Synthesis and X-ray Structure of the First Cluster-Stabilized Phosphaallene, $[\mu_3\text{-}\eta^2\text{-}t\text{-BuP(C=CH(C}_6\text{H}_5))]\text{FeCo}_2\text{(CO)}_9$

Rene Mathieu,*[1a] Anne-Marie Caminade,[1b] Jean-Pierre Majoral,*[1b] and Jean-Claude Daran[1c]

Contribution from the Laboratoire de Chimie de Coordination du CNRS, Unité n° 8241 liée par convention à l'Université Paul Sabatier, 31077 Toulouse Cedex, France, the Laboratoire de Synthèse, Structure et Réactivité de Molécules Phosphorées, UA 454, Université Paul Sabatier, 31062 Toulouse Cedex, France, and the Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France. *Received June 17, 1986*

Abstract: The complex $[\mu_3\text{-}\eta^2\text{-}t\text{-BuP(C}{=}\text{CH(C}_6\text{H}_5))]\text{FeCo}_2\text{(CO)}_6$ (**6**) has been obtained in 3% yield by the following sequence of reactions: (i) synthesizing $[\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{CPh})\text{H}]\text{Fe(CO)}_4$ (**1**) by the reaction of $[\text{HFe(CO)}_4]^-$ with $\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{CPh})\text{Cl}$, (ii) complexing the CC triple bond by reaction with $\text{Co}_2\text{(CO)}_8$ leading to $[\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{CPh})\text{H}]\text{FeCo}_2\text{(CO)}_{10}$ (**4**), and (iii) refluxing **4** in *n*-hexane. The major product of the latter reaction is the phosphinidene cluster $(t\text{-Bu})\text{PFeCo}_2\text{(CO)}_9$ (**5**), isolated in 50% yield. Phenylacetylene has been detected in the reaction media, but it has been shown that **6** does not result from the reaction of **5** with the alkyne. Rather **6** is the result of intramolecular migration of hydrogen from phosphorus to the β-carbon of the alkynyl group. The structure of **6** has been determined by X-ray diffraction. **6** is orthorhombic, space group *Pbca* with $a = 11.994$ (3) Å, $b = 27.008$ (2) Å, $c = 14.939$ (2) Å, and $Z = 8$. The structure has been solved and refined to R and R_w values of 0.0311 and 0.0331, respectively, by using 1434 reflections. **6** consists of a metallic triangle, Co_2Fe, having each metal atom surrounded by three carbonyl groups. The phosphaallenyl ligand is bonded by the phosphorus to the two cobalt atoms and by the C_α carbon to iron.

Various stable phosphacumulenes of the type R—P=C=X (X = CR_2, NR, or P—Ar) have been isolated in the free state,[2] but only recently have their complexing properties been studied.[3]

We thought that a possible way to complex phosphaalkenylidene ligands was to start with a secondary alkyl–alkynyl phosphane and to assist the migration of the hydrogen atom from phosphorus to the unsaturated carbon atoms through complexation of the triple bond.

In a first approach, dicobalt octacarbonyl has been retained, as its good propensity to react with alkynes is well-known.[4] Still, to avoid side reactions due to the reactivity of the lone pair of phosphorus toward cobalt,[5] we have first complexed the secondary phosphine by the Fe(CO)_4 group.

In this paper, we relate the results of this study that show that our objective has been fulfilled by the isolation of the title compound in low yield.

Results and Discussion

Synthesis of $\text{Fe(CO)}_4\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{C}(\text{C}_6\text{H}_5))(\text{H})$ (1). As the $\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{CC}_6\text{H}_5)(\text{H})$ phosphane is not very stable,[6] we have used an indirect method to synthesize **1**, starting from the chlorophosphane $\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{CC}_6\text{H}_5)\text{Cl}$ (**2**) and $[\text{HFe(CO)}_4]^-$ (**3**). We have shown recently that **3** reacts with dichlorophosphanes RPCl_2 to give $\text{Fe(CO)}_4\text{PRHCl}$ complexes[7] in one step. It seemed that this reaction could be extended to the case of the monochlorophosphane, **2**. This is actually the case, and the reaction of **2** with 1 equiv of **3** in a dichloromethane solution leads quantitatively to **1** at room temperature. Complex **1** is a yellow-brown liquid which has been identified by mass spectrometry (*m*/*z* 358 with successive loss of four CO groups), and the spectroscopic data[8] are in perfect agreement with the $\text{Fe(CO)}_4\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{C}(\text{C}_6\text{H}_5))(\text{H})$ formulation for **1**.

Synthesis of $\text{Fe(CO)}_4[\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{C}(\text{C}_6\text{H}_5))\text{H}]\text{Co}_2\text{(CO)}_6$ (4). Upon addition of a stoichiometric amount of $\text{Co}_2\text{(CO)}_8$ to a solution of **1** in pentane at room temperature, slow evolution of carbon monoxide was observed. The reaction was stopped when carbon monoxide evolution ceased and crystallization in pentane afforded a black complex, **4**, in good yield. The IR spectrum of this complex in the ν_{CO} stretching region shows a very complex pattern that suggests the fixation of Co(CO)_n fragments. Furthermore, no absorption is observed in the region characteristic of free carbon–carbon triple-bond vibration.

The exact formulation of **4** has been established by mass spectroscopy (*m*/*z* 644 with successive loss of 10 CO groups), and the chemical analysis is in good agreement with the $\text{Fe(CO)}_4[\text{P}(t\text{-Bu})(\text{C}{\equiv}\text{CC}_6\text{H}_5)\text{H}]\text{Co}_2\text{(CO)}_6$ formulation.

The proton NMR spectrum confirms the presence of the *t*-Bu (δ 1.42, $^3J_{\text{PH}} = 17$ Hz), H (δ 6.09, $J_{\text{PH}} = 339.8$ Hz), and C_6H_5 (δ 7.41) groups. The phosphorus NMR spectrum reveals a shift of the ^{31}P resonance toward a lower field compared to **1** (δ 64.2, $^1J_{\text{PH}} = 339.6$, $^3J_{\text{PH}} = 17$ Hz).

All these data are in good agreement with a reaction of $\text{Co}_2\text{(CO)}_8$ with the carbon–carbon triple bond of the alkynyl substituent, and we propose for **4** the structure shown in Figure 1.

Another example of complexation of the triple bond of a complexed alkynylphosphine has recently been reported, and the X-ray structure of the reaction product has been established.[9]

Study of the Thermal Stability of 4. Since our initial aim was to provoke the migration of hydrogen from phosphorus to one of

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(1) Full addresses: (a) Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex, France. (b) Laboratoire de Synthèse, Structure et Réactivité des Molécules Phosphorées, UA 454, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France. (c) Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris Cedex 05, France.

(2) (a) Appel, R.; Paulen, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 785–786. (b) Yoshifuji, M.; Toyota, K.; Shibayame, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809–1812. (c) Appel, R.; Fölling, P.; Josten, B.; Siray, M.; Winkhaus, V.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 619–620.

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(8) IR (hexane solution) 2178 ($\nu_{\text{C}{\equiv}\text{C}}$), ν_{CO} 2056, 1983, 1954, 1946 cm^{-1}; ^1H NMR δ 7.62 (C_6H_5), 1.58 (d, $J = 18.6$ Hz, *t*-Bu), 6.15 (d, $^1J^{\text{PH}} = 374$ Hz, PH); ^{31}P NMR δ 30.0 (doublet of octet, $^1J_{\text{PH}} = 374$, $^3J_{\text{PH}} = 18.6$ Hz).

(9) Sappa, E.; Prediere, G.; Tiripicchio, A.; Camellini, M. *J. Organomet. Chem.* **1985**, *297*, 103–115.

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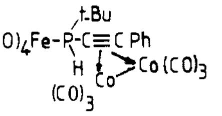

Figure 1. Structure of complex **4**.

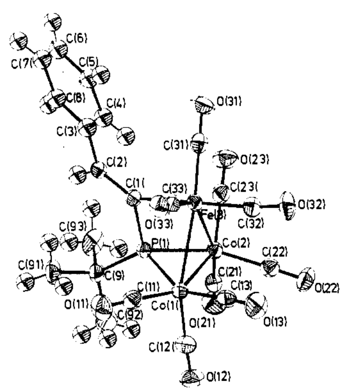

Figure 2. ORTEP drawing of **6** showing the atomic numbering scheme.

the unsaturated carbon atoms, we have investigated if such a migration could be induced by thermal activation of **4**.

When **4** was heated in refluxing hexane, monitoring the reaction by infrared spectroscopy revealed rapid formation of new complexes and the disappearance of **4**. Dark crystals of **5** were isolated from the reaction mixture.

Mass spectrometry of **5** shows a parent ion at *m/z* 514 with successive loss of nine CO groups. This is consistent with the $FeCo_2(CO)_9P(t\text{-}Bu)$ formulation. This is corroborated by the comparison of spectroscopic data of **5**[10] with published data of the same complex prepared by another route:[11] ν_{CO} 2090, 2047, 2036, 2028, 2008, 1979, 1975 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.31 (J = 18.6 Hz). Examination of the IR spectrum of the mother solution after isolation of **5** shows that another compound, **6**, is present. It has been separated from **5** by chromatography on Florisil and isolated by crystallization. Its IR spectrum in the ν_{CO} stretching region reveals only terminal carbonyl groups. The proton NMR spectrum of **6** shows the presence of the *t*-Bu group (δ 1.50, J_{PH} = 17.0 Hz), the phenyl group (multiplet centered at δ 7.44), and a doublet centered at δ 8.33 with a coupling constant of 22.9 Hz. The intensity of this doublet is consistent with the presence of one hydrogen.

These results suggest that **6** is the result of migration of the hydrogen atom from phosphorus to one carbon of the alkynyl triple bond.

The low yield of **6** prevented recording of the ^{13}C NMR spectrum. Thus it was difficult on the sole basis of spectroscopic data to know if the migration had occurred to the C_α or C_β carbon of the triple bond, even though the value of the coupling constant with phosphorus suggests that hydrogen is bonded to the C_α carbon.

For these reasons, an X-ray structure determination of **6** was undertaken. The resulting structure is shown in Figure 2. Principal bond lengths and bond angles are gathered in Table I. **6** consists of a metallic triangle containing two cobalt and one iron atoms. Each metal atom is surrounded by three carbonyl groups. To this triangle is coordinated the *t*-BuP=C=CH(Ph) fragment which results from the migration of the hydrogen atom from phosphorus to the β-carbon of the alkynyl triple bond. This fragment is bonded by the phosphorus to the two cobalt atoms and by the C(1) carbon to iron. A similar type of bonding for a phosphaalkene, Ph—P=C(OEt)Ph, has been recently found in a triiron complex, $Fe_3(\mu_3\text{-}PPh)(\mu\text{-}PhPC(OEt)Ph)(CO)_9$.[12] The assumption that the fragment is a phosphaphenylethenylidene is supported by a relatively short P(1)—C(1) distance which compares well with the value found in a $RP{=}CH_2$ ligand bonded to a triiron unit[13] (1.76 (1) Å) and is slightly shorter than that of the bonded PhP=C(OEt)Ph ligand[10] (1.800 (6) Å). The C(1)–C(2) bond length is typical of a carbon–carbon double bond. The P(1), C(1), C(2), and Fe(3) atoms are in a plane which is nearly perpendicular to the triangle of metals. If the phosphaphenylethenylidene ligand as a whole is considered a four-electron-donating ligand, **6** is a 48-valence-electron cluster. However, examination of the valence electrons around each metal leads to a more puzzling situation. Two cases can indeed be considered which are presented in Figure 3, parts a and b.

Table I. Bond Distances (Å) and Bond Angles (deg) with esd's in Parentheses Referring to the Last Digit

	Distances		
Co(1)–Co(2)	2.556 (2)	P(1)–C(9)	1.895 (9)
Co(1)–Fe(3)	2.649 (2)	C(11)–O(11)	1.14 (1)
Co(2)–Fe(3)	2.638 (2)	C(12)–O(12)	1.15 (1)
Co(1)–P(1)	2.181 (2)	C(13)–O(13)	1.13 (1)
Co(1)–C(11)	1.77 (1)	C(21)–O(21)	1.12 (1)
Co(1)–C(12)	1.79 (1)	C(22)–O(22)	1.16 (1)
Co(1)–C(13)	1.81 (1)	C(23)–O(23)	1.14 (1)
Co(2)–P(1)	2.167 (3)	C(31)–O(31)	1.14 (1)
Co(2)–C(21)	1.79 (1)	C(32)–O(32)	1.13 (1)
Co(2)–C(22)	1.79 (1)	C(33)–O(33)	1.14 (1)
Co(2)–C(23)	1.78 (1)	C(1)–C(2)	1.33 (1)
Fe(3)–C(31)	1.78 (1)	C(2)–C(3)	1.480 (9)
Fe(3)–C(32)	1.80 (1)	C(9)–C(91)	1.53 (1)
Fe(3)–C(33)	1.76 (1)	C(9)–C(92)	1.50 (1)
Fe(3)–C(1)	2.020 (8)	C(9)–C(93)	1.52 (1)
P(1)–C(1)	1.753 (9)		
	Angles		
Fe(3)–Co(1)–Co(2)	60.88 (5)	C(9)–P(1)–Co(1)	123.6 (3)
Fe(3)–Co(2)–Co(1)	61.32 (5)	C(9)–P(1)–Co(2)	125.8 (3)
Co(2)–Fe(3)–Co(1)	57.80 (5)	C(9)–P(1)–C(1)	115.3 (4)
C(11)–Co(1)–P(1)	95.0 (3)	0(11)–C(11)–Co(1)	177.2 (10)
C(12)–Co(1)–P(1)	102.9 (3)	O(12)–C(12)–Co(1)	176.7 (9)
C(12)–Co(1)–C(11)	102.1 (5)	O(13)–C(13)–Co(1)	177.3 (9)
C(13)–Co(1)–P(1)	150.5 (3)	O(21)–C(21)–Co(2)	178.2 (9)
C(13)–Co(1)–C(11)	103.4 (5)	O(22)–C(22)–Co(2)	179.0 (9)
C(13)–Co(1)–C(12)	95.7 (4)	O(23)–C(23)–Co (2)	172.4 (10)
C(21)–Co(2)–P(1)	100.8 (3)	O(31)–C(31)–Fe(3)	179.4 (9)
C(22)–Co(2)–P(1)	145.6 (3)	O(32)–C(32)–Fe(3)	173.3 (9)
C(22)—Co(2)–C(21)	95.5 (4)	O(33)–C(33)–Fe(3)	177.9 (9)
C(23)–Co(2)–P(1)	100.5 (3)	P(1)–C(1)–Fe(3)	88.1 (4)
C(23)–Co(2)–C(21)	104.2 (4)	C(2)–C(1)–Fe(3)	141.3 (7)
C(23)–Co(2)–C(22)	104.6 (4)	C(2)—C(1)–P(1)	130.3 (7)
C(32)–Fe(3)–C(31)	92.4 (4)	C(3)–C(2)–C(1)	131.5 (7)
C(33)–Fe(3)–C(31)	100.5 (5)	C(4)–C(3)–C(2)	122.7 (3)
C(33)–Fe(3)–C(32)	93.3 (5)	C(8)–C(3)–C(2)	117.2 (3)
C(1)–Fe(3)–C(31)	87.0 (4)	C(91)–C(9)–P(1)	108.3 (6)
C(1)–Fe(3)–C(32)	174.0 (4)	C(92)–C(9)–P(1)	109.9 (7)
C(1)–Fe(3)–C(33)	92.7 (4)	C(92)–C(9)–C(91)	108.7 (9)
Co(2)–P(1)–Co(1)	72.00 (8)	C(93)–C(9)–P(1)	107.4 (7)
C(1)–P(1)–Co(1)	105.6 (3)	C(93)–C(9)–C(91)	111.8 (8)
C(1)–P(1)–Co(2)	106.3 (3)	C(93)–C(9)–C(92)	110.7 (9)

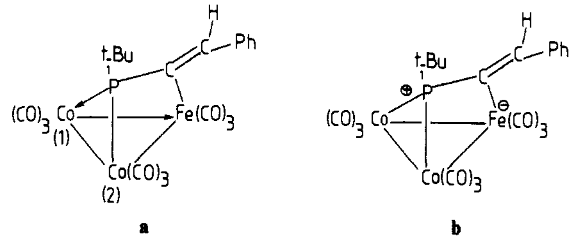

Figure 3. Two descriptions (a and b) of the bonding mode of the phosphaethenylidene ligand in **6**.

In part a, the phosphaalkenyl ligand is considered as σ-bonded to Fe(3) by C(1) while the P(1) atom gives one electron to the

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[10] IR (hexane solution) ν_{CO} 2091, 2047, 2037, 2030, 2007, 1980, 1966 cm^{-1}; ^{1}H NMR (C_6D_6 solution) of 1.30 (d, J = 18.45 Hz).

[11] Müller, M.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 2311–2321.

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Co(2) atom and two electrons to Co(1). In this hypothesis, not considering the Co(1)–Fe(3) bond, each cobalt atom is surrounded by 18 valence electrons and the iron atom by 16 electrons. The Co(1)–Fe(3) bond should be established by a dative bond from cobalt to iron.

In part b, the molecule is considered as a zwitterion; the phosphorus atom carries the positive charge while the iron atom carries the negative charge. This closely resembles the mode of bonding of ylides to transition metals.[14] This situation seems more realistic considering the structural data and especially the quite short Fe(3)–C(1) bond distance.

To summarize, **4** in boiling hexane gives two products: (i) the main product, (t-Bu)PFeCo$_2$(CO)$_9$ (**5**), in which the phosphorus atom has lost the phenylethynyl group and one hydrogen and (ii) **6**, obtained in low yield, in which hydrogen has migrated from phosphorus to the β-carbon of the ethynyl group. Furthermore, gas chromatography analysis of the hexane solution evidences the presence of phenylacetylene. The presence of the alkyne raises the question of the origin of **6**. Does it occur by intramolecular rearrangement of **4** or by the reaction of **5** with phenylacetylene?

Consequently, we tested the reactivity of **5** toward phenylacetylene in boiling hexane: no reaction occurred. So, **6** is produced from **4** by intramolecular rearrangement.

The mechanism shown in Scheme I is proposed for the thermal reaction of **4**. The first step would be phosphorus–hydrogen bond breaking through intermediate A, a common reaction of dialkylphosphine with cluster compounds.[15] In this intermediate, the alkynyl group would be η^2-bonded to Co(2) only. The second step would be the coordination of the alkynyl group to iron, the vacant site being created by the opening of the Fe–P bond. Then, migration of the hydride to the C$_\alpha$ carbon on the alkynyl group would lead to **5** after elimination of phenylacetylene, while migration to the C$_\beta$ carbon would lead to **6**.

Experimental Section

All reactions were performed under a nitrogen atmosphere by using the standard Schlenk tube technique. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer in hexane solutions. ^{1}H NMR spectra were obtained with a Bruker WH90 spectrometer and ^{31}P NMR data with a Bruker AC80 instrument. [PPh$_4$][HFe(CO)$_4$][16] was prepared by published procedures.

Synthesis of (Phenylethynyl)-*tert*-butylchlorophosphine (2). A diethyl ether solution of *n*-butyllithium (1.6 M, 30 mL, 0.050 mol) was added dropwise to a well-stirred solution of phenylacetylene (5 g, 5.375 mL, 0.049 mol) in diethyl ether (20 mL) maintained at −70 °C. The resulting white suspension was stirred for 2 h at room temperature and cooled to −70 °C. A solution of *tert*-butyldichlorophosphine (7.63 g, 0.048 mol) in diethyl ether (20 mL) then was added dropwise. After the mixture was stirred for 2 h at room temperature, the precipitate was filtered out and the solvent evaporated. **2** was distilled: bp 86 °C (0.1 mmHg); 8.62 g (80% yield); ^{31}P NMR (CDCl$_3$) δ 82; ^{1}H NMR (CDCl$_3$) δ 0.88 (d, $^3J_{PH}$ = 15 Hz, 9 H, C(CH$_3$)$_3$), 7.2 (m, 5 H, C$_6$H$_5$); IR (neat) 2160 cm^{-1} (C≡C); mass spectrum, *m/e* 224.

Synthesis of 1. To 1.1 g of *t*-BuPCl(C≡CPh) dissolved in 10 cm^3 of CH$_2$Cl$_2$ was added [PPh$_4$][HFe(CO)$_4$] (2.6 g) dissolved in 10 cm^3 of CH$_2$Cl$_2$. After stirring for 2 h, the solution was evaporated to dryness. Extraction of the residue with 4 × 10 cm^3 of pentane and evaporation of the extracts to dryness left 1.3 g of **1** as a brown liquid (ca. 80% yield).

Synthesis of 4. To 0.6 g of **1** in solution in 10 cm^3 of pentane was added 0.6 g of Co$_2$(CO)$_8$ in 10 cm^3 of pentane, and the solution was stirred until carbon monoxide evolution ceased. The solution was then evaporated to dryness. The residue was dissolved in 15 cm^3 of hexane and cooled to −20 °C. **4** was obtained as brown crystals (0.9 g, 89% yield).

Anal. Calcd for $C_{22}H_{15}Co_2FeO_{10}P$: C, 40.99; H, 2.33. Found: C, 41.28; H, 2.52.

Synthesis of 5 and 6. **4** (0.6 g) was heated for 2 h in refluxing hexane. The solution was then filtered and evaporated to dryness. The residue was dissolved in 10 cm^3 of hexane and cooled to −20 °C, to give 0.20 g of **5** as maroon crystals. The mother solution was evaporated to dryness and chromatographed on a column of Florisil. Elution with hexane gave successively **5** (0.04 g) and **6** (0.02 g after crystallization in hexane). The total yield of **5** is 50% while for **6** it is 3.5%.

Table II. Crystal Data

empirical formula	$C_{21}H_{15}O_9PCo_2Fe$
formula wt	616.01
cryst system	orthorhombic
space group	*Pbca*
a, Å	11.994 (3)
b, Å	27.008 (2)
c, Å	14.939 (2)
V, Å^3	4839
Z	8
cryst size, mm	0.36 × 0.16 × 0.1
μ(Mo Kα), cm^{-1}	21.3
D_{calcd}, g/cm^3	1.69
temp, °C	20
radiation	Mo Kα (graphite monochromator)
scan range θ, deg	0.8 + 0.345 tan θ
2θ range, deg	3–46
scan type	$\omega/1.33 \times \theta$
standard	2100, 404
reflcns collected	3521
reflcns merged	3353
reflcns obsd	1434
criteria	$1 \geq 2\sigma(1)$
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.0311
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o^2]^1/_2$	0.0331 (unit wt)
final shift/error max (av)	0.16 (0.07)

Table III. Fractional Atomic Coordinates with esd's in Parentheses

atom	*x/a*	*y/b*	*z/c*
Co(1)	0.1922 (1)	0.19412 (4)	0.03251 (8)
Co(2)	0.0181 (1)	0.15055 (4)	0.09185 (8)
Fe(3)	0.2155 (1)	0.11893 (5)	0.14487 (8)
P(1)	0.1245 (2)	0.12397 (8)	−0.0151 (1)
C(11)	0.313 (1)	0.1919 (4)	−0.0356 (7)
O(11)	0.3889 (7)	0.1920 (3)	−0.0817 (5)
C(12)	0.1084 (8)	0.2389 (4)	−0.0243 (7)
O(12)	0.0515 (6)	0.2679 (3)	−0.0571 (5)
C(13)	0.2329 (9)	0.2346 (3)	0.1234 (7)
O(13)	0.2573 (7)	0.2616 (3)	0.1782 (5)
C(21)	−0.1064 (9)	0.1650 (3)	0.0309 (7)
O(21)	−0.1860 (6)	0.1741 (3)	−0.0053 (5)
C(22)	−0.0010 (8)	0.1970 (4)	0.1756 (7)
O(22)	−0.0142 (7)	0.2276 (2)	0.2291 (5)
C(23)	−0.0136 (8)	0.0938 (4)	0.1471 (7)
O(23)	−0.0453 (6)	0.0581 (3)	0.1781 (5)
C(31)	0.2110 (8)	0.0619 (4)	0.2051 (6)
O(31)	0.2075 (7)	0.0257 (3)	0.2440 (5)
C(32)	0.2054 (8)	0.1551 (4)	0.2461 (7)
O(32)	0.2045 (6)	0.1741 (3)	0.3135 (4)
C(33)	0.3604 (9)	0.1276 (3)	0.1360 (7)
O(33)	0.4538 (6)	0.1344 (2)	0.1321 (5)
C(1)	0.2092 (8)	0.0779 (3)	0.0319 (6)
C(2)	0.2404 (7)	0.341 (3)	−0.0006 (5)
C(3)	0.3182 (3)	−0.0038 (1)	0.0344 (3)
C(4)	0.4033 (3)	0.0074 (1)	0.0942 (3)
C(5)	0.4782 (3)	−0.0292 (1)	0.1202 (3)
C(6)	0.4680 (3)	−0.0769 (1)	0.0863 (3)
C(7)	0.3829 (3)	−0.0881 (1)	0.0265 (3)
C(8)	0.3079 (3)	−0.0515 (1)	0.0005 (3)
C(9)	0.0800 (8)	0.1126 (4)	−0.1351 (6)
C(91)	0.1845 (9)	0.1010 (4)	−0.1905 (6)
C(92)	0.026 (1)	0.1584 (4)	−0.1725 (7)
C(93)	−0.0015 (9)	0.0695 (4)	−0.1346 (7)

Anal. Calcd for $C_{13}H_9Co_2FeO_9P$ (**5**): C, 30.35; H, 1.75. Found: C, 30.04; H, 1.90.

Anal. Calcd for $C_{21}H_{15}Co_2FeO_9P$ (**6**): C, 40.90; H, 2.43. Found: C, 40.79; H, 2.66.

X-ray Studies. Preliminary unit-cell dimensions and symmetry information were derived from precession photographs; the selected crystal was then set up on an Enraf-Nonius CAD4 automatic diffractometer. Accurate cell dimensions and an orientation matrix were obtained from least-squares refinements of the setting angles of 25 well-centered reflections (24 < 2θ < 28).

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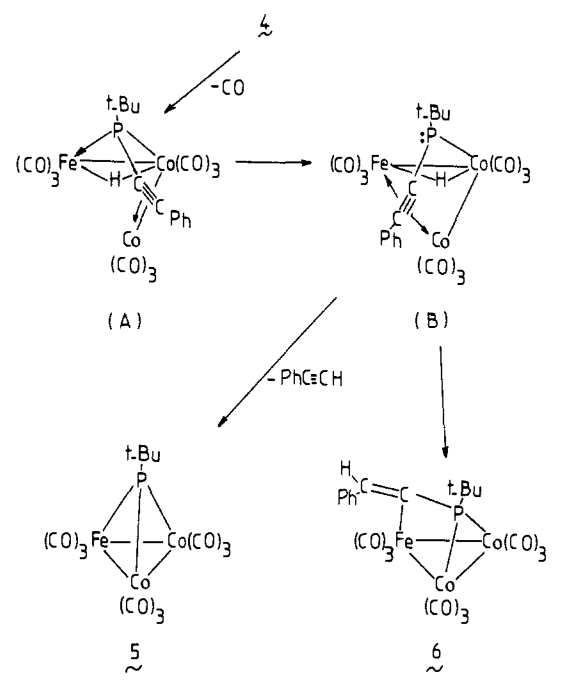
Scheme I



Crystal data and data collection parameters are listed in Table II. Intensities of two standard reflections were monitored every hour. They showed no variation during data collection. Corrections were made for Lorentz and polarization effects. ψ scan curves showed significant intensity variations. Absorption corrections were then applied via an empirical correction technique.[17]

Computations were performed using the CRYSTALS system[18] adapted on a VAX 11/725. Atomic scattering factors for neutral Fe, Co, P, C, O, and H were taken from the International Tables for Crystallography.[19] Anomalous dispersion for Fe and Co atoms were taken into account.

The positions of Fe and Co atoms were determined by Harker vector analysis of three-dimensional Patterson maps. All remaining non-hydrogen atoms were found by successive electron density map calculations. All non-hydrogen atoms were refined anisotropically, except phenyl rings, which were refined as isotropic rigid groups (C–C = 1.39 Å). Hydrogen atoms were located on a difference electron density map. Their atomic coordinates were refined with a fixed overall isotropic thermal parameter for two rounds of least-squares refinement with fixed parameters for heavy atoms. They were not further refined in the final stages of calculations. The criteria for a satisfactory completed analysis were the ratio of parameter shifts to standard deviations (Table II) and no significant features in the final difference map. Atomic coordinates are given in Table III.

Supplementary Material Available: A listing of anisotropic thermal parameters and hydrogen atomic coordinates (3 pages); tables of observed structure amplitudes and structure factors calculated from the final atomic parameters (12 pages). Ordering information is given on any current masthead page.

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Construction of an Enzyme-Targeted Organophosphonate Using Immobilized Enzyme and Whole Cell Synthesis

L. M. Reimer, D. L. Conley, D. L. Pompliano, and J. W. Frost*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received November 1, 1985*

Abstract: A potential inhibitor of plant aromatic amino acid biosynthesis, 3-deoxy-D-*arabino*-heptulosonic acid 7-phosphonate, is constructed. The centerpiece of the convergent strategy is methyl (methyl 3-deoxy-D-*arabino*-heptulopyranosid)onate. This intermediate is derived from 3-deoxy-D-*arabino*-heptulosonic acid 7-phosphate produced by immobilized enzyme synthesis or via 3-deoxy-D-*arabino*-heptulosonic acid which results from the whole cell synthesis. By the integration of organic chemical synthesis with immobilized enzyme or whole cell synthesis, the desired product organophosphonate can be conveniently made from D-fructose or D-glucose, respectively.

Disruption of amino acid biosynthesis in plants is purported to be an extremely effective vehicle for herbicide action.[1-3] The historical roots for this notion can be found in herbicidal disruption of plant aromatic amino acid biosynthesis (the shikimate pathway). Inhibition and inactivation of shikimate-pathway enzymes continues to be the focus of widespread interest in the development of specific, enzyme-targeted herbicides. Derivatives of metabolites intermediate in the common pathway offer promise as effective enzyme inhibitors. Like the naturally occurring metabolites, such putative herbicidal agents can be constructed from simple carbohydrates.

The appeal of enzyme-targeted herbicides derivable from carbohydrates must be tempered by the complexity of the chemical syntheses demanded by such an approach. In this report the construction of 3-deoxy-D-*arabino*-heptulosonic acid 7-phosphonate (DAH phosphonate, **1**)[4] is detailed. Synthetic organic, immobilized enzyme, and whole cell syntheses are exploited to achieve

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(2) Disruption of aromatic amino acid biosynthesis: (a) Jaworski, E. G. *J. Agric. Food Chem.* **1972**, *20*, 1195. (b) Amrhein, N.; Holländer, H. *Naturwissenschaften* **1981**, *68*, 43. (c) Holländer-Czytko, H.; Amrhein, N. *Plant Sci. Lett.* **1983**, *29*, 89. (d) Amrhein, N.; Schab, J.; Steinrücken, H. C. *Naturwissenschaften* **1980**, *67*, 356. (e) Steinrucken, H. C.; Amrhein, N. *Biochem. Biophys. Res. Commun.* **1980**, *94*, 1207. (f) Amrhein, N.; Johanning, D.; Schab, J.; Schulz, A. *FEBS Lett.* **1983**, *157*, 191. (g) Boocock, M. R.; Coggins, J. R. *FEBS Lett.* **1983**, *154*, 127. (h) Mousedale, D. M.; Coggins, J. R. *Planta* **1984**, *160*, 78.

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