (**6**), formed almost exclusively. Complex **6** transformed over several hours to give 4-[CpRu-(PPh$_3$)S$_2$CNH]C$_6$H$_4$NCS (**7**) as the thermodynamically stable product. Thus, the −NCS function in **6** has a significantly lower reactivity than that of 1,4-phenylene diisothiocyanate, probably due to electronic effects of the coordinated ruthenium center. When the ratio was stoichiometric or there was an excess of **2**, a mixture of **6** and **7** formed immediately, followed by the formation of 4-[CpRu(PPh$_3$)$_2$SC(S)NH]C$_6$H$_4$[NHCS$_2$Ru(PPh$_3$)Cp] (**8**) and **4b**. Although the ratio of all these species constantly changed as the reaction progressed, the amount of **8** always remained very low. No evidence for the bis-κ^1S-dithiocarbamato intermediate 1,4-[CpRu-(PPh$_3$)$_2$SC(S)NH]C$_6$H$_4$[NHC(S)SRu(PPh$_3$)$_2$Cp] was detected. As in previous experiments, the NH and aromatic *ortho* proton resonances for all complexes containing κ^2S,S-coordinated dithiocarbamato ligand(s), e.g., **7**, **8**, and **4b**, shifted to higher fields while the reaction was in progress. Characteristic NMR data for complexes **4b** and **6**−**8** are listed in Table 1.

The transient appearance of κ^1S-dithiocarbamato intermediates **5**, **6**, and **8** in the above reactions suggested that CpRu(dppe)SH might be reactive toward isothiocyanates, in contrast with its silanethiolato analogue. Indeed, reactions with RNCS (R = Ph, 1-Naphth) proceeded smoothly in benzene at room temperature to give the corresponding κ^1S-dithiocarbamato complexes, CpRu(dppe)SC(S)NHR (R = Ph (**9a**), 1-Naphth (**9b**)), as the sole products (eq 5) which were characterized by their multinuclear NMR spectra. The ^{31}P NMR spectra

$$\text{CpRu(dppe)SH} + \text{RNCS} \xrightarrow{\text{rt}} \underset{\mathbf{9a,b}}{\text{CpRu(dppe)SC(S)NHR}} \quad (5)$$

exhibited singlet resonances at about δ 78, consistent with the chelating coordination mode of dppe and equivalent phosphorus environments. The ^{1}H NMR spectra exhibited singlet resonances attributable to the NH proton at about δ 9.45, which did not change as the reactions progressed. Spectroscopic monitoring also showed that both reactions were considerably slower than the corresponding reactions of **2**, PhNCS being consumed after 4 h, and 1-NaphthNCS reacted only

Table 1. Characteristic NMR Resonances for Complexes 4b and 6−8

	^{1}H NMR (δ, ppm)[a]			^{13}C{^{1}H} NMR (δ, ppm)[a]	^{31}P{^{1}H} NMR (δ, ppm)[b]
	Cp	C_6H_4	NH	Cp	
4-[CpRu(PPh$_3$)$_2$SC(S)NH]C$_6$H$_4$NCS (**6**)	4.76	6.48 (dt, J_1 = 2 Hz, J_2 = 9 Hz, 2H), 7.15 (dt, J_1 = 2 Hz, J_2 = 9 Hz, 2H)	9.07	83.1	42.3
4-[CpRu(PPh$_3$)S$_2$CNH]C$_6$H$_4$NCS (**7**)	4.42	6.35 (dt, J_1 = 2 Hz, J_2 = 9 Hz, 2H), 6.76 (dt, J_1 = 2 Hz, J_2 = 9 Hz, 2H)	7.32	76.5	54.1
4-[CpRu(PPh$_3$)$_2$SC(S)NH]C$_6$H$_4$-[NHCS$_2$Ru(PPh$_3$)Cp] (**8**)	4.45, 4.75		∼7.35, 9.14		42.2, 54.1
1,4-[CpRu(PPh$_3$)S$_2$CNH]$_2$C$_6$H$_4$ (**4b**)	4.43	6.92 (s, 4H)	∼7.55	76.5[c]	54.1

[a] Recorded in benzene-d_6 relative to TMS, unless noted otherwise. [b] Recorded in benzene-d_6 relative to 85% H_3PO_4. [c] Recorded in DMSO-d_6.

after 3 days. Surprisingly, when acceleration of the latter reaction by moderate heating was attempted, the formation of a 1:1 mixture of the starting materials was observed instead. Upon standing at room temperature for 3 days, **9b** was nearly completely reformed, suggesting an equilibrium that favors **9b** at room temperature (eq 6). Heating **9a** in benzene-d_6 partially decomposed it, but no CpRu(dppe)SH was observed.

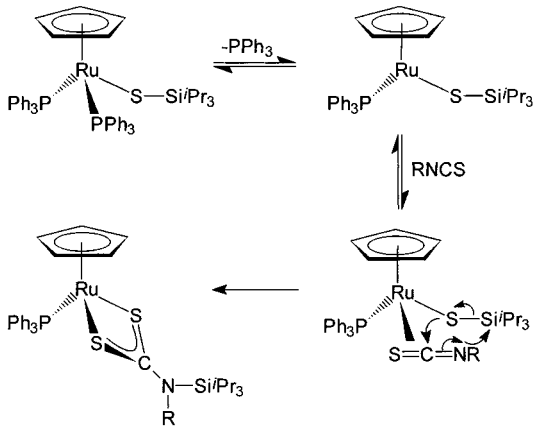
$$\text{CpRu(dppe)SH} + \text{1-NaphthNCS} \underset{80\ ^\circ\text{C}}{\overset{\text{rt}}{\rightleftharpoons}} \underset{\mathbf{9b}}{\text{CpRu(dppe)SC(S)NHNaphth}} \quad (6)$$

Discussion

Insertion of isothiocyanates into the silicon−sulfur bond of a silanethiolato complex to generate *N*-silyl κ^2*S*,*S*-dithiocarbamato complexes (eqs 1, 2) has not been reported until now. While numerous κ^2*S*,*S*-dithiocarbamato complexes of various metals have been reported, including relevant complexes of the type CpRu(PR$_3$)-S$_2$CNR′$_2$,[6−9] the great majority of these were prepared by reacting metal halides with robust *N*,*N*-dialkyl dithiocarbamate anions, the latter being generated from CS_2 and dialkylamides. Silylated dithiocarbamato complexes, however, are not known, and the reactions described here are a novel method for the preparation of κ^2*S*,*S*-dithiocarbamates. The synthesis of dppe-substituted κ^1*S*-dithiocarbamato complexes **9a**,**b** is also interesting from a preparative point of view since an attempt to prepare analogous *N*,*N*-dialkyl dithiocarbamato complexes by the conventional method, reaction of CpRu(dppe)Cl with [S$_2$CNR$_2$]$^-$, failed and gave octahedral (dppe)Ru(S$_2$CNEt$_2$)$_2$ instead.[9c] Nevertheless, at least one cyclopentadienyl κ^1*S*-dithiocarbamato ruthenium complex, CpRu(PEt$_3$)$_2$SC(S)NEt$_2$, has been reported recently.[7]

The inertness of CpRu(dppe)SSi^{i}Pr$_3$ and the observation that no κ^1*S*-dithiocarbamato intermediates were detected starting from **1** suggest a dissociative pathway (Scheme 1), rather than direct nucleophilic addition of the S−Si bond to isothiocyanates. It has been demonstrated recently[3] that **1** is extraordinarily susceptible to ligand exchange with CO, phosphines, phosphites, and SO_2 due to the steric and electronic effects of the −SSi^{i}Pr$_3$ group, which facilitates dissociation of at least one PPh$_3$ ligand and stabilizes the resulting 16e coordinatively unsaturated species. It is reasonable to assume that isothiocyanates coordinate to the ruthenium atom via the C=S bond in a κ^2 fashion. Precoordination of CS_2 has been suggested as the mechanism whereby it inserts into the Ru−S bonds of the analogous CpRu(PPh$_3$)$_2$SR (R = alkyl, aryl, H) thiolato complexes to give thioxanthato complexes.[10,11] Coordination via the C=NR bond can be ruled out since **1** is inert toward CyN=C=NCy.[12] Subsequently, the silanethiolato sulfur may attack the activated −NCS carbon, followed by silyl group transfer from sulfur to nitrogen. In any event, both sulfur atoms remain permanently in the coordination sphere of the ruthenium atom and eventually form the κ^2*S*,*S*-dithiocarbamato structure. This scenario points to a pivotal role of the metal atom in the insertion of isothiocyanates into the S−Si bond of **1**. When access to ruthenium is blocked, as in CpRu(dppe)SSi^{i}Pr$_3$, no reaction occurs.

Scheme 1



The mechanism outlined in Scheme 1 is markedly different from that of the insertion of SO_2.[3] Although SO_2 can displace a PPh$_3$ ligand and coordinate to the ruthenium atom of **1** and it can also insert into the S−Si bond of **1**, the two reactions are neither concerted not connected. It appears that nucleophilic attack by the silanethiolato sulfur atom on the sulfur atom in SO_2 takes place directly. The subsequent transfer of the silyl group is probably facilitated by the formation of a strong Si−O bond. Accordingly, such insertions readily take

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(11) Complex **1** also reacted readily with CS_2 to give a 1:1 mixture of CpRu(PPh$_3$)S$_2$CSSi^{i}Pr$_3$ and free PPh$_3$.[12] Interestingly, this compound subsequently decomposed to CpRu(PPh$_3$)S$_2$CSRu(PPh$_3$)$_2$Cp[10] and probably ^{i}Pr$_3$SiOH, suggesting partial deinsertion of CS_2 and hydrolysis of the S−Si bond.

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place with CpRu(dppe)SSi^{i}Pr$_3$ and other ligand-substituted derivatives of **1**, which are resistant to loss of PPh_3. On the other hand SO_2 can also act as a ligand and coordinate to ruthenium, but then it is not susceptible to nucleophilic attack while in the coordination sphere of the metal. The reactivity of PhNSO is intermediate between that of SO_2 and isothiocyanates: it can coordinate to **1** in a manner similar to SO_2, but it is indifferent toward direct nucleophilic attack, as is PhNCS.

While the reactions of **1** with isothiocyanates are unprecedented, those of **2** are not. CpNi(PBu_3)SH[13] and $[(CO)_5WSH]^-$ [14] react with PhNCS to give CpNi(PBu_3)-SC(S)NHPh and $[(CO)_5WSC(S)NHPh]^-$, respectively. The latter ultimately transformed into the κ^2S,S-dithiocarbamato derivative $[(CO)_4WS_2CNHPh]^-$ via loss of CO. Another interesting example is that of $[Au(SH)_2]^-$, which gave the unusual mononuclear bis-κ^1S-dithiocarbamato complex $[PhNHC(S)SAuSC(S)NHPh]^-$.[15] Although the mechanism(s) of these reactions was not studied in detail, it was suggested that direct nucleophilic addition of the S−H bond to the isothiocyanates probably took place.[14] It appears to be the most reasonable explanation for the formation of κ^1S-dithiocarbamato complexes **5**, **6**, and **9a**,**b** as well. Complexes **5** and **6** then spontaneously transformed into their thermodynamically stable κ^2S,S-dithiocarbamato derivatives via loss of PPh_3. Note, however, that **2** is substitution labile,[10] although to a lesser extent than **1**,[3] and ligand exchange with isothiocyanates may be possible. Thus, a mechanism analogous to that outlined in Scheme 1 cannot be excluded as a route to **3d**,**e**. This conclusion is particularly relevant to the reaction of **2** with phenyl and 1-naphthyl isothiocyanates (eq 3). The κ^1S-dithiocarbamato intermediate **5** was observed only as a minor species even in early stages of the reaction, while the naphthyl analogue could not be detected. Although no quantitative information is available about the rate of the $\kappa^1 \rightarrow \kappa^2$ transformation, spectroscopic monitoring suggests that the conversion of κ^1S-dithiocarbamato intermediates is probably too slow to be the only pathway leading to κ^2S,S-dithiocarbamates. This assumption is further supported by the much slower reactions of CpRu(dppe)SH with the same substrates, which are "pure" additions. Of particular importance here is the 1-naphthyl isothiocyanate derivative **9b**, the only known example for reversible formation of a κ^1S-dithiocarbamato complex. It is reasonable to expect that **2** could form the naphthyl analogue of **5** and that the failure to observe it may be due to an equilibrium favoring **2** or that its formation is very slow. Thus, the relatively fast formation of **3e** must take place, at least in part, via the alternative pathway outlined in Scheme 1.

Our results demonstrate that **1** and **2** react with isothiocyanates to give a common type of product, namely, κ^2S,S-dithiocarbamato complexes, and verify the assumption that silanethiolates and hydrosulfides have analogous chemistry.

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Experimental Section

All manipulations were carried out under an inert atmosphere (N_2 or Ar), using standard Schlenk technique and a drybox. Solvents were dried and freshly distilled under nitrogen prior to use. CpRu(PPh_3)$_2$SSi^{i}Pr$_3$, CpRu(dppe)SSi^{i}Pr$_3$, CpRu(PPh_3)$_2$SH, and CpRu(dppe)SH were prepared according to literature procedures.[3] Phenyl-, *p*-tolyl-, and 1-naphthyl isothiocyanate, as well as 1,4-phenylene diisothiocyanate were purchased from Aldrich and were used as received. ^{1}H, ^{13}C-{^{1}H}, and ^{31}P{^{1}H} NMR measurements were performed on a JEOL CPF 270 spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced to TMS and the ^{31}P NMR spectra to 85% H_3PO_4. Elemental analyses were carried out by the Laboratoire d'Analyse Elementaire at the University of Montreal.

CpRu(PPh_3)S_2CN(Si^{i}Pr$_3$)Ph (3a). A solution of **1**, freshly prepared from CpRu(PPh_3)$_2$Cl (1.0 g, 1.37 mmol) in 50 mL of THF−acetone as reported,[3] was treated with phenyl isothiocyanate (0.19 g, 1.37 mmol) at room temperature. The red-orange color of **1** changed to yellow-brown shortly after the reagents were mixed. The reaction mixture was stirred overnight. Then the solvent was removed under reduced pressure, and the residue was redissolved in CH_2Cl_2. This solution was filtered through Celite, concentrated under reduced pressure, and layered with hexane. Cooling to −20 °C gave a lemon yellow, cotton-like crystalline material, which was filtered and dried. Yield: 0.72 g (0.96 mmol, 70%). Anal. Calcd for $C_{39}H_{46}NPRuS_2Si$: C, 62.20; H, 6.16; N, 1.86. Found: C, 62.04; H, 6.38; N, 1.92. ^{1}H NMR (C_6D_6): δ 1.06 (d, J = 7 Hz, 18H, CH_3), 1.77 (sept, J = 7 Hz, 3H, CH), 4.40 (s, 5H, Cp), 7.05 (m, 14H, *m*,*p*-PPh+NPh), 7.66 (m, 6H, *o*-PPh). ^{13}C-{^{1}H} NMR (C_6D_6): δ 13.7 (CH), 18.7 (CH_3), 77.3 (d, J_{PC} = 3 Hz, Cp), 127.0 (*p*-NPh), 128.5 (*o*,*m*-NPh), 130.5 (*p*-PPh), 133.9 (d, J_{PC} = 11 Hz, *o*-PPh), 139.1 (d, J_{PC} = 38 Hz, *ipso*-PPh), 141.9 (*ipso*-NPh), 228.4 (d, J_{PC} = 5 Hz, S_2CN); the *m*-PPh doublet was covered by the solvent resonance but was clearly observed in $CDCl_3$ at 127.3 (J_{PC} = 9 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 54.0.

CpRu(PPh_3)S_2CN(Si^{i}Pr$_3$)Tol (3b). This material was prepared similarly to **3a**, using *p*-tolyl isothiocyanate (0.20 g, 1.37 mmol). Yellow microcrystals formed. Yield: 0.61 g (0.80 mmol, 58%). Anal. Calcd for $C_{40}H_{48}NPRuS_2Si$: C, 62.63; H, 6.31; N, 1.83; S, 8.36. Found: C, 62.83; H, 6.46; N, 1.87; S, 8.80. ^{1}H NMR (C_6D_6): δ 1.09 (d, J = 7 Hz, 18H, CH_3 (^{i}Pr)), 1.79 (sept, J = 7 Hz, 3H, CH), 2.01 (s, 3H, CH_3 (Tol)), 4.40 (s, 5H, Cp), 6.92 ("d", J = 8 Hz, 2H, Tol), 7.05 (m, 11H, *m*,*p*-Ph+Tol), 7.66 (m, 6H, *o*-Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 13.7 (CH), 18.8 (CH_3 (^{i}Pr)), 20.8 (CH_3 (Tol)), 77.3 (d, J_{PC} = 2 Hz, Cp), 128.5 (C-2,2′, Tol), 129.2 (C-3,3′, Tol), 130.2 (*p*-Ph), 133.9 (d, J_{PC} = 11 Hz, *o*-Ph), 136.6 (C-1, Tol), 139.2 (d, J_{PC} = 38 Hz, *ipso*-Ph), 139.3 (C-4, Tol), 228.6 (d, J_{PC} = 5 Hz, S_2CN); the *m*-Ph doublet was hidden under the solvent resonances but was clearly observed in $CDCl_3$ at 127.3 (J_{PC} = 9 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.9.

CpRu(PPh_3)S_2CN(Si^{i}Pr$_3$)Naphth (3c). This complex was prepared as **3a**, using 1-naphthyl isothiocyanate (0.25 g, 1.37 mmol). Large, dark orange crystals formed from CH_2Cl_2−hexane at room temperature. Yield: 0.61 g (0.76 mmol, 56%). Anal. Calcd for $C_{43}H_{48}NPRuS_2Si$: C, 64.31; H, 6.02; N, 1.74. Found: C, 63.99; H, 5.85; N, 1.79. ^{1}H NMR (C_6D_6): δ 1.02, 1.09 (both d, J = 6 Hz, 9H each, CH_3), 1.79 (sept, J = 6 Hz, 3H, CH), 4.40 (s, 5H, Cp), 7.07 (m, 9H, *m*,*p*-Ph), 7.17, 7.35, 7.53 (all m, 2H, Naphth), 7.63 (m, 6H, *o*-Ph), 8.28 ("d", 1H, Naphth). ^{13}C{^{1}H} NMR (C_6D_6): δ 14.2 (CH), 19.2 (CH_3), 77.5 (Cp), 124.9, 125.2, 125.7, 125.8, 132.4 (all Naphth), 133.8 (d, J_{PC} = 11 Hz, *o*-Ph), 134.7, 139.1 (both Naphth), 139.4 (d, J_{PC} = 39 Hz, *ipso*-Ph), 228.6 (d, J_{PC} = 8 Hz, S_2CN); the *m*-Ph, *p*-Ph, and three missing Naphth resonances were buried under those of the solvent but were identified in $CDCl_3$ at 127.3 (d, J_{PC} = 9 Hz, *m*-Ph), 127.6, 127.9, 128.3 (all Naphth), and 128.5 (*p*-Ph). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.7.

CpRu(PPh$_3$)S$_2$CNHPh (3d). A solution of **2** (30 mg, 0.04 mmol) in 0.7 mL of benzene-d_6 was treated with phenyl isothiocyanate (5 μL, 0.04 mmol) at room temperature, and the reaction was monitored by NMR spectroscopy. Complex **2** was consumed in about 1 h, and a mixture of **3d** and **5** (95:5) was present at this point. Conversion of **5** into **3d** was complete in an additional 2 h. Complex **3d** was characterized by NMR spectroscopy as follows. ^{1}H NMR (C_6D_6): δ 4.43 (s, 5H, Cp), 6.74 (m, 1H, *p*-NPh), 6.93 (m, 2H, *m*-NPh), 7.04 (m, 9H, *m*,*p*-PPh), 7.10 (*o*-NPh), 7.43 (s, 1H, NH), 7.74 (m, 6H, *o*-PPh). ^{13}C{^{1}H} NMR (C_6D_6): δ 76.5 (Cp), 119.7 (*m*-NPh), 123.8 (*p*-NPh), 128.7 (*p*-PPh), 134.0 (d, J_{PC} = 11 Hz, *o*-PPh), 138.1 (d, J_{PC} = 38 Hz, *ipso*-PPh), 138.2 (*ipso*-NPh); the missing *m*-PPh doublet and *o*-NPh resonances were hidden under those of the solvent. ^{31}P{^{1}H} NMR (C_6D_6): δ 54.2.

CpRu(PPh$_3$)S$_2$CNHNaphth (3e). Complex **2** (0.30 g, 0.41 mmol) was dissolved in 40 mL of benzene, and solid 1-naphthyl isothiocyanate (80 mg, 0.43 mmol) was added at once. The yellow solution was stirred overnight at room temperature. The solvent was evaporated under reduced pressure, and the resulting oily residue was dissolved in CH_2Cl_2 and filtered through Celite. The solution was concentrated to about 5 mL and was layered with hexane in a Schlenk tube. Cooling to −20 °C gave orange microcrystals. Yield: 0.15 g (0.23 mmol, 57%). Anal. Calcd for $C_{34}H_{28}NPRuS_2$: C, 63.14; H, 4.36; N, 2.17; S, 9.92. Found: C, 63.16; H, 4.61; N, 2.16; S, 9.19. ^{1}H NMR (C_6D_6): δ 4.42 (s, 5H, Cp), 7.04 (m, 9H, *m*,*p*-Ph), 7.09 (m, 1H, Naphth), 7.25 (m, 2H, Naphth), 7.32, 7.50 (both m, 1H, Naphth), 7.74 (m, 6H, *o*-Ph), 7.82 (s, 1H, NH), 7.94 (m, 2H, Naphth). ^{13}C{^{1}H} NMR (C_6D_6): δ 76.5 (Cp), 120.8, 121.2, 125.3, 125.6, 125.9 (2C), 127.0 (all Naphth), 128.7 (*p*-Ph), 132.7 (Naphth), 134.0 (d, J_{PC} = 11 Hz, *o*-Ph), 134.4 (Naphth), 138.3 (d, J_{PC} = 38 Hz, *ipso*-Ph), 217.4 (d, J_{PC} = 5 Hz, S_2CN); the *m*-Ph doublet and one missing Naphth resonance were hidden under those of the solvent, but both were detected in $CDCl_3$ at 127.4 (J_{PC} = 9 Hz) and 128.6, respectively. ^{31}P{^{1}H} NMR (C_6D_6): δ 54.2.

1,4-[CpRu(PPh$_3$)S$_2$CN(Si^{i}Pr$_3$)]$_2$C$_6$H$_4$ (4a). This complex was prepared in the same way as **3a**, using 1,4-phenylene diisothiocyanate (0.13 g, 0.68 mmol). Well-formed orange crystals readily deposited from CH_2Cl_2−hexane at room temperature. Yield: 0.97 g (0.62 mmol, 91%). Anal. Calcd for $C_{72}H_{86}N_2P_2Ru_2S_4Si_2$: C, 60.56; H, 6.07; N, 1.96; S, 8.98. Found: C, 62.59; H, 7.36; N, 1.85; S, 8.25. Calcd for **4a**·1.6C_6H_{14}: C, 62.59; H, 6.98; N, 1.79; S, 8.19. ^{1}H NMR (C_6D_6): δ 1.09 (d, J = 7 Hz, 36H, CH_3), 1.77 (sept, J = 7 Hz, 6H, CH), 4.39 (s, 10H, Cp), 7.06 (m, 22H, *m*,*p*-Ph+C_6H_4), 7.65 (m, 12H, *o*-Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 13.7 (CH), 18.8 (CH_3), 77.2 (Cp), 128.5 (C-2,2′,3,3′, C_6H_4), 130.7 (*p*-Ph), 133.9 (d, J_{PC} = 11 Hz, *o*-Ph), 138.9 (d, J_{PC} = 38 Hz, *ipso*-Ph), 140.3 (C-1,4, C_6H_4), 228.1 (d, J_{PC} = 5 Hz, S_2CN); the *m*-Ph doublet was hidden under the solvent resonances but was observed in $CDCl_3$ at 127.1 (J_{PC} = 9 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 54.7.

1,4-[CpRu(PPh$_3$)S$_2$CNH]$_2$C$_6$H$_4$ (4b). Complex **2** (50 mg, 0.07 mmol) in 1 mL of benzene-d_6 was added to 1,4-phenylene diisothiocyanate (20 mg, 0.10 mmol) in an NMR tube. The reaction, monitored by NMR spectroscopy at 22 °C, instantly consumed **2** and formed yellow-colored **6**. The NMR data for **6** are listed in Table 1; the aromatic resonances are as follows. ^{1}H NMR (C_6D_6): δ 6.94 (m, 18H, *m*,*p*-Ph), 7.39 (m, 12H, *o*-Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 122.9 (C-2,2′, C_6H_4), 125.3 (C-3,3′, C_6H_4), 129.5 (*p*-Ph), 134.1 (br "t", *o*-Ph), 137.2 (C-4, C_6H_4), 138.2 (t, J_{PC} = 20 Hz, *ipso*-Ph), 140.2 (C-1, C_6H_4); the *m*-Ph doublet was completely covered by that of the solvent peak.

Complex **6** completely transformed to **7** overnight at room temperature to give a red-orange solution. The NMR data for **7** are compiled in Table 1; the aromatic resonances are as follows. ^{1}H NMR (C_6D_6): δ 7.04 (m, 9H, *m*,*p*-Ph), 7.69 (m, 6H, *o*-Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 119.8 (C-2,2′, C_6H_4), 125.8 (C-3,3′, C_6H_4), 129.5 (*p*-Ph), 133.9 (d, J_{PC} = 11 Hz, *o*-Ph), 136.7 (C-1, C_6H_4), 137.3 (C-4, C_6H_4), 137.8 (d, J_{PC} = 39 Hz, *ipso*-Ph), 215.1 (d, J_{PC} = 5 Hz, S_2CN); the *m*-Ph resonance was hidden under that of the solvent.

Table 2. Crystallographic Data and Structure Refinement for Complexes 3c and 4a

	3c	4a
empirical formula	$C_{43}H_{48}NPRuS_2Si$	$C_{72}H_{86}N_2P_2Ru_2S_4Si_2$·0.7$C_6H_{14}$
fw	803.07	774.32
T (K)	293(2)	293(2)
radiation, λ (Å)	Mo Kα, 0.70930	Mo Kα, 0.70930
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.689(14)	10.660(5)
b (Å)	21.888(12)	13.263(7)
c (Å)	16.930(12)	15.606(7)
α (deg)	90	74.92(4)
β (deg)	94.09(8)	84.72(4)
γ (deg)	90	85.76(4)
V (Å^3)	3951(6)	2118(2)
Z	4	2
D_{calcd} (Mg m^{-3})	1.350	1.2138
μ (mm^{-1})	0.604	0.555
F(000)	1672	812
cryst size (mm)	0.38 × 0.28 × 0.22	0.62 × 0.25 × 0.20
transmn range	0.80 to 0.86	0.77 to 0.85
limiting indices	$-13 \le h \le 13$	$-13 \le h \le 13$
	$-27 \le k \le 27$	$-16 \le k \le 16$
	$-20 \le l \le 20$	$-19 \le l \le 19$
no. of reflns collected	30 122	16 658
no. of ind reflns (R_{int})	7804 (0.085)	8329 (0.108)
GoF on F^2	1.069	0.932
final R indices	R1 = 0.0647,	R1 = 0.0670,
($I > 2\sigma(I)$)	wR2 = 0.1396[a]	wR2 = 0.1656[a]
R indices (all data)	R1 = 0.1264,	R1 = 0.1134,
	wR2 = 0.1697[a]	wR2 = 0.1888[a]

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

The solution of **7**, containing unreacted 1,4-phenylene diisocyanate, was "titrated" with additional **2** in benzene-d_6, and concomitant formation of **4b** and small amounts of **8** (Table 1) was observed. Complex **4b** readily precipitated from the reaction mixture at room temperature as orange microcrystals. The crystalline material is poorly soluble in benzene or chloroform and insoluble in hexane. Eventually it was dissolved in DMSO-d_6 but recrystallized in the NMR tube while a ^{13}C NMR spectrum was acquired. This precipitate could not be redissolved even in hot DMSO-d_6. Anal. Calcd for $C_{54}H_{46}N_2P_2Ru_2S_4$: C, 58.15; H, 4.16; N, 2.51. Found: C, 58.36; H, 4.07; N, 2.23. Some NMR data for **4b** are shown in Table 1; resonances in the aromatic region are as follows. ^{1}H NMR (C_6D_6): δ 6.92 (s, 4H, C_6H_4), 7.03 (m, 18H, *m*,*p*-Ph), 7.71 (m, 12H, *o*-Ph). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 120.7 (C-2,2′,3,3′, C_6H_4), 128.0 (d, J_{PC} = 9 Hz, *m*-Ph), 129.3 (*p*-Ph), 133.7 (d, J_{PC} = 10 Hz, *o*-Ph), 137.6 (C-1,4, C_6H_4), 137.9 (d, J_{PC} = 38 Hz, *ipso*-Ph); the S_2CN carbon resonance was not identified.

CpRu(dppe)SC(S)NHR (R = Ph (9a), Naphth (9b)). To a solution of CpRu(dppe)SH (30 mg, 0.05 mmol) in 0.7 mL of benzene-d_6 were added phenyl isothiocyanate (6 μL, 0.05 mmol) and 1-naphthyl isothiocyanate (10 mg, 0.05 mmol), respectively, at room temperature. The first reaction was complete in about 4 h, while it took 3 days to obtain **9b**. When the reactions were judged complete by NMR, the solvent was evaporated under reduced pressure to give oily residues. These were washed with ether to give lemon yellow solids, but attempts to purify the products by crystallization failed so far. Both **9a**,**b** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Data for **9a** are as follows. ^{1}H NMR (C_6D_6): δ 1.73, 2.47 (both m, 2H each, PCH_2), 4.55 (s, 5H, Cp), 6.94 (m, 12H, *m*,*p*-PPh), 7.07 (m, 8H, *o*-PPh), 7.57 (m, 3H, *m*,*p*-NPh), 7.81 (m, 2H, *o*-NPh), 9.40 (s, 1H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.3 (t, J_{PC} = 23 Hz, CH_2P), 82.1 (Cp), 121.3 (*m*-NPh), 123.9 (*p*-NPh), 127.8 (*m*-NPh), 128.1, 128.5 (both br t, *m*-PPh), 129.7,

129.9 (both *p*-PPh), 132.1 (br t, *o*-PPh); the weak *ipso*-NPh and *ipso*-PPh resonances were not identified. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 78.7.

Data for **9b** are as follows. ^1H NMR (C_6D_6): δ 1.89, 2.42 (both m, 2H each, PCH_2), 4.65 (s, 5H, Cp), 6.93 (m, 12H, *m*,*p*-Ph), 7.03 (m, 8H, *o*-Ph), 7.45, 7.60, 7.75, 8.03 (all m, Naphth), 9.49 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 82.5 (Cp), 123.0, 124.4, 125.3, 125.7, 125.9, 126.4, 127.9, (all Naphth), 128.3 (br t, *m*-Ph), 128.5, 128.6 (both Naphth), 128.7 (br t, *m*-Ph), 129.4 (Naphth), 129.6, 130.1 (both *p*-Ph), 131.7, 132.6 (both br t, *o*-Ph), 133.9 (t, $J_{PC} = 18$ Hz, *ipso*-Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 77.7.

Crystal Structure Determination of Complexes 3c and 4a. Orange crystals of both complexes were obtained from methylene chloride−hexane solutions. Intensity data were collected on a Rigaku AFC6S diffractometer. Data collection and structure solution parameters are shown in Table 2. In both cases, the space group was confirmed by the PLUTON program.[16] Data reduction and absorption correction were performed using DATRD2 and ABSN, respectively, in NRC-VAX.[17] The structures were solved by the Patterson method using SHELXS96 and difmap synthesis using SHELXL96.[18] All non-hydrogen atoms are anisotropic except for the disordered Cp group in **4a**, which was modeled as a variable metric rigid group. The hydrogen atoms are isotropic and constrained to the parent site using a riding model. The isotropic factors were adjusted to 50% higher value of the parent site (methyl) and 20% higher (others).

For **4a**, the VOID routine of the PLUTON program indicated an unoccupied volume of 534 Å^3 in the unit cell. The SQUEEZE routine of the same program indicated 68 missed electrons situated in this void, which correspond to 1.4 molecules of hexane per unit cell. This has been accounted for in calculating the absorption coefficient, density, formula weight, and electrons per cell, *F*(000). The final refinement is against corrected structure factors produced by the SQUEEZE routine by subtracting the solvent contribution.

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Supporting Information Available: Tables of atomic coordinates and thermal parameters, bond lengths and angles, torsion angles, and structure refinement details and ORTEP drawings of **3c** and **4a** with full numbering scheme, as well as a packing diagram of **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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