C≡P Ligands

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Mechanisms of Cyaphide (C≡P^{-}) Formation**

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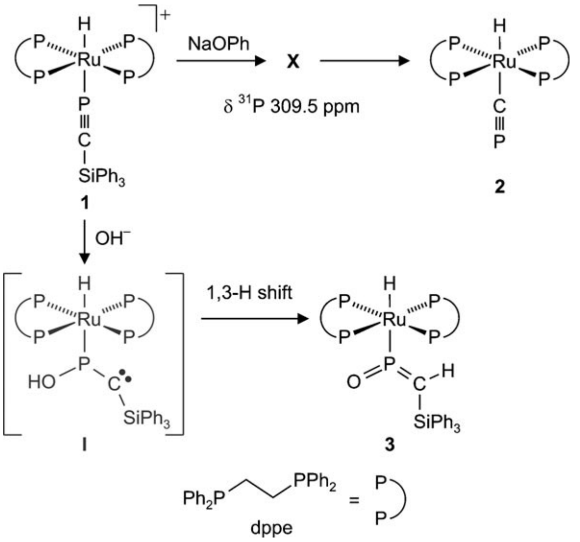
Many complexes and coordination polymers with unique properties have been constructed with the cyanide ion.[1] However, analogous chemistry with the heavier phosphorus congener of cyanide has not been developed. We reported the synthesis and X-ray crystallographic characterization of a complex with a terminal cyaphide ligand, $[\mathrm{RuH(dppe)_2(C{\equiv}P)}]$ (**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 $[\mathrm{RuH(dppe)_2(P{\equiv}CSiPh_3)}]^+$ (**1**) was treated with 1.2 equivalents of NaOPh in dry [D$_8$]THF (Scheme 1) and the subsequent reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy, a new quintet at $\delta = 309.5$ ($J_{PP} = 27$ Hz) ppm and a doublet at $\delta = 62.7$ ($J_{PP} = 27$ Hz) ppm were seen for intermediate **X**. Over time, this intermediate species disappeared and broader resonances at $\delta = 164.8$ 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 ^{31}P NMR spectrum ($\delta = 332.0$ (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 $\lambda^5\sigma^3$-phosphaketenylruthenium complex **3** (Figure 1).[4]



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

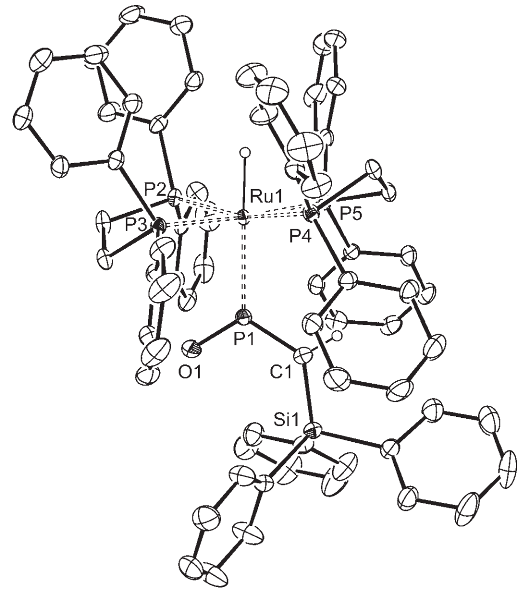


Figure 1. Molecular structure of **3**. One acetonitrile molecule in the crystal lattice and hydrogen atoms (except that bonded to Ru) are omitted for clarity. Thermal ellipsoids are set at 30% probability. Selected bond lengths [Å] and angles [°]: O1-P1 1.509(2), P1-C1 1.663(3), C1-Si1 1.823(3), Ru1-P1 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 $\lambda^5\sigma^3$-phosphaketenyl complex is trigonal-planar ($\Sigma_P = 360°$). Both the P1−O1 (1.509(2) Å) and P1−C1 (1.663(3) Å) bonds are short and typical for low-coordinate σ^3-type structures, R−P(=X)$_2$ (X = CR$_2$, 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-phosphaoximato complex. While oximato complexes are numerous, only one other report of a ruthenium phosphaoximato complex exists.[6,7] Curiously, this species, containing the κ^2-P,C-$[P(=O)C\mathit{t}Bu(C=O)]^{2-}$ ion, has a markedly low-frequency resonance in the ^{31}P 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 phosphoniocarbene **I**, $R_2P\text{-}C\text{-}R'$,[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}).

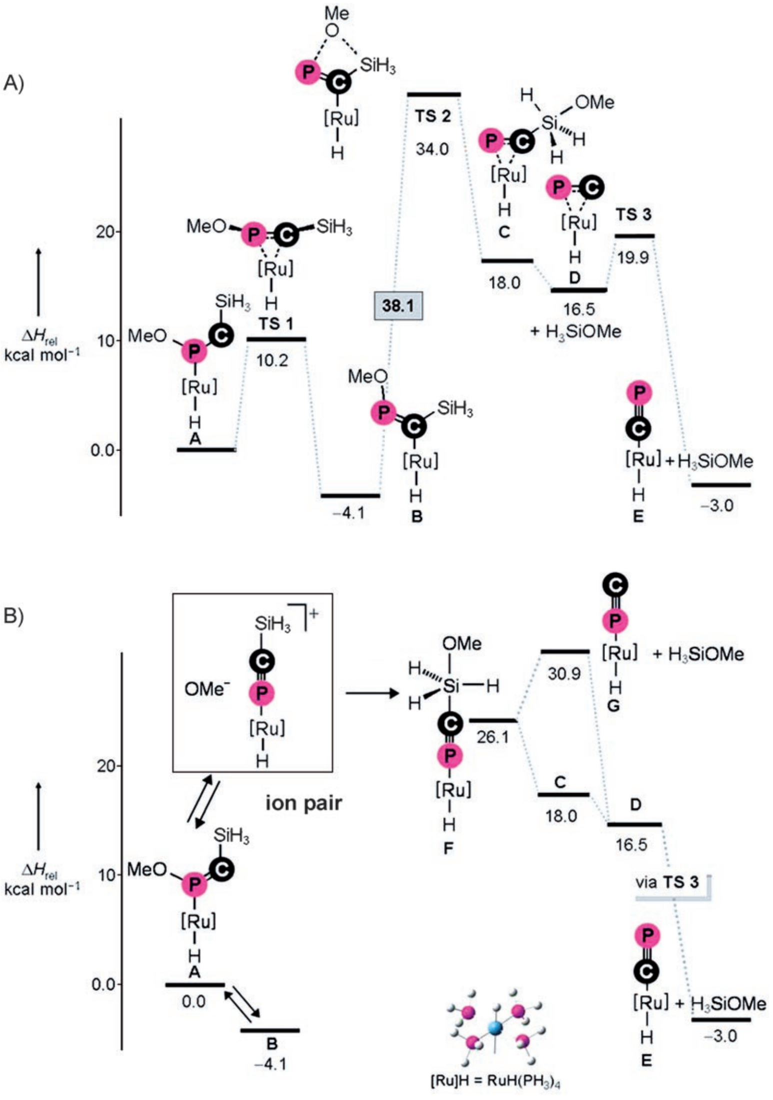

Figure 2. Calculated reaction paths (DFT) for the interaction of the silylphosphaalkyne complex $[RuH(PH_3)_4(P{\equiv}C\text{-}SiH_3)]^+$ with methoxide, MeO^- to give **E** + H_3SiOMe overall. A) nucleophilic attack at phosphorus; B) nucleophilic attack at silicon.

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 PH_3 molecules, $SiPh_3$ by a SiH_3 group, and phenoxide by methoxide. Based on the experimental results that suggested hydroxide attack at phosphorus, we hypothesized that the elimination of Ph_3SiOPh 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 2 A. This P-metalated phosphinocarbene **A** rearranges via **TS 1** with a modest barrier (10.2 kcal mol^{-1}) to the C-metalated phosphaalkene **B**, which is 4.1 kcal mol^{-1} more stable than **A**. Calculated ^{31}P-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 $\delta(^{31}P)_{calcd}$ of $\delta = 97$ ppm versus H_3PO_4, which is typical for phosphinocarbenes,[8] the $\delta(^{31}P)_{calcd}$ 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 $SiPh_3$ instead of OMe and SiH_3, respectively.

We then inspected the intramolecular elimination of the silylether $MeOSiH_3$ from **B**. The first intermediate of this pathway is the η^2-bonded phosphaalkyne silicate complex **C** which is obtained via transition state **TS 2**. The slightly exothermic dissociation of $MeOSiH_3$ 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 (**TS 3**) 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 **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 **TS 2** 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 2 B). 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 [RuH-$(PH_3)_4(P{\equiv}C\text{-}SiH_3)]^+$ directly led to the silicate complex **C**, implying that the actual barrier for the **F**→**D** conversion is probably much lower than 26.1 kcal mol^{-1}. An interesting feature is the large energy difference of 33.9 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 kcal mol^{-1}) is weaker than the Ru−C σ bond in **E** ($\Delta E_\sigma = 62.1$ 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** ($\Delta E_\pi = 16.1$ kcal mol^{-1}) is reduced compared to the Ru−C π bond of **E** ($\Delta E_\pi =$ 23.6 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 $C{\equiv}P^-$ 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 phosphaoximato complex is not possible if phenolate attacks at phosphorus. Second, despite being kinetically more favorable, the initial attack at the phosphorus center of $P{\equiv}C\text{-}SiPh_3$ 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 $Ph_3Si{-}OPh$ by phenolate attack at silicon subsequently drives the reaction to completion.

Experimental Section

3: $[RuH(dppe)_2(P{\equiv}C\text{-}SiPh_3)][OTf]$ (**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: ^{1}H (300 MHz, [D$_8$]THF): $\delta = 2.91$ (d, $^2J_{HP} =$ 9.14 Hz, (O)P=CH, 1 H), −10.17 ppm (dq, *trans*-$^2J_{HP} = 69.9$ Hz, *cis*-$^2J_{HP} = 20.5$ Hz, RuH, 1 H). ^{13}C{^{1}H} (75.5 MHz, [D$_8$]THF): $\delta =$ 110.5 ppm (d, $^1J_{CP} = 5.3$ Hz, (O)P=*C*H-SiPh$_3$). ^{31}P{^{1}H} (121.5 MHz, [D$_8$]THF): $\delta = 332.0$ (quintet, $^2J_{PP} = 28$ Hz, (O)P=CHSiPh$_3$), 67.7 ppm (d, $^2J_{PP} = 28$ Hz, dppe). For further details see the Supporting Information.

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Keywords: coordination modes · cyaphides · density functional calculations · multiple bonds · reaction mechanisms

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[4] Structure data: **3**: Colorless crystals suitable for X-ray analysis were obtained directly from the reaction vessel when wet CH_3CN was used as solvent in place of THF; $C_{71}H_{65}OP_5RuSi{\cdot}C_2H_3N$, monoclinic, space group $P2_1/c$, $a =$ 15.718(1), $b = 22.248(1)$, $c = 19.197(1)$ Å, $V = 6218.5(6)$ Å^3, $Z =$ 4, $\rho_{calcd} = 1.345$ Mg m^{-3}, crystal dimensions 0.54 × 0.40 × 0.09 mm^3, Bruker SMART Apex diffractometer with CCD area detector, Mo$_{K\alpha}$ radiation (0.71073 Å), 200 K, $2\Theta_{max} =$ 56.74°, 67 870 reflections, 15 535 independent ($R_{int} = 0.0268$), direct methods; refinement against full matrix (versus F^2) with SHELXTL (v.6.12) and SHELXL-97; 744 parameters, $R1 =$ 0.0459 and w$R2$ (all data) = 0.1290, max./min. residual electron density 1.499/−0.539 e Å^{-3}. The main residual electron density is located at the heavy atom ruthenium. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. CCDC-634845 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] A comparison of the calculated versus experimental ^{31}P NMR chemical shifts of $[\mathrm{RuH(PH_3)_4\{O{=}P{=}CH(SiH_3)\}}]$, $\delta(^{31}\mathrm{P})_{\mathrm{calcd}} = 345$ ppm versus $\delta(^{31}\mathrm{P})_{\mathrm{exp.}} = 332$ ppm in **3**, and $[\mathrm{RuH(PH_3)_4(C{\equiv}P)}]$, $\delta(^{31}\mathrm{P})_{\mathrm{calcd}} = 140$ ppm versus $\delta(^{31}\mathrm{P})_{\mathrm{exp.}} = 165$ ppm in **2**, make us confident that the chosen level of theory, B3LYP/GIAO 6-311+G* (C,H,O,Si,P), LACV3P(Ru), is sufficient. The shieldings are referenced against the calculated value of $\mathrm{P(CF_3)_3}$ which was set to $\delta = -3$ ppm versus 30% $\mathrm{H_3PO_4}$. The GIAO calculations were performed with Gaussian03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford, CT, **2004**.

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