$C \equiv P Ligands$

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, $[RuH(dppe)_2-(C\equiv P)]$ (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 $[RuH(dppe)_2(P \equiv CSiPh_3)]^+$ (1) was treated with 1.2 equivalents of NaOPh in dry $[D_8]$ THF (Scheme 1) and the



Scheme 1. Synthesis of phosphaoximato complex 3.

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subsequent reaction was monitored by ³¹P{¹H} 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 ³¹P 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]



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 ($\Sigma_P = 360^\circ$). 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 = 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-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)CtBu-(C=O)]²⁻ ion, has a markedly low-frequency resonance in the ³¹P NMR spectrum (δ = 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**, R₂P-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 ($\Delta H_r = -33.9 \text{ kcal mol}^{-1}$).

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 $0.0 \text{ kcal mol}^{-1}$ in the relative energy diagram shown in Figure 2A. This P-metalated phosphinocarbene A rearranges via **TS1** with a modest barrier $(10.2 \text{ kcal mol}^{-1})$ to the C-metalated phosphaalkene **B**, which is 4.1 kcal mol⁻¹ more stable than **A**. Calculated ³¹P-NMRspectroscopic 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 H₃PO₄, 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 SiPh₃ instead of OMe and SiH₃, respectively.

We then inspected the intramolecular elimination of the silylether MeOSiH₃ from **B**. The first intermediate of this pathway is the η^2 -bonded phosphaalkyne silicate complex **C** which is obtained via transition state **TS2**. The slightly exothermic dissociation of MeOSiH₃ from **C** (ΔH_r (**C** \rightarrow **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** \rightarrow **E**) = -19.5 kcal mol⁻¹). Note that the overall reaction



Figure 2. Calculated reaction paths (DFT) for the interaction of the silylphosphaalkyne 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 MeOSiH₃ very unlikely.

A more direct route to cyaphide complex **E** is simply nucleophilic attack at silicon by methoxide followed by MeOSiH₃ 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 kcalmol⁻¹ higher in energy than **A**. Elimination of MeOSiH₃ 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 kcalmol⁻¹ higher in energy

Communications

than **F**. Note that attempts to find a less symmetric pathway for the attack of methoxide on the silicon atom in [RuH- $(PH_3)_4(P=C-SiH_3)]^+$ directly led to the silicate complex C, implying that the actual barrier for the $\mathbf{F} \rightarrow \mathbf{D}$ conversion is probably much lower than 26.1 kcalmol⁻¹. An interesting feature is the large energy difference of $33.9 \text{ kcal mol}^{-1}$ between the cyaphide complex \mathbf{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** ($\Delta E_{\sigma} = 62.1 \text{ kcalmol}^{-1}$), 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** (ΔE_{π} = $23.6 \text{ kcal mol}^{-1}$) 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 $C \equiv P^-$ 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=C-SiPh₃ 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 Ph₃Si-OPh by phenolate attack at silicon subsequently drives the reaction to completion.

Experimental Section

3: [RuH(dppe)₂(P=C-SiPh₃)][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 CH₃CN and residual solvent removed in vacuo. Yield 0.065 g of **3** (53.3%). Selected NMR spectroscopy data: ¹H (300 MHz, [D₈]THF): δ =2.91 (d, ²J_{HP}=9.14 Hz, (O)P=CH, 1H), -10.17 ppm (dq, *trans-2*J_{HP}=69.9 Hz, *cis-2*J_{HP}=20.5 Hz, RuH, 1H). ¹³C{¹H} (75.5 MHz, [D₈]THF): δ =110.5 ppm (d, ¹J_{CP}=5.3 Hz, (O)P=CH-SiPh₃). ³¹P{¹H} (121.5 MHz, [D₈]THF): δ =332.0 (quintet, ²J_{PP}=28 Hz, (O)P=CHSiPh₃), 67.7 ppm (d, ²J_{PP}=28 Hz, dppe). For further details see the Supporting Information.

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[10] A comparison of the calculated versus experimental ³¹P NMR chemical shifts of [RuH(PH₃)₄[O=P=CH(SiH₃)]], δ (³¹P)_{calcd} = 345 ppm versus $\delta(^{31}P)_{exp} = 332$ ppm in **3**, and [RuH(PH₃)₄(C= P)], $\delta(^{31}P)_{calcd} = 140 \text{ ppm versus } \delta(^{31}P)_{exp.} = 165 \text{ ppm in } 2$, 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 P(CF₃)₃ which was set to $\delta = -3$ ppm versus 30% H₃PO₄. The GIAO calculations were performed with Gaussian 03, 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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