gested.[27] The aryl hydroxylamine is postulated to react with unoxidized aryl amine to generate a hydrazo compound that is then oxidized to the azo derivative.[27] This information suggested that isobutylhydroxylamine might be an intermediate in valanimycin biosynthesis. Accordingly, [1-^{13}C]isobutylhydroxylamine was synthesized from [1-^{13}C]isobutylamine by a modification of the methodology of Polonski and Chimiak[28] and administered to *S. viridifaciens*. To our satisfaction, the resulting valanimycin exhibited a ^{13}C enrichment which was about 6 times higher than that obtained with isobutylamine (Table I, expt 12). Additional proof for the intact incorporation of isobutylhydroxylamine into valanimycin was obtained by administration of [1-^{13}C,^{15}N]isobutylhydroxylamine, which was synthesized from [1-^{13}C,^{15}N]-isobutylamine. The valanimycin ammonia adduct isolated from this experiment exhibited high enrichment as well as the anticipated ^{13}C–^{15}N coupling (Table I, expt 13). The findings from these two experiments supply the first evidence for the intermediacy of a hydroxylamine in the biosynthesis of an aliphatic azoxy compound, and they provide support for the hypothesis that N–N bond formation involves the reaction of a hydroxylamine with an amine.[29]

Acknowledgment. We thank Dr. Tomio Takeuchi for a culture of *Streptomyces viridifaciens* and the National Institutes of Health (Grant CA-25142) and The Robert A. Welch Foundation (Grant C-729) for financial support.

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Phosphorus Analogue (C≡P$^-$) of a Bridging Cyanide (C≡N$^-$) Ligand: Synthesis and Structure of (Cl)(PEt$_3$)$_2$Pt(μ-C≡P)Pt(PEt$_3$)$_2$

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The cyanide ion (C≡N$^-$) is a common ligand in transition metal complexes.[1] It coordinates through the carbon at single metal centers (A, Chart I) or bridges two metals as in B,[2a] C,[2b] or D[2c] in Chart I. To our knowledge, the phosphorus analogue (C≡P$^-$) of the C≡N$^-$ ligand is unknown.[2d] In this communication, we report the synthesis and structure of the first example of a complex containing the cyaphide[3] (C≡P$^-$) ligand. In this complex, (Cl)(PEt$_3$)$_2$Pt(μ-C≡P)Pt(PEt$_3$)$_2$, the C≡P$^-$ ligand bridges the two Pt atoms in a manner not found in any of the known C≡N$^-$-bridged structures (B, C, or D).

The complex is prepared as outlined in Scheme I. In 20 mL of benzene, **1**[4] (0.395 g, 0.500 mmol) reacts with equimolar Pd(PEt$_3$)$_4$[5] (0.289 g, 0.500 mmol) at room temperature for 8 h under Ar to give only two products, **2**[6] and **3**,[7] as established by ^{31}P NMR studies of the mixture. Complex **2** is isolated in 86% yield as air-stable, colorless crystals by evaporating the reaction solution to dryness and recrystallizing the residue from hexanes at −78 °C; under these conditions **3** partially decomposes to unidentified materials. However, when equimolar Pt(PEt$_3$)$_4$ (0.334 g, 0.500 mmol) in 5 mL of benzene is added to the reaction mixture of **2** and **3** and the solution is stirred at room temperature under Ar for 30 min, moderately air-stable, light brown crystals of **4**[8] are isolated in an overall 80% yield (based on **1**) by evaporating the reaction solution to dryness and recrystallizing the residue from hexanes at −78 °C. Under these conditions, **4** precipitates after **2**.

The structure of **4**, as established by a single-crystal X-ray diffraction study,[9] shows that it contains a bridging C≡P$^-$ ligand

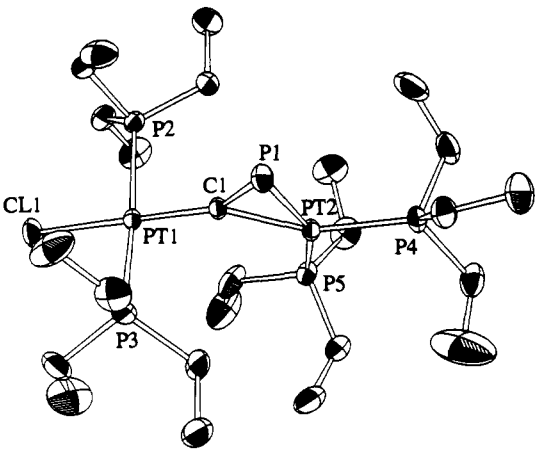
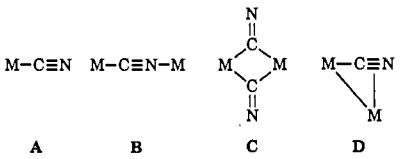
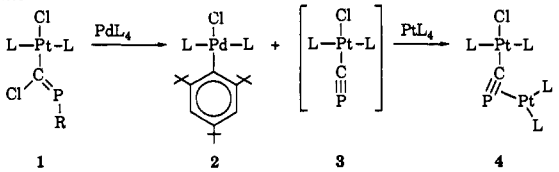


Figure 1. ORTEP drawing of (Cl)(PEt$_3$)$_2$Pt(μ-C≡P)Pt(PEt$_3$)$_2$ (**4**). Selected bond distances (Å) and angles (deg) are C(1)–P(1) = 1.666 (6), Pt(1)–C(1) = 1.950 (6), Pt(2)–C(1) = 2.083 (5), Pt(2)–P(1) = 2.337 (2), Pt(2)–P(4), = 2.269 (2), Pt(2)–P(5) = 2.277 (2), Pt(1)–C(1)–P(1) = 144.0 (3), Pt(1)–C(1)–Pt(2) = 139.7 (3), C(1)–Pt(2)–P(1) = 43.8 (2), P(4)–Pt(2)–P(5) = 104.20 (6).

Chart I



Scheme I



R = 2,4,6-tri-tert-butylphenyl
L = PEt$_3$

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(6) **2**: ^{1}H NMR (C$_6$D$_6$) δ 7.42 (t, 2 H, J_{PH} = 0.97 Hz, R), 1.89 (s, 18 H, CH$_3$ of R), 1.68 (t, q, 12 H, J_{HH} = 7.08 Hz, J_{PH} = 2.69 Hz, CH$_2$ of Et), 1.34 (s, 9 H, CH$_3$ of R), 0.88 (5 lines; 18 H, J_{HH} = 7.08 Hz, CH$_3$ of Et); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 85% H$_3$PO$_4$ external standard) δ −2.75 (s, PEt$_3$). Anal. Calcd for C$_{30}$H$_{59}$ClP$_2$Pd: C, 57.83; H, 9.47. Found: C, 57.60; H, 9.56.
(7) **3**: ^{31}P{^{1}H} NMR (C$_6$D$_6$, 85% H$_3$PO$_4$ external standard) δ 68.0 (t, J_{PP} = 9.16 Hz, J_{PtP} = 303 Hz from ^{195}Pt satellites, C≡P), 7.3 (d, J_{PP} = 9.16 Hz, J_{PtP} = 2871 Hz, PEt$_3$).
(8) **4**: ^{31}P{^{1}H} NMR (C$_6$D$_6$, 85% H$_3$PO$_4$ external standard) δ 107.0 (t, d, d, $^3J_{P_1P_2}$ = 10.68 Hz, $^2J_{P_1P_4}$ = 10.68 Hz, $^2J_{P_1P_5}$ = 13.73 Hz, $^1J_{Pt_2P_1}$ = 58 Hz, $^2J_{Pt_1P_1}$ = 255 Hz, C≡P$_1$), 18.6 (d, d, $^2J_{P_1P_4}$ = 10.68, $^2J_{P_4P_5}$ = 35.10 Hz, $^1J_{Pt_2P_4}$ = 3619 Hz, $^3J_{Pt_1P_4}$ = 137 Hz, P$_4$), 15.0 (t, d, d, $^4J_{P_5P_2}$ = 4.52 Hz, $^2J_{P_5P_4}$ = 35.10, $^2J_{P_5P_1}$ = 13.73 Hz, $^1J_{Pt_2P_5}$ = 3155 Hz, P$_5$), 4.9 (d, d, $^3J_{P_2P_1}$ = 10.68 Hz, $^4J_{P_2P_5}$ = 4.52 Hz, $^1J_{Pt_1P_2}$ = 2936 Hz, P$_2$, P$_3$). Anal. Calcd for C$_{25}$H$_{60}$ClP$_5$Pt$_2$: C, 31.89; H, 6.38. Found: C, 31.72; H, 6.61.

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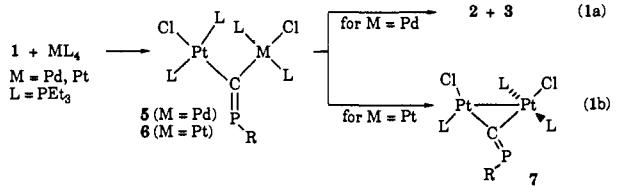
carbon-bonded to Pt(1) and η^2-bonded to Pt(2); the Pt atoms are not bonded to each other [Pt(1)—Pt(2) = 3.7868 (3) Å]. The atoms Pt(1), Cl(1), C(1), P(1), Pt(2), P(4), and P(5) are all nearly coplanar (within 0.061 Å), while P(2) and P(3) are 2.292 and 2.279 Å out of this plane. The C(1)—P(1) distance (1.666 (6) Å) is longer than those of triple bonds in phosphaalkynes RC≡P [1.52 (1) Å for R = 2,4,6-tri-*tert*-butylphenyl[10] and 1.536 (2) Å for R = *tert*-butyl][11] but is very similar to that (1.67 (2) Å) in the η^2(C,P)-coordinated phosphaalkyne in $(Ph_3P)_2Pt(\eta^2$-*t*-BuC≡P).[12] The C(1)—P(1) distance in **4** is also very similar to that of a C=P double bond, as found in Ph(H)C=PR (1.67 Å, where R = 2,4,6-tri-*tert*-butylphenyl).[13] Although there are no CN^- complexes analogous to **4** that would allow a comparison of Pt—CP vs Pt—CN bond lengths, the Pt(1)—C(1) distance (1.950 (6) Å) in **4** is shorter than the Pt—CN distances (1.992 (2) Å) in $K_2[Pt(CN)_4]$[14] and in $(Ph_3P)_2Pt(CN)(C{\equiv}CCN)$ (2.02 (3) Å).[15]

Since we have been unable to isolate and fully characterize **3**, its tentative assignment to the cyaphide structure in Scheme I is based on its ^{31}P NMR spectrum in the reaction mixture with **2**. Of the two ^{31}P signals, the one at 7.3 ppm is assigned to the PEt_3 ligands because the chemical shift is characteristic of a PEt_3 bound to Pt(II) and the ^{195}Pt–P coupling constant (2871 Hz) is typical of *trans*-$Pt^{II}(PEt_3)_2X_2$ complexes;[16] the small J_{PP} (9.16 Hz) is reasonable for coupling to the more distant phosphorus on the C≡P ligand. The signal at 68.0 ppm, which we assign to the cyaphide phosphorus, is split (J_{PP} = 9.16 Hz) into a triplet by the equivalent PEt_3 phosphorus atoms, and the ^{195}Pt satellites show a relatively small J_{Pt-P} (= 303 Hz) coupling constant. Supporting the structural assignment for **3** is its reaction with $Pt(PEt_3)_4$ which traps **3** (Scheme I) as the η^2(C, P)-complex **4**, which is obtained in high yield (80%).

The transfer of the chloro and 2,4,6-tri-*tert*-butylphenyl groups from **1** to the Pd in the first step (Scheme I) presumably occurs by initial oxidative addition (eq 1) of the C—Cl bond to the Pd(0) to give intermediate **5**; migration of the R group from the phosphorus to the Pd would give the observed products **2** and **3**.



The oxidative addition step is presumably very similar to that involved in the reaction (eq 1) of **1** with $Pt(PEt_3)_4$.[4] However, in this case, a PEt_3 ligand dissociates from intermediate **6**, which allows the formation of a Pt—Pt bond with a bridging arylisocyaphide (C≡PR)[17] ligand in **7**. These remarkable reactions of **1** with $Pd(PEt_3)_4$ and $Pt(PEt_3)_4$ have yielded the first examples of complexes containing C≡P⁻ and C≡PR ligands.

Acknowledgment. H.J. was supported in part by a government scholarship from the Republic of Korea. We thank the National Science Foundation (Grant CHE-9103948) for partial support of this research.

Supplementary Material Available: Description of the data collection and structure solution, completely labeled ORTEP drawing of **4**, and tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes for **4** (16 pages); listing of calculated and observed structure factors for **4** (25 pages). Ordering information is given on any current masthead page.

(9) Crystallographic data for **4**: mol wt 941.23; space group $P2_1/n$; a = 11.686 (1) Å, b = 12.232 (2) Å, c = 25.964 (4) Å; V = 3635 (2) Å^3, d_{calcd} = 1.72 g/cm^3 for Z = 4 at −50 ± 1 °C, μ = 80.7 cm^{-1} (Mo Kα). Diffraction data were collected at −50 ± 1 °C with an Enraf-Nonius CAD4 automated diffractometer. A total of 13 067 reflections were collected. Of the 6369 unique data, 4824 were considered observed, having $F_o^2 > 3.0\sigma(F_o^2)$. R = 0.024 and R_w = 0.033. Details of data collection and refinement are given in the supplementary material.

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(17) By analogy with the name arylisocyanide for C≡NR, we suggest arylisocyaphide for C≡PR. Also see footnote 3.

Syntheses and Absolute Configurations of Trehazolin and Its Aglycon

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Trehazolin (**1**) is a powerful trehalase inhibitor obtained from a culture broth of *Micromonospora* strain SANK 62390. Its structure was elucidated as a pseudodisaccharide shown in Figure 1 from degradation and ^1H NMR analysis.[1] A Suntory group presented the structure of trehalostain[2,3] as the C-2 epimer of **1**. However, trehalostatin has been postulated to be the same compound as trehazolin through comparison of their physical data. Therefore, it was necessary to determine the correct structure including absolute configuration. As a result, we were able to correlate the absolute configuration of natural trehazolin aglycon with that of D-glucose. We were also able to synthesize trehazolin itself.

The starting compound, (2*R*,3*S*,4*R*)-4-(benzoyloxy)-2,3-bis-[(methoxymethyl)oxy]-5-hexenal (**2**), was obtained from D-glucose[4] and was converted to the corresponding oxime (**3**) by treatment with hydroxylamine. Oxidation of **3** with aqueous sodium hypochlorite and spontaneous [2 + 3] cycloaddition[5] gave isoxazoline **4**. Cleavage of the N–O bond of **4** and coincident hydrolysis of the imine group with Raney nickel and boric acid in methanol–dioxane–H_2O (15:5:3) under an atmosphere of hydrogen[6] caused spontaneous elimination of the benzoyloxy group to give an α,β-unsaturated cyclopentenone (**5**). The primary alcohol of **5** was protected to give silyl ether **6**. The ketone of **6** was reduced to a 5:2 mixture of alcohols, **7** and its epimer, by treatment with sodium borohydride and cerium chloride.[7] The mixture was separable chromatographically on a silica gel column. Benzylation of the secondary alcohol of **7** with benzyl bromide and sodium hydride gave **8**, and deprotection of the silyl group of **8** with tetrabutylammonium fluoride[8] gave **9**.

Sharpless' epoxidation[9] of allylic alcohol **9** with diisopropyl L-tartrate, titanium(IV) isopropoxide, and *tert*-butyl hydroperoxide in dichloromethane gave **10** in 94% yield. Use of diisopropyl

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