angles differing by *ca* 11° (Table 2). (ii) The rotation of the ligands around the M—C bond. The aromatic rings make an angle of 61·4 (1)° with the O—Mo—O plane. In $ReO_2(mes)_2$ the corresponding angle is 66° and in $OsO_2(mes)_2$ the two independent aromatic rings make angles of 40 and 56°. These values reflect the steric repulsion between the O atoms and the C atoms of the methyl groups. Indeed short C···O contacts are found in (*B*) (2·99 and 3·14 Å) as well as in (*C*) (2·93 to 2·95 Å). Values of 3·13 (1) and 3·18 (1) Å are found in $MoO_2(mes)_2$ which appears to be less strained.

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Structures of 4-Diphenylphosphinodibenzothiophene and Carbonyl(η^5-cyclopentadienyl)(4-diphenylphosphinodibenzothiophene)iodoiron(II)

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Abstract. (I) $C_{24}H_{17}PS$, $M_r = 368\cdot43$, triclinic, $P\bar{1}$, $a = 10\cdot218\ (1)$, $b = 10\cdot257\ (1)$, $c = 9\cdot577\ (1)$ Å, $\alpha = 90\cdot11\ (1)$, $\beta = 110\cdot37\ (1)$, $\gamma = 92\cdot68\ (1)°$, $V = 939\cdot6\ (1)$ Å^3, $Z = 2$, $D_x = 1\cdot30$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot61$ cm^{-1}, $F(000) = 384$, $T = 295$ K, $R = 0\cdot040$, 2465 unique observed reflections. (II) $[FeI(C_5H_5)(CO)\{P(C_6H_5)_2(C_{12}H_7S)\}]$, $M_r = 644\cdot29$, monoclinic, $P2_1/n$, $a = 10\cdot381\ (2)$, $b = 17\cdot706\ (4)$, $c = 14\cdot066\ (3)$ Å, $\beta = 91\cdot86\ (2)°$, $V = 2584\ (1)$ Å^3, $Z = 4$, $D_x = 1\cdot66$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 19\cdot70$ cm^{-1}, $F(000) = 1280$, $T = 295$ K, $R = 0\cdot055$, 1720 unique observed reflections. Compound (I) was prepared by treating 4-lithiodibenzothiophene with diphenylphosphinous chloride. Compound (II) was prepared by refluxing a benzene solution of (I), dicarbonyl(η^5-cyclopentadienyl)iodoiron(II) and a catalytic amount of dicarbonyl(η^5-cyclopentadienyl)iron(II) dimer. (I) is a dibenzothiophene molecule to which a diphenylphosphinous group is substituted at the fourth position in the first ring. In (II), the Fe atom is in roughly tetrahedral coordination with the P atom of ligated (I), an η^5-cyclopentadienyl group, the C atom of a carbonyl group and an I atom. The I and carbonyl sites of (II) are disordered.

Introduction. The activation and cleavage of S—H and C—S bonds of S-containing species by transition-metal complexes is of fundamental importance in coal desulfurization (Calhorda, Carrondo, Dias, Dominges, Simoes & Teixeira, 1986). Dibenzothiophenes are among the most abundant organosulfur compounds found in coal (Attar & Messenger, 1983), and the interaction of these aromatic heterocycles with metals is widely assumed to be central to the mechanism of catalytic desulfurization (Lesch, Richardson, Jacobson & Angelici, 1984). To study the type of bonding of a dibenzothiophene-containing ligand to Fe and the effects of substituents at the 4-position of the ligand

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(Fig. 1), carbonyl(η^5-cyclopentadienyl)(4-diphenylphosphinodibenzothiophene)iodoiron(II), (II), was synthesized from CO-ligand exchange by reaction of 4-diphenylphosphinodibenzothiophene, (I), with $CpFe(CO)_2I$, catalyzed by $[CpFe(CO)_2]_2$ (Cp = cyclopentadienyl) (Albers & Coville, 1984). In a related Ru coordination complex of the dibenzothiophene compound, (I), this ligand was chelated to the Ru atom through both S and P atoms (Bucknor, Draganjac, Rauchfuss, Ruffing & Rheingold, 1984). In this study the structures of both (I) and (II) were determined in order to investigate possible dibenzothiophenic-S to metal coordination and to examine conformational variations resulting from complexation.

Experimental. Compound (I) prepared by treatment of 4-lithiodibenzothiophene with diphenylphosphinous chloride in tetrahydrofuran at room temperature. Solution containing product mixed with water, extracted with dichloromethane to obtain colorless crystals of (I) in 65% yield. Data for (I): ^{31}P NMR δ 9·38. Elemental analysis found: C 77·75%, H 4·55%, S 8·72%; calculated: C 78·24%, H 4·65%, S 8·70%. Crystals suitable for X-ray diffraction grown from dichloromethane with diffusion of a hexane layer. Preparation of (II) by addition of 2·1 mmol of (I) and 2·0 mmol $CpFe(CO)_2I$ to 10 ml benzene. Solution brought to reflux under argon and 10 mg of $[(C_5H_5)Fe(CO)_2]_2$ added to induce CO substitution (Albers & Coville, 1984) by (I). No reaction observed without the catalyst. Reaction progress monitored by TLC (silica gel; benzene as eluent). Solution cooled, solvent removed on rotary evaporator. Product purified by column chromatography (silica gel; hexane/EtOAc 1:1 as eluent). Structure of (II) confirmed by ^{1}H NMR, ^{13}C NMR, FABMS and FTIR. Data for (II): ^{1}H NMR ($CDCl_3$) δ 8·30–8·25 (*m*, 1H), 8·23–8·20 (*m*, 2H), 7·95–7·85 (*m*, 2H), 7·75–7·65 (*m*, 2H), 7·55–7·45 (*m*, C_6H_5), 4·45 (η^5-C_5H_5); ^{13}C NMR ($CDCl_3$) δ 220·86, 142·31, 140·04, 136·53, 134·80, 134·13, 133·50, 132·89, 131·02, 130·59, 128·44, 127·29, 124·55, 124·20, 123·43, 122·54, 121·65, 82·97 (η^5-C_5H_5); $^{31}P\{^1H\}$ NMR (int. std. H_3PO_4) δ 66·27 (singlet); FTIR (cm^{-1}, Nujol mull) ν_{CO} 1949, ν_{PPh} 1373, 742; FABMS: 644 (M^+), 616 (M^+-CO), 551 [$M^+-(\eta^5$-C_5H_5 + CO)], 517 (M^+-I); elemental analysis found: C 55·80%, H 3·37%; calculated: C 55·90%, H 3·41%. Crystals suitable for X-ray diffraction grown from toluene with diffusion of a hexane layer. Crystals used for data collection 0·35 × 0·30 × 0·22 mm, colorless, blocky fragment cut from larger crystal (I), and 0·22 × 0·21 × 0·05 mm, green, platy (II). Rigaku AFC5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, scan speeds 8° min^{-1} (I) and 2° min^{-1} (II), maximum of three scan repetitions to obtain $\sigma F/F < 0{\cdot}10$. Lattice parameters from least-squares fit of 25 (I) and 22 (II) strong reflections in 2θ range 38–48° (I) and 25–33° (II). For (I), 3517 reflections measured (h 0 to 12, k −12 to 12, l −11 to 11), 205 redundant reflections deleted, data set comprised 3312 unique reflections. 2465 reflections were considered observed [$I > 3\sigma(I)$], $(\sin\theta)/\lambda_{\max}$ = 0·60 Å^{-1}. Three standard reflections ($\bar{2}10$, $\bar{2}00$, $0\bar{2}\bar{2}$) varied by −1·0, −3·0 and −0·1%, respectively; no decay correction applied. For (II), 4997 reflections measured (h 0 to 12, k 0 to 21, l −16 to 16), 445 redundant and/or systematically extinct reflections deleted, data set made up of 4552 unique reflections. 1720 reflections were considered observed [$I > 3\sigma(I)$], $(\sin\theta)/\lambda_{\max}$ = 0·60 Å^{-1}. Three standard reflections ($\bar{1}10$, $\bar{1}20$, $01\bar{1}$) varied by −1·0, −1·8 and +0·5%, respectively; no decay correction applied. Data for (I) and (II) corrected for Lorentz, polarization and absorption [empirical ψ-scan method, 5 reflections, transmission range 0·88–1·0 for (I); analytical correction, transmission range 0·707–0·907 for (II)]. Direct methods provided the atomic positions of most of the atoms in both compounds, the remaining non-H atoms were found by least-squares/Fourier methods. Full-matrix least-squares refinement of F magnitudes performed on both structures. Compound (I) refined uneventfully, all H positions found from difference Fourier synthesis and included in the model. Final refinement performed with 304 variables including all positional parameters, anisotropic thermal parameters for the non-H atoms, isotropic thermal parameters for the H atoms, one scale factor and an isotropic secondary-extinction coefficient of $0{\cdot}10909 \times 10^{-5}$ ($0{\cdot}47031 \times 10^{-6}$). Compound (II) was found to have disordered I/CO sites, constrained site occupancy refinement led to occupancy values of 0·58 for I(1) and 0·42 for I(2). Occupancy values for I and CO may be of low accuracy due to correlations between their positional, thermal and population parameters. The two CO positions could not be resolved in the presence of the I atoms and were thus calculated to be along the Fe(1)—I vectors with Fe—C and Fe—O distances fixed at 1·756 and 2·924 Å, respectively (C—O = 1·168 Å). The Fe—CO distances used are the average of two Fe—CO bond distances reported for $Fe(CS)(CO)_2(PPh_3)_2$ by Touchard, Fillaut, Dixneuf & Toupet (1986). Occupancy values for the two CO groups were set at (1·0−occupancy of the related I atom) and their B's were fixed at 4·0 Å^2. H atoms placed in assumed positions (C—H = 0·95 Å) and fixed, H atom B's set at $1{\cdot}2 \times B_{eq}$

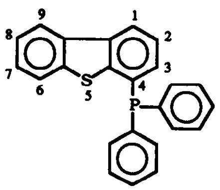

Fig. 1. IUPAC atom designations for dibenzothiophene.

Table 1. *Positional and equivalent isotropic thermal parameters for the non-*H *atoms and their e.s.d.'s*

$$B_{eq} = 8\pi^2/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha].$$

	x	y	z	B_{eq}(Å^2)
(I)				
S(1)	0·55052 (7)	0·84945 (7)	0·92273 (8)	3·35 (3)
P(1)	0·37058 (7)	0·79074 (7)	0·56742 (8)	2·99 (3)
C(1)	0·5605 (3)	0·7773 (2)	0·6447 (3)	2·8 (1)
C(2)	0·6434 (3)	0·7478 (3)	0·5612 (4)	3·5 (1)
C(3)	0·7887 (3)	0·7513 (3)	0·6248 (4)	4·0 (1)
C(4)	0·8561 (3)	0·7841 (3)	0·7725 (4)	3·7 (1)
C(5)	0·7774 (3)	0·8140 (3)	0·8610 (3)	2·9 (1)
C(6)	0·6311 (3)	0·8093 (2)	0·7953 (3)	2·8 (1)
C(7)	0·7126 (3)	0·8765 (3)	1·0645 (3)	3·1 (1)
C(8)	0·8247 (3)	0·8539 (3)	1·0163 (3)	3·0 (1)
C(9)	0·9606 (3)	0·8715 (3)	1·1187 (4)	3·9 (1)
C(10)	0·9817 (4)	0·9103 (3)	1·2635 (4)	4·4 (1)
C(11)	0·8691 (4)	0·9334 (3)	1·3073 (4)	4·4 (1)
C(12)	0·7344 (3)	0·9159 (3)	1·2105 (3)	3·8 (1)
C(13)	0·3053 (3)	0·6503 (3)	0·6461 (3)	3·0 (1)
C(14)	0·3864 (3)	0·5496 (3)	0·7187 (4)	3·9 (1)
C(15)	0·3287 (4)	0·4459 (3)	0·7733 (4)	4·8 (1)
C(16)	0·1890 (4)	0·4411 (3)	0·7551 (4)	4·7 (1)
C(17)	0·1072 (4)	0·5409 (4)	0·6839 (4)	4·7 (2)
C(18)	0·1652 (3)	0·6457 (3)	0·6319 (4)	4·1 (1)
C(19)	0·3298 (3)	0·7399 (3)	0·3734 (3)	3·0 (1)
C(20)	0·3443 (3)	0·8349 (3)	0·2756 (3)	3·6 (1)
C(21)	0·3168 (3)	0·8052 (4)	0·1272 (4)	4·3 (1)
C(22)	0·2736 (4)	0·6803 (4)	0·0742 (4)	4·7 (2)
C(23)	0·2560 (4)	0·5859 (4)	0·1680 (4)	5·0 (2)
C(24)	0·2846 (3)	0·6149 (3)	0·3171 (4)	4·0 (1)
H(1)	0·597 (3)	0·727 (3)	0·458 (4)	4·2 (7)*
H(2)	0·837 (3)	0·726 (3)	0·557 (3)	4·2 (7)*
H(3)	0·958 (3)	0·785 (3)	0·812 (3)	4·0 (7)*
H(4)	1·035 (3)	0·864 (3)	1·090 (3)	4·0 (7)*
H(5)	1·079 (4)	0·926 (3)	1·335 (4)	5·1 (8)*
H(6)	0·877 (3)	0·958 (3)	1·405 (4)	5·4 (8)*
H(7)	0·661 (3)	0·928 (3)	1·244 (3)	3·4 (6)*
H(8)	0·484 (4)	0·550 (3)	0·736 (4)	6·0 (9)*
H(9)	0·393 (4)	0·387 (3)	0·833 (4)	5·7 (9)*
H(10)	0·144 (4)	0·371 (4)	0·784 (4)	7 (1)*
H(11)	0·007 (4)	0·544 (3)	0·664 (4)	6 (1)*
H(12)	0·109 (4)	0·711 (3)	0·576 (4)	5·2 (8)*
H(13)	0·374 (3)	0·923 (3)	0·310 (3)	4·9 (8)*
H(14)	0·322 (4)	0·873 (4)	0·060 (4)	7 (1)*
H(15)	0·247 (3)	0·663 (3)	−0·025 (4)	4·5 (7)*
H(16)	0·220 (4)	0·497 (4)	0·133 (4)	6 (1)*
H(17)	0·269 (3)	0·547 (3)	0·382 (4)	5·0 (8)*

	x	y	z	B_{eq}(Å^2)
(II)				
I(1)†	0·6899 (2)	0·0851 (1)	0·9026 (1)	4·30 (9)
I(2)†	0·6007 (3)	0·0530 (2)	1·1431 (2)	6·0 (2)
Fe(1)	0·5656 (2)	0·1589 (1)	1·0290 (1)	3·5 (1)
S(1)	1·0334 (3)	0·3143 (2)	1·1319 (2)	4·2 (2)
P(1)	0·7355 (3)	0·2227 (2)	1·0860 (2)	2·8 (2)
C(1)	0·822 (1)	0·2856 (7)	1·0061 (9)	3·0 (7)
C(2)	0·766 (1)	0·3001 (8)	0·915 (1)	3·6 (7)
C(3)	0·818 (1)	0·350 (1)	0·853 (1)	4·8 (8)
C(4)	0·929 (1)	0·3859 (8)	0·874 (1)	3·8 (8)
C(5)	0·993 (1)	0·3723 (7)	0·962 (1)	3·2 (7)
C(6)	0·938 (1)	0·3228 (7)	1·0269 (8)	2·8 (6)
C(7)	1·148 (1)	0·3760 (8)	1·090 (1)	3·5 (7)
C(8)	1·116 (1)	0·4036 (8)	0·9995 (9)	3·4 (7)
C(9)	1·199 (1)	0·4530 (9)	0·954 (1)	4·6 (8)
C(10)	1·313 (1)	0·4729 (9)	1·000 (1)	4·8 (9)
C(11)	1·342 (1)	0·4464 (9)	1·092 (1)	4·5 (8)
C(12)	1·262 (1)	0·3979 (8)	1·135 (1)	4·3 (8)
C(13)	0·868 (1)	0·1655 (7)	1·135 (1)	3·1 (7)
C(14)	0·947 (1)	0·1275 (8)	1·0715 (9)	3·3 (7)
C(15)	1·043 (1)	0·0800 (9)	1·102 (1)	4·2 (8)
C(16)	1·065 (1)	0·0687 (8)	1·199 (1)	4·1 (8)
C(17)	0·990 (1)	0·1044 (9)	1·261 (1)	4·2 (8)
C(18)	0·888 (1)	0·1525 (8)	1·233 (1)	4·0 (7)
C(19)	0·692 (1)	0·2856 (8)	1·1825 (9)	2·8 (6)
C(20)	0·707 (1)	0·3615 (8)	1·178 (1)	3·6 (7)
C(21)	0·659 (1)	0·4093 (7)	1·247 (1)	3·6 (7)
C(22)	0·595 (1)	0·381 (1)	1·322 (1)	4·2 (8)
C(23)	0·582 (1)	0·303 (1)	1·329 (1)	5 (1)
C(24)	0·626 (1)	0·2570 (8)	1·259 (1)	4·0 (7)
C(25)	0·455 (1)	0·2559 (9)	1·004 (2)	6 (1)
C(26)	0·443 (2)	0·206 (2)	0·925 (1)	7 (1)
C(27)	0·389 (2)	0·140 (1)	0·959 (2)	7 (1)
C(28)	0·367 (1)	0·149 (1)	1·053 (2)	8 (1)
C(29)	0·412 (1)	0·220 (1)	1·084 (1)	5 (1)
C(30)‡	0·6501	0·1087	0·9431	4·0
O(1)‡	0·7063	0·0754	0·8860	4·0
C(31)‡	0·5903	0·0841	1·1096	4·0
O(2)‡	0·6068	0·0344	1·1631	4·0

* Isotropic temperature factor.

† Site occupancy is 0·58 for I(1) and 0·42 for I(2).

‡ Calculated coordinates; fixed isotropic temperature factor; site occupancies are 0·42 [C(30), O(1)] and 0·58 [C(31), O(2)].

of associated C atom. Final refinement with 307 variables including non-H and non-CO positional and anisotropic thermal parameters, and one scale factor. Regeneration of H and CO positions followed by refinement to convergence repeated until shifts became insignificant. Convergence of (I) yielded $R = 0{\cdot}040$, $wR = 0{\cdot}055$, $S = 1{\cdot}49$ and $(\Delta/\sigma)_{max} = 0{\cdot}15$ while (II) converged at $R = 0{\cdot}055$, $wR = 0{\cdot}062$, $S = 1{\cdot}39$ and $(\Delta/\sigma)_{max} = 0{\cdot}14$ [$w = 1/\sigma^2(|F_o|)$]. Final difference syntheses produced $(\Delta\rho)_{max} = 0{\cdot}85$ e Å^{-3} and $(\Delta\rho)_{min} = -0{\cdot}21$ e Å^{-3} for (I) and $(\Delta\rho)_{max} = 0{\cdot}68$ e Å^{-3} and $(\Delta\rho)_{min} = -0{\cdot}75$ e Å^{-3} for (II). Atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974). All computer programs from the *TEXSAN* crystal structure analysis package (Molecular Structure Corporation, 1985).

Discussion. Atomic coordinates and equivalent isotropic temperature factors for (I) and (II) are listed in Table 1 while selected bond distances and angles are presented in Table 2.* Figs. 2 and 3 depict the molecular conformations of (I) and (II) respectively. The disordered I/CO sites of (II) are shown as if both I and CO are present simultaneously (an obviously impossible occurrence) so that all of the atoms could be included. Compound (I) is composed of a dibenzothiophene molecule to which a diphenylphosphine group is substituted at the fourth position in the first ring. Fe coordination in (II) is roughly tetrahedral with one of the sites occupied by an η^5-cyclopentadienyl ligand having an average Fe—C distance of 2·09 Å. The coordination sphere of the Fe atom is completed by a bond to the P atom of ligated (I), a bond to the C of a

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* Lists of structure factors, anisotropic thermal parameters, calculated H-atom parameters [(II) only], additional distances and angles, and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51531 (63 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and their e.s.d.'s*

(I)			
S(1)—C(7)	1·748 (3)	C(4)—C(5)	1·399 (4)
S(1)—C(6)	1·752 (3)	C(5)—C(6)	1·404 (4)
P(1)—C(19)	1·826 (3)	C(5)—C(8)	1·447 (4)
P(1)—C(13)	1·831 (3)	C(7)—C(12)	1·393 (4)
P(1)—C(1)	1·833 (3)	C(7)—C(8)	1·404 (4)
C(1)—C(2)	1·395 (4)	C(8)—C(9)	1·396 (4)
C(1)—C(6)	1·399 (4)	C(9)—C(10)	1·382 (5)
C(2)—C(3)	1·394 (4)	C(10)—C(11)	1·384 (5)
C(3)—C(4)	1·373 (4)	C(11)—C(12)	1·369 (4)
C(7)—S(1)—C(6)	91·3 (1)	C(1)—C(6)—S(1)	125·0 (2)
C(19)—P(1)—C(13)	102·8 (1)	C(5)—C(6)—S(1)	112·1 (2)
C(19)—P(1)—C(1)	102·2 (1)	C(12)—C(7)—C(8)	121·6 (3)
C(13)—P(1)—C(1)	102·9 (1)	C(12)—C(7)—S(1)	126·0 (2)
C(2)—C(1)—C(6)	116·4 (3)	C(8)—C(7)—S(1)	112·4 (2)
C(3)—C(2)—C(1)	121·4 (3)	C(9)—C(8)—C(7)	118·4 (3)
C(4)—C(3)—C(2)	121·3 (3)	C(9)—C(8)—C(5)	129·6 (3)
C(3)—C(4)—C(5)	119·4 (3)	C(7)—C(8)—C(5)	112·0 (2)
C(4)—C(5)—C(6)	118·6 (3)	C(10)—C(9)—C(8)	119·8 (3)
C(4)—C(5)—C(8)	129·2 (3)	C(9)—C(10)—C(11)	120·4 (3)
C(6)—C(5)—C(8)	112·2 (2)	C(12)—C(11)—C(10)	121·5 (3)
C(1)—C(6)—C(5)	122·9 (2)	C(11)—C(12)—C(7)	118·3 (3)
(II)			
I(1)—Fe(1)	2·585 (2)	C(1)—C(2)	1·41 (2)
I(2)—Fe(1)	2·488 (4)	C(2)—C(3)	1·37 (2)
Fe(1)—C(31)	1·756*	C(3)—C(4)	1·34 (2)
Fe(1)—C(30)	1·756*	C(4)—C(5)	1·41 (2)
C(30)—O(1)	1·168*	C(5)—C(6)	1·40 (2)
C(31)—O(2)	1·168*	C(5)—C(8)	1·47 (2)
Fe(1)—P(1)	2·223 (4)	C(7)—C(12)	1·39 (2)
S(1)—C(7)	1·74 (1)	C(7)—C(8)	1·39 (2)
S(1)—C(6)	1·76 (1)	C(8)—C(9)	1·40 (2)
P(1)—C(13)	1·82 (1)	C(9)—C(10)	1·38 (2)
P(1)—C(19)	1·82 (1)	C(10)—C(11)	1·39 (2)
P(1)—C(1)	1·84 (1)	C(11)—C(12)	1·35 (2)
C(1)—C(6)	1·40 (2)		
P(1)—Fe(1)—I(2)	93·0 (1)	C(6)—C(5)—C(4)	119 (1)
P(1)—Fe(1)—I(1)	95·6 (1)	C(6)—C(5)—C(8)	112 (1)
I(2)—Fe(1)—I(1)	89·8 (1)	C(4)—C(5)—C(8)	129 (1)
C(7)—S(1)—C(6)	91·8 (6)	C(5)—C(6)—C(1)	122 (1)
C(13)—P(1)—C(19)	105·2 (6)	C(5)—C(6)—S(1)	112 (1)
C(13)—P(1)—C(1)	100·9 (6)	C(1)—C(6)—S(1)	126 (1)
C(13)—P(1)—Fe(1)	115·6 (4)	C(12)—C(7)—C(8)	120 (1)
C(19)—P(1)—C(1)	102·9 (6)	C(12)—C(7)—S(1)	127 (1)
C(19)—P(1)—Fe(1)	111·5 (4)	C(8)—C(7)—S(1)	113 (1)
C(1)—P(1)—Fe(1)	119·1 (4)	C(7)—C(8)—C(9)	120 (1)
C(6)—C(1)—C(2)	116 (1)	C(7)—C(8)—C(5)	112 (1)
C(6)—C(1)—P(1)	126 (1)	C(9)—C(8)—C(5)	128 (1)
C(2)—C(1)—P(1)	118 (1)	C(10)—C(9)—C(8)	119 (1)
C(3)—C(2)—C(1)	123 (1)	C(9)—C(10)—C(11)	120 (1)
C(4)—C(3)—C(2)	121 (1)	C(12)—C(11)—C(10)	121 (1)
C(3)—C(4)—C(5)	119 (1)	C(11)—C(12)—C(7)	119 (1)

* Fixed distance.

carbonyl group and a bond to an I atom. Least-squares-plane calculations show that the ring planarity of (I) is slightly superior to that of (II). For (I), mean deviations from best-fit planes are 0·0065 and 0·0047 Å for rings C(13) and C(19), respectively; equivalent values for (II) are 0·0069 and 0·0103 Å. C—P—C angles are quite consistent in (I), varying by only 0·7° as opposed to 4·3° in (II). A major conformational difference between (I) and (II) occurs in the relationship of the phenyl rings to the dibenzothiophene moiety, as illustrated by torsion angles C(1)—P(1)—C(13)—C(14) [−11·713 (1)° (I) and −55 (1)° (II)] and C(1)—P(1)—C(19)—C(24) [96·047 (6)° (I) and −179 (1)° (II)]. Stereo drawings of (I) and (II), oriented so that the view direction is normal to dibenzothiophene (Figs. 4 and 5), illustrate the phenyl ring reorientation when (I) is ligated in (II). Distances within the dibenzothiophene portions of (I) and (II) are identical within standard errors.

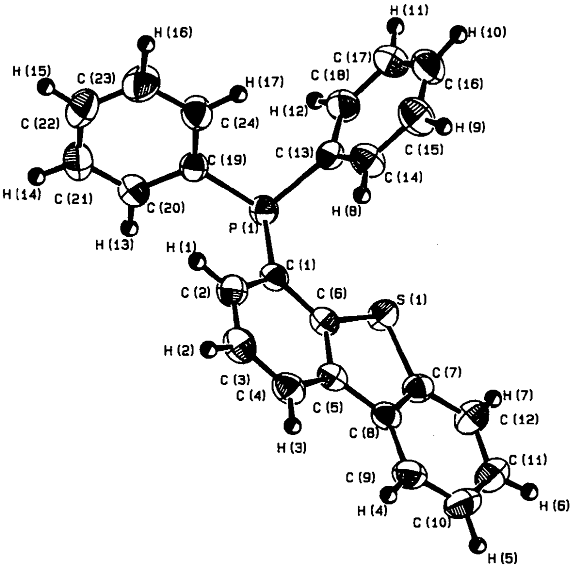

Fig. 2. Molecular structure and numbering scheme for (I); thermal ellipsoids at the 50% probability level. H atom *B*'s are isotropic.

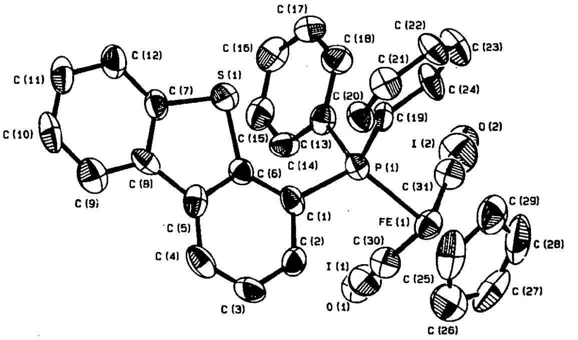

Fig. 3. Molecular structure and numbering scheme for (II); thermal ellipsoids at the 50% probability level. The I/CO sites are disordered and the CO *B*'s are fixed isotropic. H atoms are omitted to improve clarity.

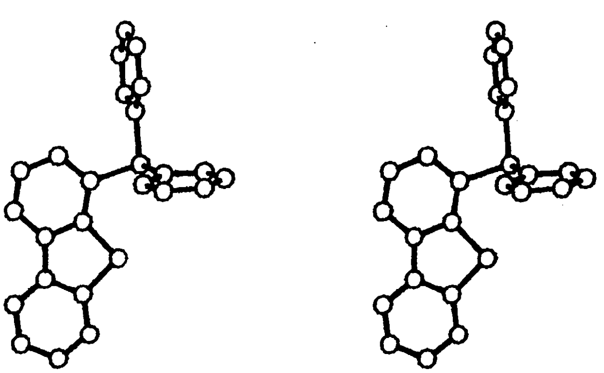

Fig. 4. Stereoview of (I) normal to the plane of the dibenzothiophene.

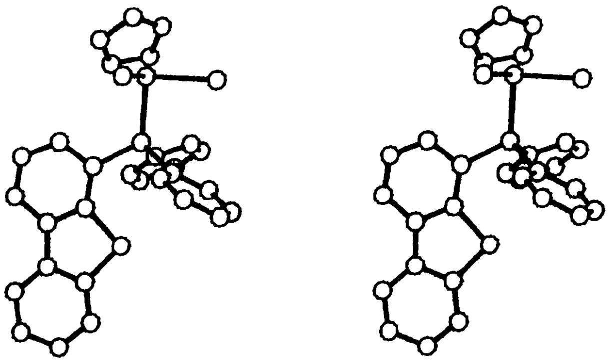

Fig. 5. Stereoview of (II) normal to the plane of the dibenzothiophene.

In ^{13}C NMR spectra of the compound it was observed that a few peaks were doubled due to coupling of ^{13}C to ^{31}P nuclei. The ^{31}P NMR spectrum of (II) exhibited a sextet, but when proton decoupled a sharp singlet was observed confirming that the coupling was between ^{1}H and ^{31}P nuclei. In (II), the Fe atom does not bind to the ring S of ligated (I). In this case, coordination of the metal center to the P atom of (I) maintains a close proximity of the Fe atom to the ring S. The possibility of Fe—S binding this affords may be important in the catalytic hydrodesulfurization of the dibenzothiophenic S.

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Studies in Werner Clathrates. II.* Structure and Thermal Analysis of Bis(isothiocyanato)tetrakis(4-phenylpyridine)nickel(II) Benzene Clathrate (1:4)

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Abstract. $C_{46}H_{36}N_6NiS_2.4C_6H_6$, $M_r = 1107{\cdot}7$, triclinic, $P\bar{1}$, $a = 9{\cdot}52\,(1)$, $b = 12{\cdot}19\,(3)$, $c = 13{\cdot}72\,(2)$ Å, $\alpha = 100{\cdot}3\,(1)$, $\beta = 90{\cdot}3\,(1)$, $\gamma = 105{\cdot}9\,(2)°$, $V = 1504{\cdot}0$ Å^3, $Z = 1$, host:guest = 1:4, $D_m = 1{\cdot}235$, $D_x = 1{\cdot}22$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 3{\cdot}95$ cm^{-1}, $F(000) = 582$, $T = 294$ K, $R = 0{\cdot}097$ ($wR = 0{\cdot}078$) for 3782 observed reflections. The host molecule has a −++− configuration and guest molecules are contained in a large channel parallel to **a** which has been mapped by volume calculations. Thermal decomposition studies indicate release of guest molecules at *ca* 307 K.

Introduction. Werner clathrates are complexes of the type MX_2L_4 where M = divalent transition-metal cation, *e.g.* Mn^{2+}–Cu^{2+}, X = anionic ligand *e.g.* halide, NCS^-, NO_2^-, NCO^-, and L = electrically neutral substituted pyridine or α-arylalkylamine. Since the pioneering work in the 1950's (Schaeffer, Dorsey, Skinner & Christian, 1957) these compounds have been used to separate a wide variety of isomeric and other organic compounds. The 4-methylpyridine (4-Mepy) derivative of the bis(isothiocyanato)nickel(II) complex

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