

Mechanisms of Cyaphide (C≡P[−]) Formation**

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Many complexes and coordination polymers with unique properties have been constructed with the cyanide ion.^[1] However, analogous chemistry with the heavier phosphorus congener of cyanide has not been developed. We reported the synthesis and X-ray crystallographic characterization of a complex with a terminal cyaphide ligand, [RuH(dppe)₂-(C≡P)] (**2**; dppe = bis-1,2-diphenylphosphinoethane).^[2,3] Herein we present experimental and computational results which suggest a possible mechanism for the formation of **2**.

When [RuH(dppe)₂(P≡CSiPh₃)]⁺ (**1**) was treated with 1.2 equivalents of NaOPh in dry [D₈]THF (Scheme 1) and the

subsequent reaction was monitored by ³¹P{¹H} NMR spectroscopy, a new quintet at δ = 309.5 (*J*_{PP} = 27 Hz) ppm and a doublet at δ = 62.7 (*J*_{PP} = 27 Hz) ppm were seen for intermediate **X**. Over time, this intermediate species disappeared and broader resonances at δ = 164.8 and 65.3 ppm appeared for product **2**. When two equivalents of NaOPh (relative to **1**) were used, the rate of reaction to form the cyaphide complex **2** was accelerated. A clue to the nature of **X** was obtained serendipitously when the reaction of NaOPh and **1** was performed in wet acetonitrile. From this reaction a new product was detected in the ³¹P NMR spectrum (δ = 332.0 (qnt, *J*_{PP} = 28 Hz), 67.7 (d, *J*_{PP} = 28 Hz) ppm). Further investigations into this crystalline material by X-ray diffraction revealed the unique λ³σ³-phosphaketenylyl ruthenium complex **3** (Figure 1).^[4]

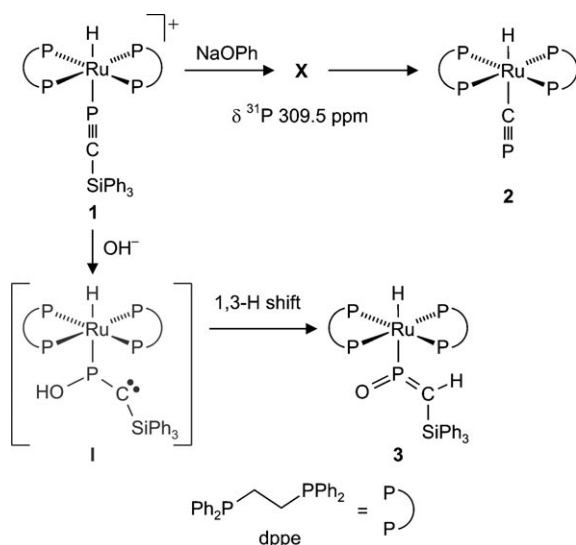
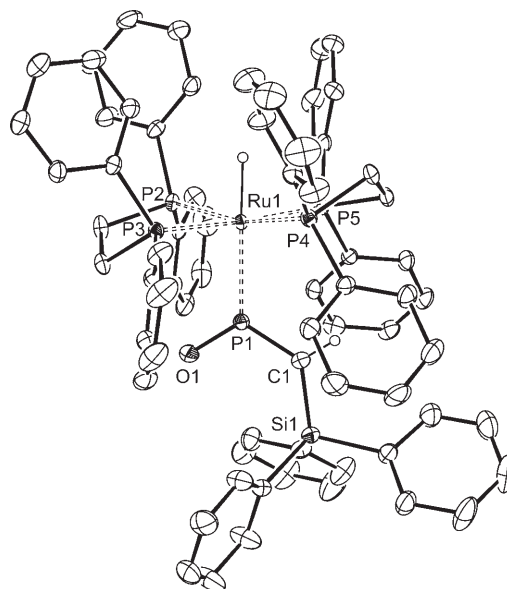
Scheme 1. Synthesis of phosphaoximato complex **3**.

Figure 1. Molecular structure of **3**. One acetonitrile molecule in the crystal lattice and hydrogen atoms (except that bonded to Ru) are omitted for clarity. Thermal ellipsoids are set at 30% probability. Selected bond lengths [Å] and angles [°]: O1-P1 1.509(2), P1-C1 1.663(3), C1-Si1 1.823(3), Ru1-P1 2.358(1), Ru1-P2 2.351(1), Ru1-P3 2.336(1), Ru1-P4 2.340(1), Ru1-P5 2.350(1); O1-P-C1 113.5(1), Ru1-P1-O1 122.7(1), Ru1-P1-C1 123.8(1), P1-C1-Si1 127.4(2), P1-Ru1-P2 93.9(1), P1-Ru1-P3 89.0(1), P1-Ru1-P4 97.5(1), P1-Ru1-P5 96.8(1), P2-Ru1-P3 81.3(1), P3-Ru1-P4 97.2(1), P4-Ru1-P5 83.5(1), P5-Ru1-P2 96.8(1).

The coordination sphere around phosphorus in this λ⁵σ³-phosphaketenylyl complex is trigonal-planar (Σ_P = 360°). Both the P1–O1 (1.509(2) Å) and P1–C1 (1.663(3) Å) bonds are short and typical for low-coordinate σ³-type structures, R–P(=X)₂ (X = CR₂, NR, O, S).^[5] In analogy with complexes

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containing oximate, $[R_2C=N-O]^-$, as ligand, **3** can also be viewed as a κ^1 -P-phosphaoximate complex. While oximate complexes are numerous, only one other report of a ruthenium phosphaoximate complex exists.^[6,7] Curiously, this species, containing the κ^2 -P,C-[P(=O)CtBu-(C=O)]²⁻ ion, has a markedly low-frequency resonance in the ³¹P NMR spectrum ($\delta = 47.0$ ppm) in comparison to **3**.

Hypothesizing that in the presence of residual water and phenoxide, hydroxide ions are formed that then attack at phosphorus to irreversibly generate **3**, we treated **1** with excess LiOH in THF. Indeed, quantitative formation of **3** was obtained through this more direct pathway. A P-metalated phosphonocarbene **I**, R_2P-C-R' ,^[8] is a likely intermediate in this reaction which converts by a 1,3-H shift into the final product **3** (Scheme 1). DFT calculations^[9] show that thermodynamically the rearrangement of **I** to **3** is strongly favored ($\Delta H_r = -33.9$ kcal mol⁻¹).

The results discussed above serve as a starting point for DFT calculations aimed at understanding the mechanism leading to the formation of cyaphide complex **2**.^[9] We used a simplified model where each 1,2-diphenylphosphinoethane (dppe) ligand was replaced by two PH₃ molecules, SiPh₃ by a SiH₃ group, and phenoxide by methoxide. Based on the experimental results that suggested hydroxide attack at phosphorus, we hypothesized that the elimination of Ph₃SiOPh from **1** might likewise occur by initial phenoxide attack at phosphorus. Therefore, our computations started with **A** as a model for intermediate **I** which is set at 0.0 kcal mol⁻¹ in the relative energy diagram shown in Figure 2A. This P-metalated phosphinocarbene **A** rearranges via **TS1** with a modest barrier (10.2 kcal mol⁻¹) to the C-metalated phosphalkene **B**, which is 4.1 kcal mol⁻¹ more stable than **A**. Calculated ³¹P-NMR-spectroscopic shifts of **A** and **B**^[10] allow us to decide which of these two isomers corresponds to the experimentally detected intermediate **X** (Scheme 1). While **A** has a $\delta(^{31}\text{P})_{\text{calcd}}$ of $\delta = 97$ ppm versus H₃PO₄, which is typical for phosphinocarbenes,^[8] the $\delta(^{31}\text{P})_{\text{calcd}}$ of **B** is $\delta = 334$ ppm, which is in reasonably good agreement with the experimentally detected resonance at $\delta = 309.5$ ppm.^[11] Consequently we propose that **X** has a structure similar to that of isomer **B**, but with [Ru] = [Ru(dppe)₂] and OPh and SiPh₃ instead of OMe and SiH₃, respectively.

We then inspected the intramolecular elimination of the silyl ether MeOSiH₃ from **B**. The first intermediate of this pathway is the η^2 -bonded phosphalkyne silicate complex **C** which is obtained via transition state **TS2**. The slightly exothermic dissociation of MeOSiH₃ from **C** (ΔH_r (**C**→**D**) = -1.5 kcal mol⁻¹), leads to the η^2 -bonded cyaphide complex **D** which rearranges via a small barrier (**TS3**) to the end-on bonded cyaphide complex **E** in the most exothermic step (ΔH_r (**D**→**E**) = -19.5 kcal mol⁻¹). Note that the overall reaction

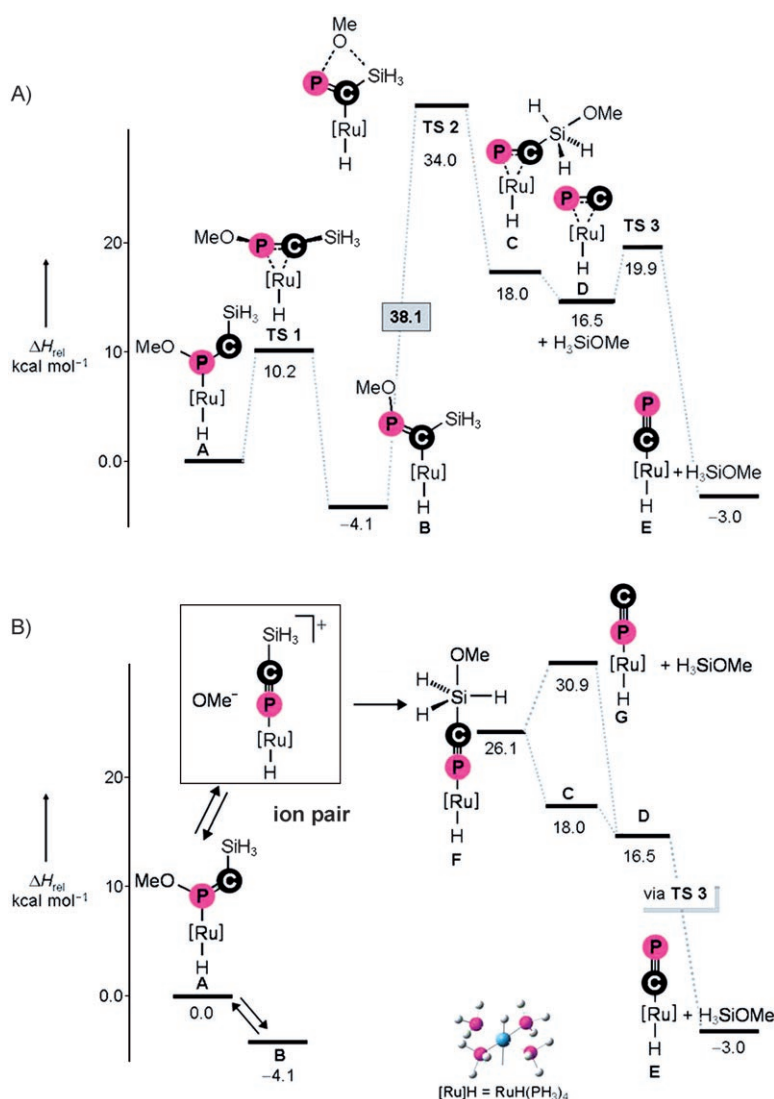


Figure 2. Calculated reaction paths (DFT) for the interaction of the silylphosphalkyne complex $[RuH(PH_3)_4](P\equiv C-SiH_3)^+$ with methoxide, MeO^- to give **E** + H_3SiOMe overall. A) nucleophilic attack at phosphorus; B) nucleophilic attack at silicon.

B→**E** is almost thermoneutral (ΔH_r (**B**→**E**) = 1.1 kcal mol⁻¹), which would explain the rather long reaction time (ca. 14 h) for complete conversion of **1** into **2**. However, the high barrier of 38.1 kcal mol⁻¹ calculated for the rate-limiting step via transition state **TS2** makes the intramolecular elimination of $MeOSiH_3$ very unlikely.

A more direct route to cyaphide complex **E** is simply nucleophilic attack at silicon by methoxide followed by $MeOSiH_3$ elimination (Figure 2B). This alternative mechanism requires that the ion pair and intermediates **A** and **B** are in equilibrium with one another and that only the ion pair, and not intermediates **A** and **B**, is on the pathway leading to **E**. Calculations put the pentacoordinate silicon intermediate **F**, with a linear O-Si-C arrangement, 26.1 kcal mol⁻¹ higher in energy than **A**. Elimination of $MeOSiH_3$ leads to the η^2 -bonded complex **D** via the phosphorus-coordinated cyaphide complex **G**. This isocyaphide complex **G** is actually calculated to be a transition state only 4.8 kcal mol⁻¹ higher in energy

than **F**. Note that attempts to find a less symmetric pathway for the attack of methoxide on the silicon atom in $[\text{RuH}(\text{PH}_3)_4(\text{P}=\text{C}-\text{SiH}_3)]^+$ directly led to the silicate complex **C**, implying that the actual barrier for the **F**→**D** conversion is probably much lower than $26.1 \text{ kcal mol}^{-1}$. An interesting feature is the large energy difference of $33.9 \text{ kcal mol}^{-1}$ between the cyaphide complex **E** and isocyaphide transition-state complex **G**, which can be understood in terms of the Ru–P versus Ru–C σ - and π -bonding interactions. The Ru–P σ bond in **G** ($49.9 \text{ kcal mol}^{-1}$) is weaker than the Ru–C σ bond in **E** ($\Delta E_\sigma = 62.1 \text{ kcal mol}^{-1}$), as a consequence of the larger energy difference between the accepting metal d-orbital and the donating lone pair on phosphorus (-3.9 eV) compared to carbon (0.6 eV). The Ru–P π bond in **G** ($\Delta E_\pi = 16.1 \text{ kcal mol}^{-1}$) is reduced compared to the Ru–C π bond of **E** ($\Delta E_\pi = 23.6 \text{ kcal mol}^{-1}$) as there is less favorable overlap. As a result, the phosphorus-coordinated isocyaphide complex **G** is even higher in energy than the η^2 -bonded complex **D**, and thus **G** is the transition state for the rotation of the $\text{C}\equiv\text{P}^-$ moiety.

The investigations presented herein are an example of an observed intermediate not being on the pathway leading to product formation. The observance of intermediate **X** merely reflects the kinetic preference of phenolate addition to phosphorus.^[12] Calculations predict a transition state that is much too high in energy from intermediate **B** for path A to be a reasonable mechanism leading to cyaphide complex **2**. Instead, direct attack of phenolate at silicon is proposed. While kinetically less favorable than the addition of phenolate to phosphorus, the nucleophilic substitution reaction at silicon is the product-forming step. Two important properties associated with phenolate as the nucleophile in the reaction with **1** are notable. First, the lack of α -hydrogen means rearrangement to a phosphaoximate complex is not possible if phenolate attacks at phosphorus. Second, despite being kinetically more favorable, the initial attack at the phosphorus center of $\text{P}=\text{C}-\text{SiPh}_3$ must be reversible. While we could not compute the proposed ion-pair intermediate with sufficient accuracy, we assume that the barrier to phenolate dissociation from phosphorus is low. The irreversible elimination of $\text{Ph}_3\text{Si}-\text{OPh}$ by phenolate attack at silicon subsequently drives the reaction to completion.

Experimental Section

3: $[\text{RuH}(\text{dppe})_2(\text{P}=\text{C}-\text{SiPh}_3)]^+[\text{OTf}]^-$ (**1**; 0.135 g, 0.10 mmol) and LiOH (0.018 g, 1.0 mmol) were combined in THF (10 mL) under argon for 4 days. The reaction mixture was filtered through diatomaceous earth and the volatile materials were removed under reduced pressure. The resulting off-white solid was washed with CH_3CN and residual solvent removed in vacuo. Yield 0.065 g of **3** (53.3%). Selected NMR spectroscopy data: ^1H (300 MHz, $[\text{D}_8]\text{THF}$): $\delta = 2.91$ (d, $^2J_{\text{HP}} = 9.14 \text{ Hz}$, (O)P=CH, 1H), -10.17 ppm (dq, $\text{trans-}^2J_{\text{HP}} = 69.9 \text{ Hz}$, $\text{cis-}^2J_{\text{HP}} = 20.5 \text{ Hz}$, RuH, 1H). $^{13}\text{C}\{^1\text{H}\}$ (75.5 MHz, $[\text{D}_8]\text{THF}$): $\delta = 110.5$ ppm (d, $^1J_{\text{CP}} = 5.3 \text{ Hz}$, (O)P=CH-SiPh₃). $^{31}\text{P}\{^1\text{H}\}$ (121.5 MHz, $[\text{D}_8]\text{THF}$): $\delta = 332.0$ (quintet, $^2J_{\text{PP}} = 28 \text{ Hz}$, (O)P=CHSiPh₃), 67.7 ppm (d, $^2J_{\text{PP}} = 28 \text{ Hz}$, dppe). For further details see the Supporting Information.

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