(relative intensity) 516 (100), 517 (50), 304 (16), 356 (8). Anal. Calcd for $C_{31}H_{25}FeO_2P$ (516.4): C, 72.1; H, 4.9. Found: C, 71.7; H, 4.9.

**1-Methyl-1-methoxy-2,4,6-triphenyl-λ$^5$-phosphinine (5a)**, identical by $^1H$ NMR with the known material,[14a] was isolated in quantitative yield by adding methanol to 4 and workup by chromatography.

**1-Ethoxy-1-methyl-2,4,6-triphenyl-λ$^5$-phosphinine (5b)** (mp 114–116 °C), identical by $^1H$ and $^{31}P$ NMR with the known material,[14b] was isolated in quantitative yield by adding ethanol to 4.

**Acknowledgment.** T.D. thanks the Deutsche Akademische Austauschedienst for the possibility to work 2 years together with K.D. in Marburg. The financial support of the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for chemicals and instrumental equipment is highly acknowledged.

**Registry No.** **3a**, 97011-51-3; **3b**, 96999-77-8; 4, 97011-50-2; **5a**, 36240-81-0; **5b**, 58159-59-4; **10a**, 96999-78-9; **10b**, 96999-79-0; **10c**, 96999-80-3; **11a**, 96999-81-4; **11c**, 96999-82-5; **12a**, 96999-84-7; **12c**, 97042-25-6; **13a**, 96999-86-9; (1,4-dimethyl-2,6-diphenylphosphinine)lithium, 96999-87-0; (4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)lithium, 96999-88-1; iron(II) chloride, 7758-94-3; dicarbonyl(η$^5$-cyclopentadienyl)iron iodide, 12078-28-3.

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# Iron Complexes of Phosphinine Derivatives: The Crystal Structure of $[\eta^5\text{-}t\text{-}BuPh_2C_5H_2P(CH_3)]_2Fe$

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The structure of the title compound was determined by single-crystal X-ray diffraction at $T = 22$ °C and refined to $R_w = 0.051$ for 1807 reflections. The space group is *Pbcn* ($Z = 8$) with $a = 19.277$ (5) Å, $b = 19.921$ (3) Å, and $c = 19.300$ (4) Å. The bis(phosphinine) sandwich complex has the gauche-eclipsed conformation, and iron is five-carbon η$^5$-bonded to both phosphinine rings (mean Fe–C distance = 2.16 Å, Fe–P = 2.91 Å). All the C–C distances in the almost planar $C_5$ part of the rings are very similar (mean 1.41 Å), and the "chair angles" between these $C_5$ planes and the C1–P–C5 planes are 33.3° and 37.4°. Thus a relationship to the "open ferrocenes" is obvious.

## Introduction

Dimroth et al.[1] have synthesized a series of new substituted phosphinine sandwich complexes of iron. The neutral complexes as well as the corresponding biphosphonium dications reveal spectroscopic features similar to those of the "open ferrocenes" of Ernst et al.[2] To elucidate the interesting stereochemical properties, a single-crystal X-ray structure analysis has been performed on a typical representative of a neutral phosphinine complex: bis(4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)iron (1).

## Experimental Section

The synthesis of 1 is reported in the preceding paper.[1] A dark brown, small needle-shaped crystal of 1 which has been obtained from benzene/hexane was investigated on a four-circle diffractometer (CAD4). The experimental details are summarized in Table I. The lattice parameters were refined from 25 machine-centered high-angle reflections.

**Table I. Experimental Data for the Crystal Structure Determination of Bis(4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)iron (1)**

| | |
|---|---|
| | Crystal Data |
| formula | $C_{44}H_{48}P_2Fe$ |
| $M_r$ | 694.7 |
| dimens | approximately 0.35 × 0.1 × 0.08 mm$^3$ |
| absorptn | $\mu = 4.8$ cm$^{-1}$, no correction |
| space group | *Pbcn*, $Z = 8$ |
| lattice consts (Mo Kα) | $a = 19.277$ (5) Å, $b = 19.921$ (3) Å, $c = 19.300$ (4) Å |
| temp | 295 K |
| density | $d_{calcd} = 1.245$ g cm$^{-3}$ |
| | Data Collection |
| diffractometer | four-circle CAD4 (Enraf-Nonius) |
| radiation | Mo Kα, graphite monochromator |
| scan type | ω scan |
| scan width | $(1.2 + 0.35 \tan \theta)$° and 25% on the left and right side of a reflection for background determination |
| measuring range | $1° < \theta < 20°$, $+h,+k,+l$ |
| reflctns | 3478, 1807 independent, $>3\sigma(F_o)$ |
| | Computing |
| computer | Telefunken TR440 and Sperry 1100/62 at the Rechenzentrum der Universität Marburg |
| programs | system STRUX[3] with programs SHELX[4] and ORTEP[5] |
| | atomic scattering factors for neutral atoms[6] |
| | anomalous scattering corrected[7] |

**Structure Determination of 1.** The systematic absences $0kl$, $k \neq 2n$, $h0l$, $l \neq 2n$, and $hk0$, $h + k \neq 2n$, are consistent with the space group *Pbcn*. The structure was solved by the heavy-

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**Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters in $[\eta^5\text{-}t\text{-BuPh}_2C_5H_2P(CH_3)]_2Fe$ (1)[a]**

| atom | $x$ | $y$ | $z$ | $B_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Fe | 0.3129 (1) | 0.2812 (1) | 0.5662 (1) | 3.02 (6) |
| P1 | 0.4634 (1) | 0.2771 (2) | 0.5772 (1) | 3.6 (1) |
| C1 | 0.3966 (5) | 0.2360 (5) | 0.6273 (5) | 3.2 (6) |
| C11 | 0.4081 (5) | 0.1643 (6) | 0.6440 (7) | 3.8 (7) |
| C12 | 0.4307 (5) | 0.1190 (6) | 0.5943 (6) | 4.1 (7) |
| C13 | 0.4399 (6) | 0.0520 (7) | 0.6110 (9) | 6.1 (9) |
| C14 | 0.4295 (8) | 0.0287 (8) | 0.6769 (12) | 8.7 (11) |
| C15 | 0.4108 (7) | 0.0758 (9) | 0.7263 (8) | 7.8 (11) |
| C16 | 0.4012 (7) | 0.1425 (7) | 0.7119 (8) | 6.2 (9) |
| C2 | 0.3493 (5) | 0.2728 (6) | 0.6684 (5) | 3.5 (6) |
| C3 | 0.3322 (4) | 0.3406 (5) | 0.6558 (6) | 3.0 (6) |
| C31 | 0.2919 (6) | 0.3817 (5) | 0.7104 (6) | 4.1 (6) |
| C32 | 0.2588 (8) | 0.3363 (7) | 0.7675 (7) | 9.2 (10) |
| C33 | 0.2382 (6) | 0.4275 (7) | 0.6809 (6) | 7.3 (9) |
| C34 | 0.3460 (6) | 0.4242 (6) | 0.7471 (6) | 6.4 (8) |
| C4 | 0.3575 (5) | 0.3735 (5) | 0.5954 (5) | 3.6 (6) |
| C5 | 0.4086 (5) | 0.3456 (5) | 0.5504 (5) | 3.3 (6) |
| C51 | 0.4335 (5) | 0.3880 (5) | 0.4911 (5) | 2.8 (5) |
| C52 | 0.4908 (6) | 0.3681 (6) | 0.4539 (6) | 4.5 (7) |
| C53 | 0.4796 (6) | 0.5917 (6) | 0.6015 (6) | 5.2 (7) |
| C54 | 0.5068 (7) | 0.5316 (7) | 0.6153 (6) | 5.3 (8) |
| C55 | 0.4329 (7) | 0.4908 (7) | 0.4229 (7) | 6.3 (8) |
| C56 | 0.4059 (5) | 0.4497 (6) | 0.4730 (6) | 4.2 (7) |
| C6 | 0.5157 (4) | 0.3167 (5) | 0.6473 (5) | 4.0 (6) |
| P2 | 0.2580 (1) | 0.1506 (2) | 0.5275 (1) | 4.0 (2) |
| C1′ | 0.2269 (4) | 0.2131 (5) | 0.5869 (5) | 3.2 (5) |
| C11′ | 0.1986 (6) | 0.1884 (6) | 0.6531 (5) | 3.4 (6) |
| C12′ | 0.2284 (6) | 0.1335 (7) | 0.6847 (7) | 5.3 (8) |
| C13′ | 0.2038 (8) | 0.1073 (7) | 0.7440 (8) | 7.0 (9) |
| C14′ | 0.1454 (8) | 0.1327 (9) | 0.7772 (8) | 7.3 (10) |
| C15′ | 0.1141 (7) | 0.1856 (9) | 0.7467 (7) | 7.6 (10) |
| C16′ | 0.1399 (6) | 0.2143 (7) | 0.6866 (6) | 5.9 (7) |
| C2′ | 0.2054 (4) | 0.2762 (6) | 0.5623 (6) | 3.6 (5) |
| C3′ | 0.2262 (5) | 0.3051 (5) | 0.4988 (6) | 3.1 (6) |
| C31′ | 0.1886 (7) | 0.3648 (6) | 0.4660 (5) | 4.3 (6) |
| C32′ | 0.1321 (10) | 0.3923 (9) | 0.5089 (8) | 16.7 (16) |
| C33′ | 0.1502 (8) | 0.3369 (7) | 0.4016 (7) | 11.6 (12) |
| C34′ | 0.2308 (7) | 0.4195 (8) | 0.4430 (11) | 15.2 (15) |
| C4′ | 0.2814 (5) | 0.2748 (6) | 0.4616 (5) | 3.3 (5) |
| C5′ | 0.3076 (5) | 0.2111 (5) | 0.4788 (5) | 3.4 (5) |
| C51′ | 0.3664 (5) | 0.1828 (6) | 0.4351 (6) | 3.3 (6) |
| C52′ | 0.4140 (6) | 0.2246 (6) | 0.4028 (5) | 4.8 (7) |
| C53′ | 0.4664 (7) | 0.1976 (9) | 0.3610 (7) | 7.2 (9) |
| C54′ | 0.4700 (8) | 0.1298 (9) | 0.3503 (7) | 7.4 (10) |
| C55′ | 0.4224 (8) | 0.0886 (7) | 0.3825 (7) | 6.4 (8) |
| C56′ | 0.3720 (6) | 0.1147 (6) | 0.4244 (6) | 4.9 (7) |
| C6′ | 0.1815 (6) | 0.1354 (6) | 0.4713 (6) | 6.2 (7) |

[a] $B_{eq} = {}^1/_3\sum_i\sum_j B_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

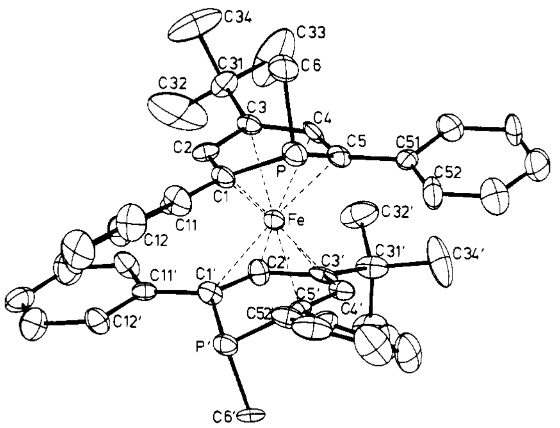


**Figure 1.** ORTEP drawing of 1. The thermal ellipsoids are drawn at the 30% probability level.

atom method and refined by the block-diagonal-matrix least-squares technique using anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were included "riding" on the calculated positions (C–H distance fixed at 0.96 Å) with a common isotropic temperature factor. The final R factors were $R_w = 0.051$ ($w = 1.2/\sigma^2(F_o)$ and $R = 0.062$. The resulting atomic coordinates are listed in Table II and bond lengths and angles in Table III. Figure 1 shows a view of complex 1 with the labeling scheme.

**Table III. Selected Interatomic Distances (Å) and Bond Angles (deg) in 1: a, "Upside" and, b, "Downside" Ligand**

| | a | b |
|---|---|---|
| Fe–C1 | 2.19 (1) | 2.18 (1) |
| Fe–C2 | 2.10 (1) | 2.08 (1) |
| Fe–C3 | 2.13 (1) | 2.17 (1) |
| Fe–C4 | 2.11 (1) | 2.11 (1) |
| Fe–C5 | 2.27 (1) | 2.19 (1) |
| mean Fe–C | 2.16 | 2.15 |
| Fe–P | 2.909 (3) | 2.907 (4) |
| P–C1 | 1.81 (1) | 1.80 (1) |
| P–C5 | 1.80 (1) | 1.80 (1) |
| P–C6 | 1.86 (1) | 1.85 (1) |
| P–C7 | | |
| C1–C2 | 1.41 (2) | 1.41 (2) |
| C2–C3 | 1.41 (2) | 1.42 (1) |
| C3–C4 | 1.42 (2) | 1.42 (1) |
| C4–C5 | 1.43 (1) | 1.40 (2) |
| mean C–C | 1.41 | 1.41 |
| C1–P–C5 | 94.6 (5) | 92.6 (5) |
| C1–P–C6 | 100.9 (5) | 102.8 (5) |
| C1–P–C7 | | |
| C5–P–C6 | 101.8 (5) | 103.1 (5) |
| C5–P–P7 | | |
| C6–P–C7 | | |
| P–C1–C2 | 121.6 (8) | 120.1 (7) |
| C1–C2–C3 | 123.5 (9) | 125.1 (9) |
| C2–C3–C4 | 120.1 (9) | 118.6 (9) |
| C3–C4–C5 | 123.7 (8) | 122.3 (9) |
| P–C5–C4 | 121.7 (8) | 122.4 (7) |

**Table IV. Distances (Å) from Least Squares Planes through the Marked Atoms and Dihedral Angles in 1: a, "Upside", and b, "Downside" Ligand[a]**

| | a | b |
|---|---|---|
| plane | A1 | A1′ |
| C1* | 0.01 | 0.01 |
| C2* | 0.01 | −0.04 |
| C3* | −0.04 | 0.05 |
| C4* | 0.05 | −0.04 |
| C5* | −0.02 | 0.02 |
| Fe | 1.61 | −1.59 |
| P | −0.68 | 0.77 |
| C11 | 0.11 | −0.04 |
| C31 | −0.31 | 0.35 |
| C51 | 0.01 | −0.08 |
| plane | B1 | B1′ |
| C1* | 0 | 0 |
| P* | 0 | 0 |
| C5* | 0 | 0 |
| Angles between Planes (deg) | | |
| A/B | 33.3 | 37.4 |
| A1/A1′ | 9.2 | |
| A/Ph1 | 25.2 | 11.2 |
| A/Ph5 | 12.8 | 35.9 |

[a] For the phenyl groups the dihedral angles only are listed (Ph1 means plane of phenyl group at C1, ...).

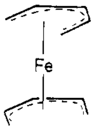
## Results and Discussion

As can be seen in Figure 1 the phosphinine sandwich complex has the gauche-eclipsed conformation and both ligands are five-carbon $\eta^5$-bonded.

The Fe–C distances are between 2.06 and 2.29 Å (mean Fe–C = 2.16 Å, Table III). The Fe–C2 and Fe–C4 bonds are somewhat shorter than the remaining Fe–C bonds. The five carbon atoms of the phosphinine rings do not deviate remarkably from planarity (Table IV), and the planes of the two ligands are nearly parallel.

Preliminary results of an X-ray structure analysis[8] of bis(1,1-dimethyl-2,4,6-triphenyl-phosphininium)iron bis(tetrafluoroborate) solvate (**2**) indicate a very similar coordination geometry of iron in the dicationic complex which has the gauche-eclipsed conformation as well and nearly the same Fe–C distances. However, a significant difference between the neutral (**1**) and the cationic (**2**) complexes was found for the Fe–P distances, which are shorter in **1** (mean 2.91 Å, Table III) than in **2** (mean 2.96 Å). In consequence, the dihedral angles in the phosphinine rings ("chair angles") between the $C_5$ planes and the C1–P–C5 planes are much smaller for **1** (mean 35°, Table IV) than for **2** (mean 47°). The severe differences between the two ligands within each complex which are documented, e.g., in the variation of dihedral angles between the phosphinine $C_5$ planes and the phenyl planes (Table IV), will be due to packing effects.

The C–C distances are equal within the esd's (mean 1.41 Å) in the phosphinine ring of **1**, indicating a high degree of $\pi$-electron delocalization. Therefore, an allyl–ene-like $\eta^3,\eta^2$-bonding scheme is not correct (for discussion of the bonding properties see ref 1 and 9). The same distances of 1.41 Å have been found for bis(2,4-dimethylpentadienyl)iron[2] which also has the gauche-eclipsed conformation. Thus, the relationship of the phosphinine sandwich complexes (II) to the "open ferrocenes" (I) is obvious.[1]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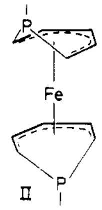

II

In the neutral phosphinine ligand of **1** the methyl group at the three-coordinate P atom is in the axial position (Figure 1). Thus, the lone electron pair at the P atom points toward the $C_5$ plane, and an interaction with the central Fe atom leading to the observed smaller "chair angle" may be discussed. Nevertheless, repulsion interaction of the positive charges at the four-coordinate P atoms of the cationic complex would explain the different chair angles as well.

**Acknowledgment.** We thank Professor K. Dimroth and Dr. T. Dave for providing the crystals.

**Registry No.** 1, 97042-29-0.

**Supplementary Material Available:** Tables of anisotropic temperature factors for non-hydrogen atoms, complete bond lengths and angles, and observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(8) Crystal data: space group $P2_1/c$, $a$ = 19.711 (8) Å, $b$ = 14.766 (10) Å, $c$ = 17.153 (10) Å, $\beta$ = 92.46 (4)°. Due to disorder of the $BF_4^-$ anions and solvent molecules only poor quality of the structural parameters could be obtained ($R$ = 0.125 for 2637 reflections). Following the suggestion of a reviewer we intend to treat the disorder by the back Fourier transform method: Rae, A. D.; Baker, A. T. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **1984**, *A40*, C-428. The results will be published separately. A different monoclinic form of **2** has been found in an other single crystal claimed by a different method showing also strong disorder effects at the $BF_4^-$ sites (Allmann, R. unpublished work, Marburg, 1984).

(9) See ref 6 in the preceding paper.

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# Integrated Molecular Systems. Fixation of Carbon Monoxide on Iron(I) in Simple and Superstructured Porphyrins

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Investigation of a series of superstructured iron porphyrins showed that the fixation of carbon monoxide on iron(I) is significantly enhanced by the presence of amide groups in the protecting chain. Axial ligation of iron also increases the CO affinity. It was thus possible to obtain and characterize by their UV–vis, IR, and ESR spectra iron(I)–carbon monoxide complexes from amide-linked superstructured porphyrins in the presence of a complexing agent in the solution. The IR and ESR data as well as the remarkable electron push (axial ligation)–pull (NHCO) stabilizing effect indicate a significant electron transfer from the iron atom to the CO ligand. The complex bearing two amide-linked chains with a pending imidazole ligand in one of them is an example of an integrated molecular system, protected from solvent interaction, ensuring a good CO affinity for iron(I) independent of the reaction medium.

## Introduction

Direct electrochemical reduction of carbon monoxide requires very high voltages, close to the discharge of the supporting electrolyte, yielding acetylene diolate and other condensed products.[2] It is therefore of interest to attempt to chemically catalyze[3] the reaction through fixation of CO on a transition metal and reduction of the ensuing complex. The aim of such a mediated reduction is to decrease the overpotential and, possibly, vary the products. Synthetic and naturally occurring iron(II) porphyrins are known to strongly bind CO.[4] We thus set out to use this property for transferring electrons from the electrode to

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