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Binuclear Metallocyclic Complex of a Non-Macrocyclic Polyhydroimidazole Ligand: Structure of Bis{μ-[1,2,4,5-tetrakis(4,5-dihydroimidazol-2-yl)benzene]-1$\kappa^2N^3,N^{3'}$:2$\kappa^2N^{3''},N^{3'''}$}-bis[isothiocyanatocopper(II)] Dithiocyanate, $[Cu_2(C_{18}H_{22}N_8)_2(NCS)_2](NCS)_2$, and the Potential Ligand 1,2,4,5-Tetrakis-(benzothiazol-2-yl)benzene, $C_{34}H_{18}N_4S_4$

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Abstract. (I) $[Cu_2(C_{18}H_{22}N_8)_2(NCS)_2](NCS)_2$, M_r = 1060.27, monoclinic, $P2_1/n$, a = 14.381 (4), b = 10.834 (3), c = 15.824 (4) Å, β = 108.988 (20)°, V = 2331.3 (10) Å^3, Z = 2, D_x = 1.510 g cm^{-3}, λ(Mo $K\alpha$) = 0.70930 Å, μ = 11.4 cm^{-1}, $F(000)$ = 1092, T = 295 (1) K, R = 0.071, wR = 0.050 for 1999/3032 unique reflections with $I > 2.5\sigma(I)$. (II) $C_{34}H_{18}N_4S_4$, M_r = 610.81, monoclinic, $P2_1/c$, a = 9.7550 (9), b = 5.9547 (5), c = 23.8871 (24) Å, β = 90.783 (8)°, V = 1387.43 (22) Å^3, Z = 2, D_x = 1.462 g cm^{-3}, λ(Cu $K\alpha$) = 1.54056 Å, μ = 33.5 cm^{-1}, $F(000)$ = 628, T = 295 (1) K, R = 0.047, wR = 0.032 for 1594/2054 unique reflections with $I > 2.5\sigma(I)$. (I) has a large Cu···Cu distance [7.472 (10) Å] with each five-coordinate Cu atom displaced by 0.259 (5) Å from the N4 plane, and an empty cavity with a parallel benzene ring separation of 4.236 (12) Å. (II) displays severe twisting of the benzothiazole rings, which may be the reason for its lack of donor function.

Introduction. The ligand 1,2,4,5-tetrakis(4,5-dihydroimidazol-2-yl)benzene (btim) has been shown to form novel binuclear metallocyclic copper(II) complexes with large Cu···Cu separations and a large empty cavity defined by the Cu square pyramids and the parallel eclipsed benzene rings (Mandal, Thompson, Newlands, Gabe & Lee, 1989, 1990). $[Cu_2(btim)_2Cl_2]Cl_2.7H_2O$ has a Cu···Cu separation of 7.610 (2) Å, a Cu—Cl distance of 2.505 (4) Å and a benzene–benzene separation of 3.93 Å; $[Cu_2(btim)_2(N_3)_2](N_3)_2.5H_2O$ has Cu···Cu separations of 7.30, 7.42 Å, copper–azide distances of 2.18, 2.27 Å and benzene–benzene separations of 4.3, 4.4 Å. These compounds are characterized by weak antiferromagnetic exchange through the ligand bridges. In its Cu coordination chemistry btim displays no tendency to form mononuclear bis-ligand derivatives, typical of the related 'half' molecule 1,2-bis(4,5-dihydroimidazol-2-yl)benzene (Wellon, Bautista, Thompson & Hartstock, 1983). This paper describes the preparation and structure of the related ligand complex $[Cu_2(btim)_2(NCS)_2](NCS)_2$ (I) and also the preparation and structure of the related ligand 1,2,4,5-tetrakis(benzothiazol-2-yl)benzene (II) (btbz), which, surprisingly, shows no tendency to bind copper.

Experimental. $[Cu_2(btim)_2(NCS)_2](NCS)_2$ was prepared by treatment of an aqueous solution of $[Cu_2(btim)_2Cl_2]Cl_2.7H_2O$ (Mandal, Thompson, Newlands, Gabe & Lee, 1989) with excess aqueous thiocyanate, followed by recrystallization from methanol to give deep blue crystals. (II) was prepared by heating pyromellitic dianhydride (1 equivalent) and *o*-aminobenzenethiol (4 equivalents) in polyphosphoric acid at 433 K for 5 h. The hot mixture was poured into ice–water giving a yellow precipitate, which was filtered off, washed with aqueous sodium bicarbonate and water and vacuum dried. Recrystallization from chloroform gave pale yellow crystals. Satisfactory elemental analyses were obtained for both compounds.

Data for both structures were collected on an Enraf–Nonius CAD-4 diffractometer controlled by the *NRCCAD* control program (Grant & Gabe, 1978). The structures were solved by direct methods and refined by cycles of least-squares calculations (on F). For (I) a secondary-extinction parameter, according to Zachariasen (1967), was refined. All calculations were performed using the *NRCVAX* crystal

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Table 1. *Crystal and data-collection parameters for* $[Cu_2(btim)_2(NCS)_2](NCS)_2$ (I) *and* $C_{34}H_{18}N_4S_4$ (II)

	(I)	(II)
Formula	$Cu_2C_{40}H_{44}N_{20}S_4$	$C_{34}H_{18}N_4S_4$
Colour	Blue	Yellow
Crystal size (mm)	0.1 × 0.2 × 0.25	0.1 × 0.2 × 0.2
No. of reflections used for lattice parameters	25	24
θ range (°)	28.00–35.00	70.00–90.00
Max. value of 2θ (°)	44.8	119.7
Range of h	$-15\rightarrow14$	$-10\rightarrow10$
k	$0\rightarrow11$	$0\rightarrow6$
l	$0\rightarrow16$	$0\rightarrow26$
Data collected	4248	5286
Unique data	3032	2054
Data with $I > 2.5\sigma(I)$	1999	1594
Merging R	0.018	0.029
Weighting scheme	Counting statistics	Counting statistics
No. of parameters in last LS cycle	299	226
Max. shift/e.s.d.	0.055	0.014
$\Delta\rho_{max}$ (e Å^{-3})	0.66	0.32
$\Delta\rho_{min}$ (e Å^{-3})	−0.74	−0.29
Secondary extinction	0.14 (4)	–
Goodness of fit	3.48	4.19

Table 2. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for* $[Cu_2(btim)_2(NCS)_2](NCS)_2$ (I) *and* $C_{34}H_{18}N_4S_4$ (II) *with e.s.d.'s in parentheses*

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq}
(I)				
Cu	0.80448 (9)	0.91874 (13)	0.09849 (8)	2.91 (7)
S1	0.5002 (3)	0.8612 (4)	0.1400 (3)	9.1 (3)
S2	0.1261 (3)	0.3464 (4)	0.1694 (3)	7.9 (3)
N1	0.6986 (7)	0.8663 (10)	0.1652 (6)	5.0 (6)
N2	0.9137 (6)	0.9712 (8)	0.2069 (5)	3.3 (5)
N3	1.0609 (6)	1.0082 (9)	0.3026 (6)	4.4 (5)
N4	0.7229 (6)	0.8802 (8)	−0.0276 (5)	3.5 (5)
N5	0.6642 (6)	0.9069 (9)	−0.1760 (5)	3.9 (5)
N6	0.7599 (5)	1.0937 (9)	0.0714 (5)	3.1 (5)
N7	0.7453 (7)	1.2791 (9)	0.0084 (5)	3.6 (5)
N8	0.8708 (6)	0.7570 (8)	0.1120 (5)	3.1 (5)
N9	0.9826 (6)	0.6145 (9)	0.1158 (6)	3.9 (5)
N10	0.2266 (8)	0.5138 (12)	0.1010 (8)	7.4 (7)
C1	0.6179 (9)	0.8635 (11)	0.1575 (8)	4.7 (7)
C2	1.0065 (8)	0.9681 (10)	0.2225 (6)	2.8 (6)
C3	0.9978 (8)	1.0278 (12)	0.3557 (7)	4.9 (7)
C4	0.8966 (8)	1.0271 (11)	0.2839 (7)	4.5 (7)
C5	0.7329 (7)	0.9370 (10)	−0.0968 (7)	3.3 (6)
C6	0.6346 (8)	0.8023 (10)	−0.0589 (7)	4.2 (6)
C7	0.5915 (8)	0.8280 (11)	−0.1588 (7)	5.2 (7)
C8	0.7791 (7)	1.1656 (11)	0.0167 (6)	2.6 (6)
C9	0.6976 (8)	1.1658 (12)	0.1119 (7)	4.3 (7)
C10	0.6932 (8)	1.2935 (11)	0.0711 (7)	4.4 (7)
C11	0.9582 (8)	0.7333 (10)	0.1099 (6)	2.8 (6)
C12	0.8266 (7)	0.6377 (11)	0.1193 (8)	4.7 (8)
C13	0.9017 (9)	0.5403 (10)	0.1259 (8)	4.7 (7)
C11	0.8147 (7)	1.0195 (10)	−0.0942 (6)	2.8 (5)
C15	0.8371 (7)	1.1285 (10)	−0.0417 (6)	2.4 (5)
C16	0.9128 (7)	1.2101 (10)	−0.0449 (7)	3.2 (6)
C17	1.0327 (7)	0.8226 (9)	0.1050 (6)	2.4 (6)
C18	1.0567 (7)	0.9325 (11)	0.1584 (6)	2.7 (5)
C19	1.1338 (7)	1.0123 (10)	0.1552 (7)	3.1 (6)
C20	0.1891 (9)	0.4437 (13)	0.1257 (8)	4.6 (8)
(II)				
S1	0.00808 (11)	0.53216 (22)	0.12549 (4)	3.45 (5)
S2	−0.25067 (12)	0.45544 (24)	0.01226 (5)	4.26 (6)
N1	0.1348 (3)	0.9085 (6)	0.14528 (13)	3.20 (19)
N2	−0.2810 (3)	0.7680 (7)	0.08710 (14)	3.36 (19)
C1	0.1116 (4)	1.0605 (9)	0.03154 (18)	3.16 (22)
C2	0.0201 (4)	0.9084 (7)	0.05477 (16)	2.77 (21)
C3	−0.0975 (4)	0.8507 (7)	0.02164 (16)	2.73 (20)
C4	0.0550 (4)	0.8079 (7)	0.10896 (16)	2.74 (20)
C5	−0.2103 (4)	0.7103 (8)	0.04420 (17)	2.77 (20)
C11	0.1005 (4)	0.5555 (8)	0.18777 (16)	2.58 (20)
C12	0.1123 (4)	0.3981 (9)	0.23021 (19)	3.27 (24)
C13	0.1887 (5)	0.4614 (10)	0.27704 (20)	3.8 (3)
C14	0.2502 (5)	0.6720 (11)	0.28040 (21)	4.2 (3)
C15	0.2393 (5)	0.8262 (9)	0.23799 (20)	3.7 (3)
C16	0.1594 (4)	0.7678 (8)	0.19045 (17)	2.83 (21)
C21	−0.3758 (4)	0.4146 (9)	0.06282 (18)	3.55 (23)
C22	−0.4642 (5)	0.2339 (10)	0.06871 (23)	4.9 (3)
C23	−0.5541 (6)	0.2481 (12)	0.1130 (3)	5.5 (4)
C24	−0.5562 (5)	0.4290 (13)	0.1486 (3)	5.6 (3)
C25	−0.4692 (5)	0.6128 (10)	0.14254 (24)	4.9 (3)
C26	−0.3765 (4)	0.6006 (9)	0.09799 (18)	3.37 (23)

structure system (Gabe, Le Page, Charland, Lee & White, 1989). H atoms in (I) were included in calculated positions (C—H distance 1.08 Å and U value of 1.1 times the value of U for the bonded atom) and were not refined. Non-H atoms were refined anisotropically. For (II), the H atoms were located in a difference Fourier map and were refined with isotropic thermal parameters, while other atoms were refined anisotropically. Crystal and data collection parameters are given in Table 1.* Atomic scattering factors and f', f'' values from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The atomic coordinates for (I) and (II) are listed in Table 2 and selected bond distances and angles are presented in Table 3. Views of the molecules and the atomic numbering schemes are shown in Figs. 1 (I) and 2 (II).

The structure of $[Cu_2(btim)_2(NCS)_2](NCS)_2$ resembles that of $[Cu_2(btim)_2Cl_2]Cl_2.7H_2O$, with the same metallocyclic structural arrangement in which two ligands and two square-pyramidal Cu centres encompass a large empty cavity. Cu—N distances in (I) are very similar to those in $[Cu_2(btim)_2Cl_2]Cl_2.7H_2O$, but the Cu···Cu separation [7.472 (10) Å] is significantly shorter. The Cu centre is displaced by 0.259 (5) Å from the mean N4 basal plane (the four N atoms are within 0.032 Å of the mean plane) and the Cu—N(isothiocyanate) distance is relatively short [2.190 (10) Å]. The benzene rings are essentially planar and eclipsed and separated by 4.24 Å, about 0.3 Å larger than in the chloro derivative. This may be associated in part with the smaller apical displacement of the Cu atoms in (I).

The hydroimidazole rings 2,3,4,5 (Fig. 1) are twisted with respect to the mean N2–N4–N6–N8 plane (plane 1) with angles of 61.7, 113.5, 72.9 and 112.8°, respectively, and because of the ease of rotation of the hydroimidazole groups around the 2-carbon linkage to the benzene ring the square-pyramidal Cu^{II} centre can be easily accommodated. Attempts to synthesize non-metallocyclic Cu derivatives with two metals bound to one ligand have, so

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes, H-atom positions, full details of bond distances and angles, and additional diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54624 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected bond lengths* (Å) *and angles* (°) *for* $[Cu_2(btim)_2(NCS)_2](NCS)_2$ (I) *and* $C_{34}H_{18}N_4S_4$ (II) *with e.s.d.'s in parentheses*

(I)			
Cu—N1	2.190 (10)	S1—C1	1.624 (13)
Cu—N2	1.995 (8)	S2—C20	1.678 (15)
Cu—N4	2.002 (8)	N1—C1	1.128 (15)
Cu—N6	2.003 (9)	N10—C20	1.077 (18)
Cu—N8	1.974 (9)		
N1—Cu—N2	97.8 (3)	N4—Cu—N8	91.6 (3)
N1—Cu—N4	98.7 (3)	N6—Cu—N8	166.8 (4)
N1—Cu—N6	97.2 (4)	Cu—N1—C1	143.9 (9)
N1—Cu—N8	96.0 (4)	Cu—N2—C2	129.8 (7)
N2—Cu—N4	163.4 (4)	Cu—N2—C4	122.6 (7)
N2—Cu—N6	91.3 (3)	S1—C1—N1	176.5 (11)
N2—Cu—N8	86.7 (3)	S2—C20—N10	173.9 (14)
N4—Cu—N6	86.6 (3)		
(II)			
S1—C4	1.751 (5)	C3—C5	1.489 (6)
S1—C11	1.734 (4)	C11—C12	1.385 (6)
S2—C5	1.741 (5)	C11—C16	1.389 (7)
S2—C21	1.746 (5)	C12—C13	1.388 (7)
N1—C4	1.303 (5)	C13—C14	1.392 (9)
N1—C16	1.384 (5)	C14—C15	1.371 (8)
N2—C5	1.290 (6)	C15—C16	1.412 (6)
N2—C26	1.391 (6)	C21—C22	1.388 (7)
C1—C2	1.392 (6)	C21—C26	1.390 (7)
C1—C3*A*	1.381 (6)	C22—C23	1.386 (9)
C2—C3	1.426 (6)	C23—C24	1.372 (11)
C2—C4	1.462 (6)	C24—C25	1.394 (9)
C3—C1*A*	1.381 (6)	C25—C26	1.407 (7)
C4—S1—C11	89.07 (21)	C12—C11—C16	123.5 (4)
C5—S2—C21	88.54 (23)	C11—C12—C13	116.4 (5)
C4—N1—C16	109.6 (4)	C12—C13—C14	121.2 (5)
C5—N2—C26	108.9 (4)	C13—C14—C15	122.1 (5)
C2—C1—C3*A*	124.0 (4)	C14—C15—C16	117.7 (5)
C1—C2—C3	116.8 (4)	N1—C16—C11	116.6 (4)
C1—C2—C4	118.4 (4)	N1—C16—C15	124.4 (4)
C3—C2—C4	124.6 (4)	C11—C16—C15	119.0 (4)
C1*A*—C3—C2	119.2 (4)	S2—C21—C22	128.3 (4)
C1*A*—C3—C5	118.9 (4)	S2—C21—C26	108.5 (3)
C2—C3—C5	121.8 (4)	C22—C21—C26	123.2 (4)
S1—C4—N1	115.9 (3)	C21—C22—C23	115.5 (6)
S1—C4—C2	121.7 (3)	C22—C23—C24	122.4 (6)
N1—C4—C2	122.1 (4)	C23—C24—C25	122.5 (6)
S2—C5—N2	117.4 (3)	C24—C25—C26	115.9 (6)
S2—C5—C3	119.7 (3)	N2—C26—C21	116.7 (4)
N2—C5—C3	123.0 (4)	N2—C26—C25	122.9 (5)
S1—C11—C12	127.6 (4)	C21—C26—C25	120.4 (5)
S1—C11—C16	108.8 (3)		

far, been unsuccessful, and in all cases stable metallocyclic structures like (I) have been obtained with differing axial ligands (Cl, N_3, H_2O) (Mandal, Thompson, Newlands, Gabe & Lee, 1990).

(II) is a closely related ligand to btim with 2-benzothiazole groups bound at the 1,2,4,5-benzene ring positions. This potentially tetradentate donor resists all attempts to form coordination complexes with Cu^{II} salts, under conditions in which btim reacts so readily. This is surprising because the analogous bidentate ligand 1,2-bis(benzothiazol-2-yl)benzene reacts fairly readily with Co^{II}, Cu^{II} and Zn^{II} salts to produce derivatives in which coordination occurs *via* the two N atoms (Rendell & Thompson, 1979). The four benzothiazole groups are twisted relative to the benzene ring and opposite groups are coplanar (Fig. 2). Dihedral angles of 29.4 and 116.2° are found between benzene ring 1 (Fig. 2) and benzothiazole rings 2 and 3 respectively, with a dihedral angle of 116.6° between 2 and 3. Within each benzothiazole the five-membered heterocyclic rings are essentially planar and almost coplanar with the benzene rings. The relative orientation of adjacent pairs of benzothiazoles is such that no two pairs present N donors in suitable chelating positions. The N2···S1 distance [3.271 (3) Å] is quite short, while the N1···S2 distance is much longer [5.585 (4) Å]. The S1···S2 distance [3.703 (2) Å] is also short. These short contacts are quite significant since they are very close to the sum of the van der Waals radii for the respective atoms. Sulfur S1 has a lone pair pointing towards the neighbouring benzothiazole, in between the N and S atoms, and there would be significant resistance to rotation of one benzothiazole group about the C—C (benzene) bond, because of these close contacts.

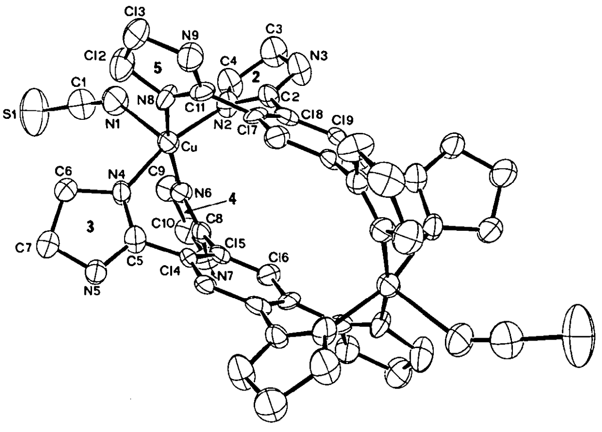

Fig. 1. An *ORTEP*II view (Johnson, 1976) of the $[Cu_2(btim)_2(NCS)_2]$ (I) cation, showing the atomic numbering scheme. Thermal ellipsoids at 50% probability level.

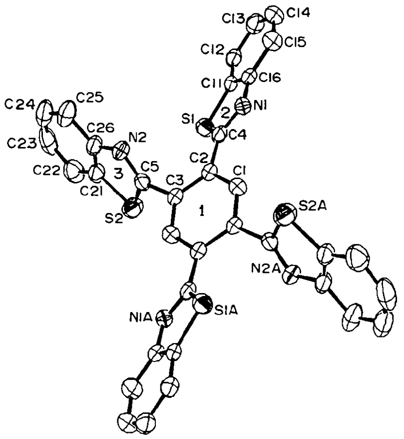

Fig. 2. An *ORTEP*II view (Johnon, 1976) of $C_{34}H_{18}N_4S_4$ (II), showing the atomic numbering scheme. Thermal ellipsoids at 50% probability level.

However, molecular models do suggest that simultaneous rotation of the two rings could bring both N donors into a position for chelate formation (S is unlikely to be a donor). The lack of donor ability of this ligand may, in part, be associated with these steric constraints and the weaker donor capacity of benzothiazoles in general when compared with *e.g.* hydroimidazoles and imidazoles. The molecule does not display any unusual intermolecular contacts and bond lengths and angles are typical of benzothiazole derivatives.

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Structures of Two Acetyl(carbonyl)(cyclopentadienyl)iron Complexes with Phosphine Ligands. III. $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Fe(CO)(COMe)(PPh}_2\text{Me)}]$ (1) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(COMe)(PPhMe}_2)]$ (2)*

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Abstract. (1) Acetyl(carbonyl)(η^5-methylcyclopentadienyl)(methyldiphenylphosphine)iron, $[\text{Fe(C}_2\text{H}_3\text{O)(CO)(C}_6\text{H}_7)(\text{C}_{13}\text{H}_{13}\text{P)}]$, $M_r = 406.25$, triclinic, $P\bar{1}$, $a = 9.435\,(3)$, $b = 8.618\,(2)$, $c = 13.381\,(4)$ Å, $\alpha = 97.52\,(2)$, $\beta = 99.65\,(2)$, $\gamma = 108.67\,(2)^\circ$, $V = 996.2\,(5)$ Å^3, $Z = 2$, $D_m = 1.35$, $D_x = 1.355$ g cm^{-3}, $\mu = 8.68$ cm^{-1}, $F(000) = 424$, $R(F) = 0.065$, $wR = 0.052$ for 1791 reflections with $F_o > 3\sigma(F_o)$. (2) Acetyl(carbonyl)(η^5-cyclopentadienyl)(dimethylphenylphosphine)iron, $[\text{Fe(C}_2\text{H}_3\text{O)(CO)(C}_6\text{H}_5)(\text{C}_8\text{H}_{11}\text{P)}]$, $M_r = 330.15$, triclinic, $P\bar{1}$, $a = 7.509\,(2)$, $b = 12.961\,(6)$, $c = 8.691\,(3)$ Å, $\alpha = 106.83\,(3)$, $\beta = 93.19\,(3)$, $\gamma = 97.93\,(3)^\circ$, $V = 797.8\,(5)$ Å^3, $Z = 2$, $D_m = 1.36$, $D_x = 1.374$ g cm^{-3}, $\mu = 10.66$ cm^{-1}, $F(000) = 344$, $R(F) = 0.034$, $wR = 0.038$ for 2069 reflections with $F_o > 3\sigma(F_o)$. $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $T = 293$ K for (1) and (2). The Fe—P bond distances are 2.185 (2) Å in (1) and 2.180 (1) Å in (2): the shortest Fe—P bond lengths observed thus far for σ-donor ligands in this type of complex. In all probability the absence of steric strain, rather than an electronic effect, is the explanation for these short distances. The torsion angles O(2)—C(2)—Fe—(CO) [C(2) = acetyl carbon] are 33° (*anti*) in (1) and 19° (*anti*) in (2). The additional methyl group in (1) does not cause ring slippage.

Introduction. In two earlier structural papers we reported the geometry of complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(COMe)}L]$ (L = phosphine ligand) for $L = \text{PPh}_2\text{Et}$ (Liu, Rahman, Koh, Eriks, Giering & Prock, 1989) and $L = \text{PPh}_3$ (Liu, Koh, Eriks, Geiring & Prock, 1990). We listed the Fe—P bond lengths for a series of phosphine ligands based on our results and those of others reported in the literature. According to our proposed model of Fe—P σ bonding, the Fe—P bond lengths should be nearly constant, close to 2.20 Å for pure σ-donor ligands in the absence of steric effects, and independent of the σ donicity of the ligand. We also reported that substituent groups on the cyclopentadienyl ring, or on the acetyl group, or on both seem to have very little influence on the Fe—P distance or on the distance from Fe to the five-membered ring. As a continuing effort to understand the requirements of Fe—P bond length, we report below the results of our structural studies of the complexes [(η^5-

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* Part II: Liu, Koh, Eriks, Giering & Prock (1990).

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