the rings were inclined by 6.6°, and the relevant distances to each ring were 1.69 and 1.70 Å. The Fe–ring center distance in pure ferrocene[12] is 1.66 Å, which is not significantly different from the values cited above.

Acknowledgment. We thank Professor D. H. Templeton for valuable discussions in the preparation of this work and the U.S. Energy Research and Development Administration for its support.

Registry No. $(C_5H_5)_2FeBiCl_4$, 61026-19-5.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic and X-Ray Structural Characterization of Bis(diphenylphosphino(phenyl)acetylene)hexacarbonyldiiron(0), an Alkyne Derivative of Iron Pentacarbonyl

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The synthesis of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ from phenylethynyldiphenylphosphine and $Fe_2(CO)_9$ is described. The compound has been characterized by microanalysis and mass, infrared, and Mössbauer spectroscopy, as well as by single-crystal x-ray diffraction. Crystals are monoclinic, space group $P2_1/n$, with $a = 12.032$ (6) Å, $b = 19.155$ (7) Å, $c = 17.644$ (6) Å, $\beta = 91.38$ (4)°, and $Z = 4$. The structure was solved by the heavy-atom method using the intensities of 3400 reflections measured on a Syntex $P\bar{1}$ diffractometer. Refinement converged at an R value of 0.065. In the binuclear molecule each iron atom is coordinated to three carbonyl groups, the phosphorus atom of one phosphinoalkyne, and the triple bond of the other. Each half of the molecule can be considered as a phosphine substitution product of a simple alkyne π complex $Fe(CO)_4(RC\equiv CR)$. Important intramolecular distances are Fe(1)–P(1) = 2.287 (2), Fe(2)–P(2) = 2.298 (2), Fe(1)–C(9) = 2.076 (8), Fe(1)–C(10) = 2.046 (8), Fe(2)–C(7) = 2.068 (8), Fe(2)–C(8) = 2.064 (6), C(7)–C(8) = 1.273 (11), and C(9)–C(10) = 1.260 (11) Å. Structural data and Mössbauer parameters ($\delta = 0.20$, $\Delta = 1.56$ mm s^{-1}) suggest a description of the iron–acetylene bonding intermediate between the metallocyclopropene and π-alkyne extremes. The relationship of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ to proposed intermediates in the reactions of iron carbonyls with alkynes is discussed.

Introduction

The simple alkyne derivatives of $Fe(CO)_5$, namely $Fe(CO)_4(RC_2R')$ (I), have long been recognized as plausible intermediates in the oligomerization of acetylenes by iron carbonyls.[1-3] Evidence for the existence and structure of these compounds is scant resting mainly on the isolation of two complexes with sterically demanding alkynes. One of these $Fe(CO)_4(Me_3SiC_2SiMe_3)$[1,4] has been spectroscopically characterized,[5] but structural data for the second complex $Fe(CO)_4(Me_3CC_2CMe_3)$ have not yet been published.[4,6] In an effort to stabilize simple alkyne π complexes derived from iron carbonyls we have carried out reactions of several dialkyl- and diarylphosphinoacetylenes with diiron enneacarbonyl and triiron dodecacarbonyl. As is well established for nonbulky alkynes,[1-3] these reactions produce many exotic organometallic compounds[7] often in low yields. The present paper describes the synthesis and infrared and Mössbauer spectra as well as a complete single-crystal x-ray structure determination of $Fe_2(CO)_6(Ph_2PC\equiv CPh)_2$ a compound which can be prepared in workable yields from $Fe_2(CO)_9$ and $Ph_2PC\equiv CPh$. Each half of this binuclear molecule is derived from $Fe(CO)_5$ by substitution of an axial carbonyl by a phosphorus atom and an equatorial carbonyl by an alkyne triple bond. A preliminary report of this work has already appeared.[8]

Experimental Section

Synthesis of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$. Diiron enneacarbonyl (1.8 g) and $Ph_2PC\equiv CPh$ (1.5 g) in degassed benzene (50 ml) were allowed to react for 3 days at room temperature. The resultant red solution was filtered, reduced to a small volume in vacuo, and introduced onto a Florisil column made up in petroleum ether (bp 80–100 °C). The first band, eluted with petroleum ether, contains the σ–π-acetylide complex $Fe_2(CO)_6(C_2Ph)(PPh_2)$ (II)[9] and traces of the phosphine substitution product $Fe(CO)_4(Ph_2PC\equiv CPh)$ which has a very similar R_f value. Elution of a second yellow band with a 9:1 mixture of petroleum ether–benzene afforded, on evaporation, dark yellow crystals of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ (III) in 16% yield; mp 176–178 °C. Anal. Calcd for $Fe_2(CO)_6(Ph_2PC_2Ph)_2$: C, 64.81; H, 3.70. Found: C, 64.94; H, 3.70. IR (cm^{-1}) (Nujol): 2020 s, 2012 s, 1988 s, 1970 sh, 1940 sh, 1805 s, 1798 s (C_6H_{12}), 2044 s, 2029 s, 1980 m, 1971 s, 1946 s, 1802 w. Mass spectrum: m/e 852.0266 (calcd 852.0259) (M^+), 824, 796, 768, 740, 712, 684 ($Fe_2L_2^+$), 628, 606, 551, 530, 474, 450, 352, 342, 328, 318, 286 (L^+). A third band, eluted with a 7:3 mixture of petroleum ether–benzene gave on crystallization a 21% yield of bright yellow $Fe(CO)_3(Ph_2PC_2Ph)_2$, mp 217–218 °C. This compound is also a product of the reaction between (η^4-C_7H_8)$Fe(CO)_3$ and Ph_2PC_2Ph.[10]

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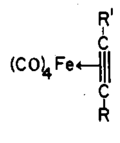

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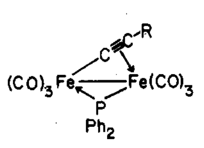

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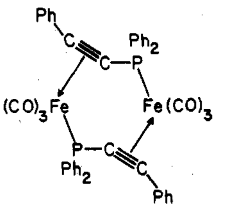

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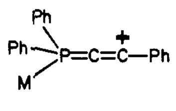

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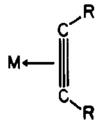

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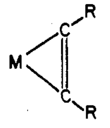

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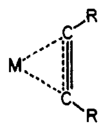

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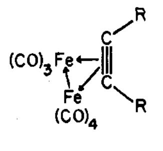

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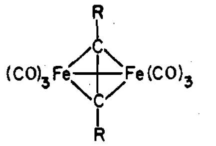

IX

Physical Measurements. Microanalyses were performed by Galbraith Microanalytical Laboratories Inc. Infrared spectra were run as Nujol mulls on cesium iodide plates or as solutions in cyclohexane using 0.5-mm matched NaCl cells on a Perkin-Elmer 180 spectrometer. Mössbauer spectra were obtained with a 10-mCi $^{57}Co/Pd$ source at room temperature and the absorber, as a powder held in a copper disk, at 77 K. The drive and associated electronics have been described elsewhere.[11] Spectra were fitted to Lorentzian line shapes by the computer program MOSS. Parameters are accurate to ±0.01 mm s^{-1} and isomer shift values are relative to sodium nitroprusside. Mass spectra at 70 eV were measured on an AEI MS 30 spectrometer.

X-Ray Data Collection and Reduction. Preliminary Weissenberg photographs, taken with nickel-filtered Cu Kα radiation revealed systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with space group $P2_1/n$ (C_{2h}^5). Precise lattice parameters at room temperature were determined by least-squares refinement of 2θ, ω, ϕ, and χ for 15 reflections on a Syntex $P\bar{1}$ diffractometer. Crystal data are $a = 12.032$ (6) Å, $b = 19.155$ (7), Å, $c = 17.644$ (6) Å, $\beta = 91.38$ (4)°, $V = 4065$ (3) Å^3. The experimental density, 1.42 g cm^{-3}, measured in a carbon tetrachloride–*n*-hexane mixture agrees with the value of 1.393 g cm^{-3} calculated for four formula units of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$, mol wt 852.38, in the unit cell; $F(000) = 1744$.

Intensity data were collected on the $P\bar{1}$ diffractometer using a variable (1–24°/min) θ–2θ scan technique and graphite-monochromatized Mo Kα (λ 0.7107 Å) radiation. The crystal was a needle of dimensions 0.46 × 0.19 × 0.10 mm mounted with its long dimension parallel to the glass fiber. Four standard reflections were monitored after every 96 reflections. These showed a decrease of <13% during the course of data collection and were used to scale the data to a common level. Reflections with $I < 1.8\sigma(I)$ were considered unreliable leaving a total of 3400 for use in structure solution and refinement. The value of μ for molybdenum radiation is only 8.6 cm^{-1} so that absorption corrections were unnecessary. The extreme error in I due to neglect of absorption is ≤5.0%. The data were corrected for Lorentz and for polarization effects in the normal way.

Structure Solution and Refinement. A sharpened Patterson map revealed the positions of the two iron atoms. A Fourier synthesis phased on the two heavy-atom positions allowed the location of the two phosphorus atoms. The remaining light atoms were located in subsequent Fourier maps. At this stage the R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) with all nonhydrogen atoms located was 0.18. A difference Fourier synthesis suggested the absence of solvent of crystallization since there were no peaks of intensity greater than 2 e/Å^3 except in the region of the heavy-atom ripple. Three cycles of least-squares refinement with all atoms having isotropic temperature factors reduced R to 0.11. The atoms were then assigned anisotropic temperature coefficients and three cycles of block-diagonal least-squares refinement led to an R value of 0.076. After three further cycles of anisotropic refinement, the R value had fallen to 0.065 and shifts were all less than one-third of their estimated standard deviations. Refinement was therefore terminated. A final difference map did not reveal any additional features of significance. No attempt was made to locate hydrogen atoms. Final positional and thermal parameters are listed in Table I. The observed and calculated structure factor amplitudes are available.[12]

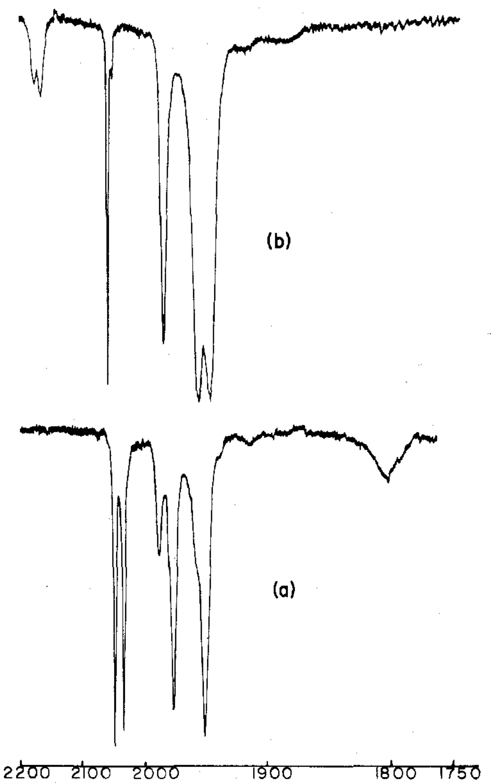

Figure 1. ν(CO) infrared spectra of (a) $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ and (b) $Fe(CO)_4(Ph_2PC_2Ph)$ in cyclohexane solution.

In least-squares calculations the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{1/2} = F_o/F_{\text{low}}$ if $F_o < F_{\text{low}}$, $w^{1/2} = 1$ if $F_{\text{low}} \le F_o \le F_{\text{high}}$ and $w^{1/2} = F_{\text{high}}/F_o$ if $F_{\text{high}} < F_o$. Values of F_{low} and F_{high} were 6 times and 16 times the minimum observable F, respectively. Atomic scattering factors were taken from Hanson, Herman, Lea, and Skillman.[13] All calculations were carried out on an IBM 370/165 using programs written or modified by G.J.P.

Results and Discussion

The reaction of diiron enneacarbonyl with the phosphinoacetylene $Ph_2PC{\equiv}CPh$ yielded three major components separable by column chromatography. The first compound eluted from the column was the σ–π-acetylide II. Compound II and analogues can be prepared more conveniently via the reaction of the phosphine complexes $Fe(CO)_4(Ph_2PC{\equiv}CR)$ with $Fe_2(CO)_9$[14]. The last band contained the *trans*-bis(phosphine) complex $Fe(CO)_3(Ph_2PC{\equiv}CPh)_2$ which has ν(CO) infrared [CHCl$_3$; 2176 w (ν(C≡C), 1982 vw, 1901 s, 1889 s (ν(C≡O) cm^{-1}] and Mössbauer ($\delta = 0.086$; $\Delta = 2.726$ mm s^{-1}) spectra [cf. *trans*-$Fe(CO)_3(PPh_3)_2$: ν(CO) (CH_3COCH_3) 1950 vw, 1894 vs cm^{-1}; $\delta = 0.161$, $\Delta = 2.76$ mm s^{-1}][15,16] typical of trans trigonal-bipyramidal stereochemistry.

The third product from this reaction was shown by microanalysis and high-resolution mass spectroscopy to have the stoichiometry $Fe_2(CO)_6(Ph_2PC_2Ph)_2$. The parent ion of m/e 852.0266 in the mass spectrum fragments by loss of six carbonyl groups to give the carbonyl-free ion $Fe_2(Ph_2PC_2Ph)_2^+$. A competing fragmentation mechanism involves elimination

Table I. Atomic Positional Parameters and Anisotropic Thermal Parameters[a] (Å^2 × 10^4) for $Fe_2(CO)_6(Ph_2PC_2Ph)_2$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.1696 (1)	0.2293 (1)	0.3044 (1)	62.4 (0.9)	24.3 (0.4)	31.7 (0.4)	9 (1)	1 (1)	2 (1)
Fe(2)	0.0280 (1)	0.4308 (1)	0.3749 (1)	65.9 (0.9)	23.0 (0.4)	27.4 (0.4)	0.6 (1.1)	−3 (1)	−6 (1)
P(1)	−0.0106 (2)	0.2492 (1)	0.3368 (1)	57 (2)	22.3 (0.7)	27.5 (0.8)	−4 (2)	−2 (2)	1 (1)
P(2)	0.1652 (2)	0.4150 (1)	0.2882 (1)	63 (2)	23.8 (0.7)	27.3 (0.8)	−7 (2)	0 (2)	2 (1)
C(1)	0.2119 (7)	0.2363 (5)	0.4006 (5)	87 (8)	40 (4)	44 (4)	14 (9)	1 (9)	−3 (6)
C(2)	0.3088 (7)	0.2141 (5)	0.2787 (5)	81 (8)	41 (4)	53 (4)	11 (9)	−3 (10)	4 (7)
C(3)	0.1343 (8)	0.1417 (5)	0.2888 (6)	102 (10)	38 (4)	66 (5)	12 (10)	3 (11)	−7 (7)
C(4)	−0.0893 (7)	0.4406 (5)	0.4321 (5)	91 (8)	34 (3)	42 (4)	−1 (9)	11 (9)	−28 (6)
C(5)	0.0446 (7)	0.5221 (4)	0.3677 (5)	93 (8)	29 (3)	45 (4)	5 (9)	−13 (9)	1 (6)
C(6)	0.1221 (7)	0.4057 (5)	0.4497 (5)	96 (8)	34 (3)	42 (4)	−1 (9)	4 (9)	1 (5)
O(1)	0.2422 (5)	0.2373 (4)	0.4638 (3)	130 (7)	74 (4)	46 (3)	22 (8)	−29 (7)	2 (5)
O(2)	0.3980 (5)	0.2038 (4)	0.2609 (4)	86 (6)	74 (4)	82 (4)	38 (8)	43 (8)	16 (6)
O(3)	0.1089 (5)	0.0835 (4)	0.2796 (5)	167 (8)	36 (3)	105 (5)	1 (8)	10 (10)	−22 (6)
O(4)	−0.1699 (5)	0.4457 (4)	0.4658 (4)	111 (6)	54 (3)	57 (3)	−7 (7)	32 (7)	−36 (5)
O(5)	0.0548 (5)	0.5820 (3)	0.3664 (4)	140 (7)	28 (2)	81 (4)	−1 (7)	−23 (8)	−2 (5)
O(6)	0.1773 (6)	0.3913 (4)	0.5013 (3)	149 (8)	55 (3)	43 (3)	10 (7)	−44 (7)	7 (5)
C(7)	−0.0399 (6)	0.3388 (4)	0.3336 (4)	60 (7)	28 (3)	30 (3)	6 (7)	−3 (7)	0 (5)
C(8)	−0.0851 (6)	0.3893 (4)	0.2974 (4)	61 (7)	25 (3)	32 (3)	1 (7)	−3 (7)	−6 (5)
C(9)	0.1670 (6)	0.3282 (4)	0.2562 (4)	60 (7)	29 (3)	23 (3)	−2 (7)	−5 (7)	3 (5)
C(10)	0.1446 (6)	0.2836 (4)	0.2056 (4)	62 (7)	28 (3)	32 (3)	0 (7)	11 (7)	2 (5)
C(11)	−0.1662 (6)	0.4140 (4)	0.2420 (4)	66 (7)	25 (3)	35 (3)	8 (7)	−11 (8)	3 (5)
C(12)	−0.2009 (8)	0.3702 (5)	0.1812 (5)	114 (10)	44 (4)	35 (4)	6 (10)	−26 (10)	2 (6)
C(13)	−0.2804 (9)	0.3956 (5)	0.1269 (6)	143 (11)	44 (4)	49 (5)	11 (11)	−38 (11)	−3 (7)
C(14)	−0.3224 (9)	0.4631 (5)	0.1342 (6)	137 (11)	50 (4)	56 (5)	29 (11)	−60 (12)	13 (8)
C(15)	−0.2906 (8)	0.5066 (5)	0.1947 (6)	125 (11)	47 (4)	59 (5)	26 (11)	−50 (12)	9 (8)
C(16)	−0.2109 (7)	0.4825 (5)	0.2487 (5)	96 (9)	34 (4)	55 (4)	28 (9)	−8 (10)	7 (7)
C(21)	−0.1252 (6)	0.2119 (4)	0.2797 (4)	80 (7)	23 (3)	36 (3)	−2 (7)	−18 (8)	4 (5)
C(22)	−0.1046 (7)	0.1853 (4)	0.2082 (5)	108 (9)	28 (3)	36 (4)	−23 (8)	−29 (9)	−1 (6)
C(23)	−0.1955 (9)	0.1632 (5)	0.1615 (6)	139 (11)	39 (4)	60 (5)	−36 (11)	−54 (12)	−2 (7)
C(24)	−0.3042 (8)	0.1711 (5)	0.1881 (6)	110 (10)	42 (4)	67 (5)	−23 (10)	−55 (12)	−5 (8)
C(25)	−0.3233 (8)	0.1966 (5)	0.2597 (6)	83 (9)	49 (4)	85 (6)	−12 (10)	−30 (12)	−17 (8)
C(26)	−0.2340 (7)	0.2174 (5)	0.3077 (5)	60 (7)	45 (4)	63 (5)	−4 (9)	−17 (9)	−16 (7)
C(31)	−0.0391 (6)	0.2186 (4)	0.4319 (4)	74 (7)	29 (4)	33 (3)	−9 (8)	13 (8)	7 (5)
C(32)	−0.0369 (9)	0.1457 (5)	0.4432 (5)	163 (12)	36 (4)	45 (4)	−27 (11)	10 (11)	27 (7)
C(33)	−0.0479 (10)	0.1194 (6)	0.5167 (6)	200 (15)	51 (5)	57 (6)	−28 (14)	19 (14)	34 (8)
C(34)	−0.0616 (10)	0.1650 (6)	0.5780 (6)	189 (14)	60 (5)	47 (5)	−57 (14)	39 (13)	11 (8)
C(35)	−0.0629 (9)	0.2360 (6)	0.5661 (5)	158 (12)	57 (5)	43 (4)	−18 (13)	40 (12)	−1 (8)
C(36)	−0.0526 (8)	0.2624 (5)	0.4926 (5)	128 (10)	47 (4)	36 (4)	−11 (1)	31 (10)	1 (7)
C(41)	0.1187 (7)	0.2670 (4)	0.1260 (4)	88 (7)	23 (3)	32 (3)	−4 (8)	11 (8)	6 (5)
C(42)	0.1512 (8)	0.2029 (5)	0.0950 (5)	129 (10)	41 (4)	41 (4)	−7 (10)	25 (10)	−25 (6)
C(43)	0.1242 (9)	0.1875 (6)	0.0176 (5)	159 (12)	59 (5)	39 (4)	−5 (13)	19 (11)	20 (8)
C(44)	0.0637 (9)	0.2344 (6)	−0.0244 (5)	182 (13)	59 (5)	42 (5)	9 (14)	8 (12)	−10 (8)
C(45)	0.0280 (10)	0.2970 (6)	0.0069 (6)	189 (14)	59 (5)	48 (5)	33 (14)	−31 (13)	3 (8)
C(46)	0.0581 (8)	0.3144 (5)	0.0816 (5)	138 (11)	45 (4)	37 (4)	5 (11)	−35 (10)	1 (7)
C(51)	0.1546 (7)	0.4656 (4)	0.2001 (4)	82 (8)	28 (3)	35 (4)	−4 (8)	−3 (8)	3 (5)
C(52)	0.2367 (9)	0.4618 (7)	0.1473 (5)	158 (13)	90 (7)	51 (5)	81 (15)	76 (13)	71 (9)
C(53)	0.2228 (11)	0.4964 (8)	0.0758 (7)	203 (16)	90 (7)	67 (6)	82 (18)	69 (16)	79 (11)
C(54)	0.1321 (10)	0.5357 (6)	0.0610 (6)	167 (13)	58 (5)	55 (5)	31 (13)	27 (13)	30 (8)
C(55)	0.0486 (9)	0.5452 (6)	0.1144 (6)	165 (13)	60 (5)	50 (5)	33 (13)	−5 (13)	36 (8)
C(56)	0.0612 (8)	0.5059 (5)	0.1857 (5)	120 (10)	48 (4)	46 (4)	22 (11)	−11 (11)	30 (7)
C(61)	0.3088 (6)	0.4304 (4)	0.3216 (4)	72 (7)	33 (3)	33 (3)	−9 (8)	−9 (8)	16 (6)
C(62)	0.3289 (7)	0.4872 (5)	0.3727 (5)	101 (8)	40 (4)	40 (4)	−47 (9)	−24 (9)	4 (6)
C(63)	0.4406 (8)	0.5025 (6)	0.3958 (5)	103 (10)	55 (4)	52 (5)	−25 (11)	−24 (11)	−1 (8)
C(64)	0.5268 (8)	0.4607 (6)	0.3675 (6)	103 (10)	62 (5)	52 (5)	−23 (12)	−27 (11)	14 (8)
C(65)	0.5075 (8)	0.4053 (5)	0.3175 (5)	92 (9)	51 (4)	51 (5)	−20 (10)	0 (10)	17 (7)
C(66)	0.3962 (7)	0.3897 (5)	0.2956 (5)	66 (8)	47 (4)	45 (4)	−3 (9)	12 (9)	14 (6)

[a] In the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

of a neutral iron atom from $Fe_2(CO)_2(Ph_2PC_2Ph)_2^+$ leading to a series of monometallic ions beginning with $Fe(CO)_2(Ph_2PC_2Ph)_2^+$ of *m/e* 684. The infrared spectrum of III in the solid state has five bands in the region for ν(CO) terminal modes and a sharp doublet at 1805 s, 1798 s cm^{-1} which, in view of the x-ray analysis (vide infra), can be assigned to $\nu(C{\equiv}C)$ of the coordinated phosphinoalkynes. The magnitude of the shift $[\Delta\nu(C{\equiv}C)]$ from the free-ligand frequency (2164 cm^{-1}) is 362 cm^{-1}, comparable to values of 388 cm^{-1} for $\Delta\nu(C{\equiv}C)$ in $[Pd(Ph_3P)(Ph_2PC_2CF_3)]_2$[17], 423 cm^{-1} in $Ni(Ph_3P)_2(PhC_2Ph)$,[18] and 469 cm^{-1} in $Pt(Ph_3P)_2(PhC_2Ph)$.[18] By contrast, values of $\Delta\nu(C{\equiv}C)$ lie in the range 200–240 cm^{-1} for platinum(II)–acetylene complexes.[2,19] Therefore, the iron–acetylene interaction in $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ is similar to that in the zerovalent platinum complexes, if indeed $\Delta\nu(C{\equiv}C)$ can be used as a measure of the strength of metal–acetylene bonding. In the $\nu(CO)_t$ region of the solution infrared spectrum there is a close resemblance of frequencies and general band shapes for $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ and $Fe(CO)_4(Ph_2PC_2Ph)$[14] (Figure 1). This similarity is, in retrospect, not unexpected since substitution of an equatorial CO ligand in $Fe(CO)_4(Ph_2PC_2Ph)$ by a π-bonded acetylene would lead to a stereochemistry at iron comparable to the iron environments in $Fe_2(CO)_6(Ph_2PC_2Ph)_2$. By analogy with the accepted ν(CO) assignments for $Fe(CO)_4(PR_3)$[20] molecules and by keeping in mind the lower C_s local symmetry in $Fe_2(CO)_6(Ph_2PC_2Ph)_2$, the sharp doublet at 2020, 2012 cm^{-1} can be attributed to symmetrical stretching of the two equatorial CO groups on each iron atom (A_1 equatorial stretching in $Fe(CO)_4PR_3$[20]) and the central band at 1971 cm^{-1} to stretching of the CO group trans to phosphorus (cf. A_1 axial stretching in $Fe(CO)_4PR_3$[20]); the remaining two bands derive

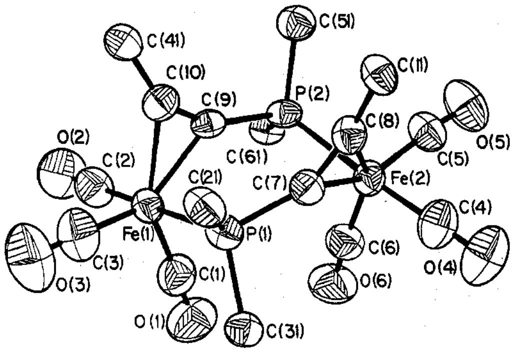

Figure 2. Perspective view of the molecular structure of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ showing the atomic numbering. Only the first carbon atom of each phenyl ring is included.

Table II. Bond Lengths (Å) and Angles (deg) for $Fe_2(CO)_6(Ph_2PC_2Ph)_2$

(a) Bond Lengths

Fe(1)-P(1)	2.287 (2)	P(1)-C(31)	1.818 (8)
Fe(1)-C(1)	1.765 (9)	P(2)-C(9)	1.756 (8)
Fe(1)-C(2)	1.771 (9)	P(2)-C(51)	1.834 (8)
Fe(1)-C(3)	1.751 (10)	P(2)-C(61)	1.836 (8)
Fe(1)-C(9)	2.076 (8)	C(1)-O(1)	1.166 (10)
Fe(1)-C(10)	2.046 (8)	C(2)-O(2)	1.142 (11)
Fe(2)-P(2)	2.298 (2)	C(3)-O(3)	1.165 (12)
Fe(2)-C(4)	1.765 (8)	C(4)-O(4)	1.153 (10)
Fe(2)-C(5)	1.765 (8)	C(5)-O(5)	1.155 (10)
Fe(2)-C(6)	1.783 (9)	C(6)-O(6)	1.147 (11)
Fe(2)-C(7)	2.068 (8)	C(7)-C(8)	1.273 (11)
Fe(2)-C(8)	2.064 (6)	C(9)-C(10)	1.260 (11)
P(1)-C(7)	1.753 (8)	C(8)-C(11)	1.444 (11)
P(1)-C(21)	1.834 (8)	C(10)-C(41)	1.467 (11)

(b) Angles

P(1)-Fe(1)-C(1)	90.0 (3)	Fe(1)-C(1)-O(1)	176.2 (8)
P(1)-Fe(1)-C(2)	179.6 (3)	Fe(1)-C(2)-O(2)	178.8 (8)
P(1)-Fe(1)-C(3)	88.4 (3)	Fe(1)-C(3)-O(3)	178.5 (9)
P(1)-Fe(1)-C(9)	86.9 (2)	Fe(1)-P(1)-C(7)	110.3 (3)
P(1)-Fe(1)-C(10)	90.5 (2)	Fe(1)-P(1)-C(21)	120.1 (3)
C(1)-Fe(1)-C(2)	90.4 (4)	Fe(1)-P(1)-C(31)	112.3 (3)
C(1)-Fe(1)-C(3)	106.7 (4)	Fe(1)-C(9)-C(10)	70.9 (5)
C(1)-Fe(1)-C(9)	108.9 (4)	Fe(1)-C(9)-P(2)	137.1 (4)
C(1)-Fe(1)-C(10)	144.4 (4)	Fe(1)-C(10)-C(9)	73.5 (5)
C(2)-Fe(1)-C(3)	91.7 (4)	Fe(1)-C(10)-C(41)	136.8 (6)
C(2)-Fe(1)-C(9)	92.8 (4)	Fe(2)-C(4)-O(4)	175.9 (8)
C(2)-Fe(1)-C(10)	89.2 (4)	Fe(2)-C(5)-O(5)	177.0 (8)
C(3)-Fe(1)-C(9)	144.0 (4)	Fe(2)-C(6)-O(6)	175.2 (8)
C(3)-Fe(1)-C(10)	108.9 (4)	Fe(2)-P(2)-C(9)	110.7 (3)
C(9)-Fe(1)-C(10)	35.6 (3)	Fe(2)-P(2)-C(51)	117.3 (3)
P(2)-Fe(2)-C(4)	172.8 (3)	Fe(2)-P(2)-C(61)	116.8 (3)
P(2)-Fe(2)-C(5)	89.9 (3)	Fe(2)-C(7)-C(8)	71.9 (5)
P(2)-Fe(2)-C(6)	90.2 (3)	Fe(2)-C(7)-P(1)	138.2 (4)
P(2)-Fe(2)-C(7)	86.4 (2)	Fe(2)-C(8)-C(7)	72.2 (5)
P(2)-Fe(2)-C(8)	88.9 (2)	C(7)-C(8)-C(11)	149.4 (8)
C(4)-Fe(2)-C(5)	91.7 (4)	P(1)-C(7)-C(8)	147.5 (7)
C(4)-Fe(2)-C(6)	96.2 (4)		
C(4)-Fe(2)-C(7)	88.7 (4)		
C(4)-Fe(2)-C(8)	84.0 (4)		
C(5)-Fe(2)-C(6)	104.4 (4)		
C(5)-Fe(2)-C(7)	149.7 (4)		
C(5)-Fe(2)-C(8)	114.0 (4)		
C(6)-Fe(2)-C(7)	105.7 (4)		
C(6)-Fe(2)-C(8)	141.5 (4)		
C(7)-Fe(2)-C(8)	35.9 (4)		
C(9)-C(10)-C(41)	149.7 (8)		
P(2)-C(9)-C(10)	149.9 (6)		
C(7)-P(1)-C(21)	102.4 (4)		
C(7)-P(1)-C(31)	107.6 (4)		
C(9)-P(2)-C(51)	103.3 (4)		
C(9)-P(2)-C(61)	103.7 (4)		
C(21)-P(1)-C(31)	103.0 (4)		
C(51)-P(2)-C(61)	103.5 (4)		

from the E_1 equatorial ν(CO) mode of $Fe(CO)_4(PR_3)$.

The relative intensity of the $\nu(C\equiv C)$ bands of the coordinated alkynes decreases substantially from the solid state to solution. Bridging carbonyl groups often exhibit similar behavior although bridge–terminal isomerism is often responsible. In the present case there was no evidence for the appearance of "free" $\nu(C\equiv C)$ bands; hence, dissociation of complex to yield coordinatively unsaturated species seems unlikely.

Description and Discussion of the Structure. The basic structural unit in the crystal is the noncentrosymmetric dimer illustrated in Figure 2. Excluding the distances and angles in the six phenyl rings which are available,[12] the remaining distances and angles in the dimer are given in Table II. Each iron atom is coordinated to three carbonyl groups, the phosphorus atom of one phosphinoalkyne, and the triple bond of a second phosphinoalkyne. Thus, the phosphinoalkyne behaves as a bridging four-electron donor. The iron atom is in the center of a trigonal bipyramid if the triple bond is considered to occupy one coordination site. The phosphorus atom and one CO group occupy the "axial" positions [P(1)–Fe(1)–C(2) is 179.6 (3)° and P(2)–Fe(2)–C(4) is 172.8 (3)°], with the remaining CO groups and the triple bond in the "equatorial" positions. Surprisingly, the Fe–C bonds to the "axial" carbonyls [average 1.768 ± 0.003 Å] do not differ significantly from those to the "equatorial" groups [average 1.766 ± 0.017 Å] in spite of the trans phosphorus atom. Unfortunately, the C(1)–Fe(1)–C(3) angle of 106.7 (4)° and the C(5)–Fe(2)–C(6) angle of 104.4 (4)° are midway between the values for the trigonal bipyramid (120°) and the octahedron (90°). An alternate description (discussed in more detail below) is a metallocyclopropene in which two iron hybrid orbitals bond to the acetylene, producing a distorted octahedral arrangement. Finally, the Fe–P distances [average 2.293 ± 0.006 Å] are longer than those found in other trigonal-bipyramidal iron carbonyl complexes [2.190 (4) Å in *trans*-$L_2Fe(CO)_3$,[21] L = $P(OCH_2)_3P$, and 2.237 (2) Å in $Fe(CO)_4PPh_2H$[22]]. Consequently, there is some justification for both stereochemical descriptions of the iron–acetylene bonding. Mössbauer data (vide infra) favor a model intermediate between the two extremes.

The principal molecular parameter of interest is the length of the coordinated acetylenic triple bond since this might be expected to provide some gauge of the strength of the metal–acetylene interaction. A recent tabulation of $-C\equiv C-$ distances in terminal acetylene π complexes[23] reveals values ranging from 1.18 (3) Å in $K[Cl_3Pt(C_2H_5)_2C(OH)C\equiv C-C(OH)(C_2H_5)_2]$[24] to 1.35 (2) Å in $(\pi-C_5H_5)(CO)Nb(PhC\equiv CPh)_2$.[25] The $-C\equiv C$ bond lengths in $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ are C(7)–C(8) of 1.273 (11) Å and C(9)–C(10) of 1.260 (11) Å, both of which differ significantly from the average bond length in uncoordinated acetylenes (1.204 (2) Å).[26] The magnitude of the lengthening of the alkyne triple bond on complexation appears similar to that in the nickel complex $(t-BuNC)_2Ni(PhC_2Ph)$.[27] The "bend-back" angles of the acetylene may also provide useful information pertaining to the perturbation of the acetylene. In the present instance, a comparison with simple acetylene complexes is of dubious significance owing to the bidentate coordination mode of the phosphinoalkyne. However, three π complexes of phosphinoalkynes have been examined crystallographically and comparison of bend-back angles for these compounds is relevant. In the related nickel complex $Ni_2(CO)_2(Ph_2PC_2Bu-t)_2$[8] the bend-back angles subtended at the alkyne carbon atoms with phosphino substituents average 25.9° while the corresponding angle at the alkyne carbon atoms having *tert*-butyl substituents is 28.6°. In the iron complex these angles are 31.3° (average) and 30.4° (average). The bend-back angles in the nickel and iron complexes, the $C\equiv C$ bond lengths (1.267 (11) Å in $Ni_2(CO)_2(t-BuC_2PPh_2)_2$ and 1.280 (14) Å in $Fe_2(CO)_6(Ph_2PC_2Ph)_2$) and $\nu(C\equiv C)$

stretching frequencies (1810 and 1802 cm^{-1}) all reinforce the opinion that the strength of the metal–acetylene interaction is slightly greater in the iron complex. The palladium–alkyne interaction in $Pd_2(PPh_3)_2(Ph_2PC_2CF_3)_2$[17] ($\Delta\nu(C{\equiv}C)$ 388 cm^{-1}; $r(C{\equiv}C)$ 1.286 Å (average)) also appears similar in strength despite the presence of a different terminal ligand (Ph_3P) and strongly electron-withdrawing substituents on the alkyne.

The $P-C_{sp}$ distances P(1)–C(7) of 1.753 (8) Å and P(2)–C(9) of 1.756 (8) Å are somewhat shorter than expected when compared with the sums of phosphorus (1.10 Å) and carbon (sp) (0.70 Å) radii. This is a typical feature of phosphinoacetylene complexes[28] and can be attributed to partial P–C multiple bonding represented by a contribution from resonance form IV. Extensive deshielding of the β carbon in ^{13}C NMR spectra of alkynylphosphonium salts has recently been attributed to an analogous effect.[29]

Mössbauer Spectrum. The Mössbauer spectrum of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ consists of a single quadrupole doublet as expected for two identical, noncubic iron sites. The Mössbauer parameters δ and Δ are the first reported for a zerovalent iron–acetylene complex and provide some important information concerning the description of the iron(0)–acetylene bond. The quadrupole splitting Δ (1.56 mm s^{-1}) is considerably smaller than for the simple trigonal-bipyramidal complexes *trans*-$Fe(CO)_3L_2$ and -$Fe(CO)_4L$ (L = phosphine)[15,16,20,21] which have Δ values in the range 2.2–2.8 mm s^{-1} consistent with the presence of a large field gradient at the iron nucleus. In contrast, quadrupole splittings in $Fe(CO)_3$(diene) and $Fe(CO)_4$(alkene) complexes (typical values are $\Delta = 1.59$ for tricarbonyl-1-phenylbutadieneiron(0) and 1.41 mm s^{-1} for tetracarbonyl(maleic anhydride)iron(0)[16,32]) are much smaller than in the phosphine derivatives. The quadrupole splitting in III thus indicates a field gradient at the ^{57}Fe nucleus much closer to $Fe(CO)_4$(alkene) than $Fe(CO)_3(PR_3)_2$. The complexes *cis*-$Fe(CO)_3L$(alkene) (L = phosphine) would certainly provide a better comparison but no Mössbauer data are available. The Δ value for III also reveals the inadequacy of the metallocyclopropene and π-bonded acetylene (V and VI) models for describing the bonding of acetylene to Fe(0). Distorted octahedral organoiron complexes have Δ values ≤ 1.00 mm s^{-1} whereas unquestionably trigonal-bypyramidal stereochemistry produces large splittings of ~ 2.5 mm s^{-1}. The structural data and quadrupole splitting for III hence emphasize the intermediate stereochemical and bonding situation represented by VII. The isomer shift reinforces this description. The value (0.20 mm s^{-1}) is more positive than for typical $Fe(CO)_4L$ or $Fe(CO)_3L_2$ (L = phosphine) species[16,31] but only slightly lower than for $Fe(CO)_4$(alkene) (cf. $Fe(CO)_4$(*trans*-cinnamaldehyde), $\delta = 0.245$ mm s^{-1}, and $Fe(CO)_4$(maleic anhydride), $\delta = 0.269$ mm s^{-1}).[16,32] Compared to the simple phosphine complexes, the isomer shift is displaced toward the values for Fe(II) compounds. It thus appears that Mössbauer spectroscopy may be capable of making a useful contribution to our understanding of metal–hydrocarbon π bonding.

Conclusions

Prior to commencement of the present structural study of $Fe_2(CO)_6(Ph_2PC{\equiv}CPh)_2$, acetylene complexes of iron in which the alkyne behaves as a simple two-electron nonbridging ligand had eluded complete characterization. Hübel and co-workers in their monumental efforts of the late 1950's[1] to rationalize the oligomerization of alkynes by iron carbonyls briefly mentioned the compounds I (R = Me_3C, Me_3Si) as being the initial products in the reaction of $Fe(CO)_5$ with the bulky acetylenes $Me_3CC_2CMe_3$ and $Me_3SiC_2SiMe_3$.[4] A reexamination of the reactions between $Me_3SiC_2SiMe_3$ and the three iron carbonyls by Pannell and Crawford confirmed the identity of the $Fe(CO)_4(Me_3SiC_2SiMe_3)$ derivative.[5] Infrared evidence for an unstable bis(tetracarbonyliron)–butadiyne complex $\{Fe(CO)_4\}_2(Me_3SiC_4SiMe_3)$ was also presented. Finally, Cotton et al.[6] mentioned unpublished work on the complete characterization of $Fe(CO)_4(Me_3CC_2CMe_3)$, the original Hübel compound.[4] Compounds of the stoichiometry $-Fe(CO)_4(RC_2R)$ as well as the binuclear complexes VIII were presumed intermediates in the oligomerization reactions of alkynes with iron carbonyls.[1,4] Recent work however has shown that the complexes of type VIII actually have structure IX in which the acetylenes behave as bridging four-electron donors.[6,33] The role of these alkyne-bridged, iron–iron double-bonded complexes in the formation of acetylene dimers or trimers, if any, has not yet been established. A further type of complex is exemplified by $Fe_2(CO)_4(t\text{-}BuC_2\text{-}t\text{-}Bu)_2$[34] where an iron–iron double bond is bridged symmetrically to two acetylenes. Again, however, no further chemistry of this type of complex has been forthcoming as yet. In retrospect, it may well be naive to expect that the isolable compounds of the type $M(CO)_4(RC_2R)$ (M = iron group metal) will provide useful models for mechanistic studies of iron carbonyl promoted acetylene oligomerizations since the electronic and/or steric features of those acetylenes which form isolable simple π-alkyne complexes may be such as to inhibit acetylene coupling. There is evidence for this in closely related but less reactive systems. Thus, the compound *trans*-$Os(CO)_3[P(OMe)_3]_2$ reacts with $CF_3C_2CF_3$ yielding the CO substitution product $Os(CO)_2[P(OMe)_3]_2(CF_3C_2CF_3)$ but this material is quite unreactive toward an excess of hexafluorobutyne.[35] The analogous iron and ruthenium phosphite complexes $M(CO)_3[P(OMe)_3]_2$ (M = Fe, Ru) react readily with the same fluoroalkyne giving metallocyclopentadienone (M = Fe), metallocyclobutenone, metallocyclopentadiene, and hexakis(trifluoromethyl)benzene derivatives (M = Ru) but the supposed intermediates $M(CO)_2[P(OR)_3]_2(CF_3C_2CF_3)$ or $M(CO)_3[P(OR)_3]_2(CF_3C_2CF_3)$[35] were not isolated. With other metals it has occasionally proven possible to isolate initial intermediates *and* demonstrate their intermediacy in the buildup of cyclic products. Notable examples are the intermediates η^5-$C_5H_5Co(Ph_3P)(PhC_2Ph)$[36] and $Ir(CO)(Ph_3P)_2(CF_3C_2CF_3)(CF_3C_2CF_3(H))$[37] which are isolable yet reactive toward acetylene addition. The phosphinoacetylene complex $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ is in this category since the complex is air stable in the solid state yet is readily attacked by activated alkynes. These reactions will be the subject of a forthcoming publication.

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Registry No. III, 61025-84-1; $Fe(CO)_3(Ph_2PC_2Ph)_2$, 30173-77-4; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Listing of structure factor amplitudes and a table of distances and angles within phenyl rings (20 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of the Macrocyclic Nickel(II) Complex $Ni(C_{18}H_{14}N_4)$: Dibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulenenickel(II)

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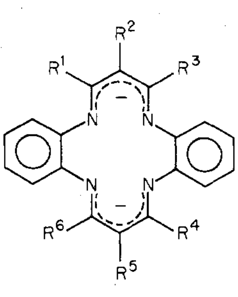
The crystal and molecular structure of the four-coordinate complex $Ni(C_{18}H_{14}N_4)$ containing the dibenzotetraaza[14]annulene ligand has been determined from three-dimensional x-ray diffraction data. The complex crystallizes in the monoclinic space group $C_{2h}{}^5$-$P2_1/c$ with cell dimensions $a = 19.456$ (4) Å, $b = 5.228$ (1) Å, $c = 14.868$ (3) Å, and $\beta = 112.28$ (1)° with $Z = 4$, the unit cell containing two independent molecules each lying on a crystallographic inversion center. The cobalt(II) complex $Co(C_{18}H_{14}N_4)$ is isostructural with cell dimensions $a = 19.52$ (1) Å, $b = 5.228$ (1) Å, $c = 14.84$ (1) Å, and $\beta = 112.46°$. The nickel structure was refined by Fourier and least-squares techniques to a conventional R value of 4.1% based on 3112 reflections with $F > 3\sigma_F$. The average Ni–N distance is 1.870 Å. Although the macrocyclic ring is essentially planar in each molecule, the delocalized propane-1,3-diiminato chelate rings and the benzenoid rings are linked by nominally single C–N bonds.

Introduction

The chemistry associated with highly conjugated and completely conjugated macrocyclic complexes is considerably different from that of their saturated counterparts. Highly delocalized conjugated ligand systems interact strongly with coordinated metals and greatly influence the physical and chemical properties of the metal.[1] With very flat macrocyclic ligands intermolecular interactions may occur.[2] Both solid-state and solution intermolecular interactions have been documented.[3]

A large number of macrocyclic complexes have been synthesized and characterized which are based on the dibenzotetraaza[14]annulene framework[4–6]



Crystallographic studies have shown that when R^1, R^3, R^4, R^6 = CH_3 strong intramolecular steric interactions of the methyl groups with the benzenoid rings cause marked deviation from ligand planarity leading to a pronounced saddle-shaped ligand.[7] These peripheral steric constraints are responsible for unusual and unique chemical reactivity observed in the metal complexes of this ligand.[8]

The crystal and molecular structure of the title compound, prototypic of the dibenzotetraaza[14]annulenes, was undertaken to extend and elucidate structural tendencies parameterized by the crystallographic characterization of the various substituted analogues. Also it was important to determine if the extent of π delocalization throughout the 14-membered inner ring of the macrocyclic ligand, as inferred from bond distances, is a detectable function of the departure from ligand planarity.

Experimental Section

A sample of the title compound was prepared according to the method of Dolphin.[9] Crystals suitable for x-ray diffraction studies were grown by slow vacuum sublimation in a sealed tube. A well-formed crystal, 0.5 × 0.15 × 0.10 mm, was selected. Zero-level precession and Weissenberg photographs had systematic absences indicating orthorhombic space groups *Fdd*2 or *Fddd*. However, examination of the upper-level photographs clearly indicated monoclinic symmetry with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, establishing $C_{2h}{}^5$-$P2_1/c$ as the unique space group.

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