

Fig. 1. Schematic drawing of the dimer (projection along  $c$ ). Adjacent pairs of alanyl moieties are mutually perpendicular and are in *cis* configuration, while the alanyl N atoms are in *trans* configuration. The centre of inversion lies between the two Cu atoms. The four carboxyl O atoms and an axial water O coordinate with Cu to form a square pyramid.

complexes (Ueki, Ashida, Sasada & Kakudo, 1968), and references cited therein), but comparable to the value of 1.975 Å in bis( $\beta$ -alanine)copper(II) tetrahydrate (Kamwaya & Teoh, 1984). The angles O(1)—Cu—O(2), O(2)—Cu—O(3), O(3)—Cu—O(4) and O(4)—Cu—O(1) fall within the range 82–96° as reported for Cu compounds by Ueki *et al.* (1968), while O(1)—Cu—O(3) and O(2)—Cu—O(4) are in the range 160–174° as summarized for Ag compounds (Rao &

Viswamitra, 1972, and references cited therein). Angles O(1)—C(1A)—O(3\*) [125.8 (1)°] and O(2)—C(1B)—O(4\*) [125.0 (1)°] are larger than the values of 122.5 and 122.2° for analogous angles previously reported by us (Kamwaya & Teoh, 1984).

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## Structure of Bis( $\mu_3$ -phenylimido)-tris(tricarbonyliron)(2Fe—Fe), [Fe<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>N)<sub>2</sub>(CO)<sub>9</sub>]

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**Abstract.**  $M_r = 601.9$ , monoclinic,  $P2_1/n$ ,  $a = 11.282$  (2),  $b = 13.658$  (1),  $c = 15.379$  (4) Å,  $\beta = 99.81$  (2)°,  $V = 2335.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.712$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.89$  mm<sup>-1</sup>,

$F(000) = 1200$ ,  $T = 291$  K,  $R = 0.029$  for 3495 observed reflections. The three Fe atoms form an approximately isosceles triangle, with Fe—Fe 2.484 (1) and 2.421 (1) Å, Fe...Fe 3.044 (1) Å, Fe—Fe—Fe 76.7 (1)°. All carbonyl groups are terminal. The NPh ligands are triply bridging, with Fe—N 1.926 (2) to 1.969 (2) Å, N...N 2.301 (6) Å.

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**Introduction.** Nitrobenzene reacts with  $\text{Ru}_3(\text{CO})_{12}$  to give  $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-NPh})$  (1) and  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-NPh})_2$  (2) (Sappa & Milone, 1973; Bhaduri, Gopalkrishnan, Sheldrick, Clegg & Stalke, 1983; Clegg, Sheldrick, Stalke, Bhaduri & Gopalkrishnan, 1984). (1) can be hydrogenated, forming  $\text{Ru}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-NPh})$  (3), in which the H atoms bridge two of the Ru—Ru bonds (Bhaduri, Gopalkrishnan, Clegg, Jones, Sheldrick & Stalke, 1984). The hydrido complex (3) can in turn be carbonylated, thus yielding aniline and regenerating  $\text{Ru}_3(\text{CO})_{12}$ . In these studies, probable intermediates in the catalytic hydrogenation of nitrobenzene to aniline with  $\text{Ru}_3(\text{CO})_{12}$  as catalyst have been isolated and structurally characterized.

More drastic conditions are required for the hydrogenation of nitroarenes when  $\text{Fe}_3(\text{CO})_{12}$  is used as the catalyst, and, because the two reactions respond differently to changes in conditions, it has been suggested that they proceed *via* different mechanisms (Alper & Amaratunga, 1980). A variety of binuclear and trinuclear iron complexes with different nitrogen ligands has been isolated from the reactions of nitroalkanes and nitroarenes with iron carbonyls, and some have been structurally characterized (Doedens, 1969; Aime, Gervasio, Milone, Rossetti & Stanghellini, 1978).

We have obtained  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NPh})_2$  (4) from the reaction of  $\text{PhNO}_2$  with  $\text{Fe}_3(\text{CO})_{12}$  in the presence of  $\text{Co}_2(\text{CO})_8$ , and report here its crystal structure. The  $\text{Co}_2(\text{CO})_8$  appears to be necessary for the reaction, but no mixed-metal species were found in the products.

**Experimental.** Crystal mounted in glass capillary,  $0.50 \times 0.38 \times 0.31$  mm. Stoe—Siemens AED diffractometer. Unit-cell parameters refined from  $2\theta$  values of 48 reflections centred at  $\pm\omega$  ( $20 < 2\theta < 25^\circ$ ). 4463 reflections with  $2\theta < 50^\circ$ ,  $h$  0→18,  $k$  0→16,  $l$  -13→13 and 2253 with  $h$  0→7,  $k$  -16→0,  $l$  -13→13. On-line profile analysis (Clegg, 1981). No significant intensity variation for three standard reflections. Semi-empirical absorption corrections based on azimuthal scan data for sets of equivalent reflections, transmission 0.233 to 0.314. 4106 unique reflections ( $R_{\text{int}} = 0.020$ ), 3495 with  $F > 4\sigma(F)$ . Multisolution direct methods. Blocked-cascade refinement on  $F$ .  $w^{-1} = \sigma^2(F) + 0.00005F^2$ . H atoms constrained to lie on ring external bisectors with  $\text{C—H} = 0.96 \text{ \AA}$ ,  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Anisotropic thermal parameters for non-H atoms. Extinction  $x = 1.3(1) \times 10^{-6} [F_c' = F_c / (1 + xF_c^2 / \sin^2\theta)^{1/4}]$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). 317 parameters,  $R = 0.029$ ,  $wR = 0.029$ , slope of normal probability plot 1.40. Max.  $\Delta/\sigma = 0.015$ , mean = 0.003. Largest peak in final difference map  $0.25 \text{ e \AA}^{-3}$ , largest hole  $-0.23 \text{ e \AA}^{-3}$ . Programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Fe(1)	8611 (1)	3252 (1)	774 (1)	37 (1)
Fe(2)	9800 (1)	2172 (1)	2425 (1)	37 (1)
Fe(3)	9368 (1)	1543 (1)	933 (1)	38 (1)
N(1)	8304 (2)	2259 (1)	1596 (1)	37 (1)
C(111)	7113 (2)	2045 (2)	1738 (2)	44 (1)
C(112)	6322 (2)	1508 (2)	1135 (2)	58 (1)
C(113)	5147 (3)	1357 (3)	1258 (3)	78 (1)
C(114)	4757 (3)	1753 (3)	1966 (3)	87 (2)
C(115)	5524 (3)	2294 (3)	2571 (2)	80 (1)
C(116)	6704 (2)	2437 (2)	2459 (2)	59 (1)
N(2)	10162 (2)	2778 (1)	1357 (1)	34 (1)
C(211)	11270 (2)	3181 (2)	1205 (2)	40 (1)
C(212)	11978 (2)	3734 (2)	1851 (2)	49 (1)
C(213)	13039 (3)	4136 (2)	1699 (2)	67 (1)
C(214)	13435 (3)	4004 (3)	917 (3)	77 (1)
C(215)	12733 (3)	3467 (2)	264 (2)	75 (1)
C(216)	11667 (2)	3050 (2)	406 (2)	56 (1)
C(11)	7052 (2)	3383 (2)	222 (2)	50 (1)
O(11)	6094 (2)	3497 (2)	-114 (1)	73 (1)
C(12)	9125 (2)	3890 (2)	-149 (2)	44 (1)
O(12)	9408 (2)	4285 (2)	-723 (1)	63 (1)
C(13)	8574 (2)	4322 (2)	1450 (2)	49 (1)
O(13)	8580 (2)	4967 (2)	1906 (2)	80 (1)
C(21)	9767 (3)	3143 (2)	3220 (2)	56 (1)
O(21)	9758 (3)	3725 (2)	3741 (2)	99 (1)
C(22)	11348 (2)	1821 (2)	2818 (2)	45 (1)
O(22)	12302 (2)	1585 (2)	3059 (1)	66 (1)
C(23)	9284 (2)	1204 (2)	3073 (2)	48 (1)
O(23)	8997 (2)	579 (2)	3469 (1)	69 (1)
C(31)	8793 (3)	1611 (2)	-223 (2)	55 (1)
O(31)	8464 (3)	1578 (2)	-970 (1)	93 (1)
C(32)	10807 (3)	995 (2)	863 (2)	56 (1)
O(32)	11719 (2)	663 (2)	857 (2)	89 (1)
C(33)	8728 (3)	371 (2)	1125 (2)	59 (1)
O(33)	8372 (2)	-380 (2)	1276 (2)	98 (1)

Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

Fe(1)—Fe(3)	2.484 (1)	Fe(2)—Fe(3)	2.421 (1)
Fe(1)—N(1)	1.926 (2)	Fe(1)—N(2)	1.937 (2)
Fe(2)—N(1)	1.938 (2)	Fe(2)—N(2)	1.943 (2)
Fe(3)—N(1)	1.964 (2)	Fe(3)—N(2)	1.969 (2)
Fe(1)—C(11)	1.827 (3)	Fe(1)—C(12)	1.842 (3)
Fe(1)—C(13)	1.797 (3)	Fe(2)—C(21)	1.810 (3)
Fe(2)—C(22)	1.812 (2)	Fe(2)—C(23)	1.811 (3)
Fe(3)—C(31)	1.788 (3)	Fe(3)—C(32)	1.807 (3)
Fe(3)—C(33)	1.801 (3)	N(1)—C(111)	1.427 (3)
N(2)—C(211)	1.421 (3)		
Fe(3)—Fe(1)—N(1)	51.0 (1)	Fe(3)—Fe(1)—N(2)	51.1 (1)
N(1)—Fe(1)—N(2)	73.1 (1)	Fe(3)—Fe(1)—C(11)	115.2 (1)
N(1)—Fe(1)—C(11)	96.2 (1)	N(2)—Fe(1)—C(11)	166.0 (1)
Fe(3)—Fe(1)—C(12)	111.9 (1)	N(1)—Fe(1)—C(12)	162.7 (1)
N(2)—Fe(1)—C(12)	97.9 (1)	C(11)—Fe(1)—C(12)	90.0 (1)
Fe(3)—Fe(1)—C(13)	138.5 (1)	N(1)—Fe(1)—C(13)	99.7 (1)
N(2)—Fe(1)—C(13)	96.4 (1)	C(11)—Fe(1)—C(13)	94.3 (1)
C(12)—Fe(1)—C(13)	95.9 (1)	Fe(3)—Fe(2)—N(1)	52.1 (1)
Fe(3)—Fe(2)—N(2)	52.3 (1)	N(1)—Fe(2)—N(2)	72.7 (1)
Fe(3)—Fe(2)—C(21)	151.3 (1)	N(1)—Fe(2)—C(21)	106.5 (1)
N(2)—Fe(2)—C(21)	106.8 (1)	Fe(3)—Fe(2)—C(22)	104.5 (1)
N(1)—Fe(2)—C(22)	156.6 (1)	N(2)—Fe(2)—C(22)	93.8 (1)
C(21)—Fe(2)—C(22)	95.6 (1)	Fe(3)—Fe(2)—C(23)	103.4 (1)
N(1)—Fe(2)—C(23)	94.6 (1)	N(2)—Fe(2)—C(23)	155.5 (1)
C(21)—Fe(2)—C(23)	96.7 (1)	C(22)—Fe(2)—C(23)	90.3 (1)
Fe(1)—Fe(3)—Fe(2)	76.7 (1)	Fe(1)—Fe(3)—N(1)	49.6 (1)
Fe(2)—Fe(3)—N(1)	51.2 (1)	Fe(1)—Fe(3)—N(2)	49.9 (1)
Fe(2)—Fe(3)—N(2)	51.3 (1)	N(1)—Fe(3)—N(2)	71.6 (1)
Fe(1)—Fe(3)—C(31)	78.0 (1)	Fe(2)—Fe(3)—C(31)	154.7 (1)
N(1)—Fe(3)—C(31)	109.9 (1)	N(2)—Fe(3)—C(31)	110.6 (1)
Fe(1)—Fe(3)—C(32)	132.9 (1)	Fe(2)—Fe(3)—C(32)	99.5 (1)
N(1)—Fe(3)—C(32)	150.7 (1)	N(2)—Fe(3)—C(32)	90.7 (1)
C(31)—Fe(3)—C(32)	98.1 (1)	Fe(1)—Fe(3)—C(33)	135.3 (1)
Fe(2)—Fe(3)—C(33)	100.5 (1)	N(1)—Fe(3)—C(33)	93.4 (1)
N(2)—Fe(3)—C(33)	151.6 (1)	C(31)—Fe(3)—C(33)	97.0 (1)
C(32)—Fe(3)—C(33)	91.8 (1)	Fe(1)—N(1)—Fe(2)	104.0 (1)
Fe(1)—N(1)—Fe(3)	79.4 (1)	Fe(2)—N(1)—Fe(3)	76.7 (1)
Fe(1)—N(1)—C(111)	121.6 (1)	Fe(2)—N(1)—C(111)	128.6 (2)
Fe(3)—N(1)—C(111)	130.7 (2)	Fe(1)—N(2)—Fe(2)	103.3 (1)
Fe(1)—N(2)—Fe(3)	79.0 (1)	Fe(2)—N(2)—Fe(3)	76.4 (1)
Fe(1)—N(2)—C(211)	123.0 (1)	Fe(2)—N(2)—C(211)	128.4 (1)
Fe(3)—N(2)—C(211)	129.8 (2)		

**Discussion.** Atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2.\* Fig. 1 shows the molecular structure.

Direct comparison can be made with the homologous Ru compound (2), and with  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NMe})_2$  (5) (Doedens, 1969). All three compounds possess the same molecular framework, with two NR nitrene ligands triply-bridging an approximately isosceles  $M_3$  triangle, to which all CO ligands are attached terminally. A very similar arrangement is observed for  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NNCPh}_2)_2$  (Baikie & Mills, 1967), but insufficient details are available for a comparison of all the relevant geometrical features.

As is the case for both (2) and (5), the two  $M-M$  bond lengths in (4) are significantly different. Comparison of all three structures suggests that the major cause of this asymmetry is the arrangement of the nine CO groups, rather than the orientation of the Ph rings in (2) and (4). In each case, the longer  $M-M$  bond is the one with a staggered rather than eclipsed arrangement of CO ligands. The structures of (5) and (4) are remarkably similar in detail, (4) benefitting from higher precision. The differences between these and (2) can be attributed to the change in metal from Fe to Ru. Despite the minor nature of these differences, (2) and (4) are not isomorphous.

Because of the short  $\text{N}\cdots\text{N}$  distance of 2.405 (11) Å in (2), some direct  $\text{N}-\text{N}$  interaction was postulated, and an alternative description of the structural core is as an  $\text{Ru}_3\text{N}_2$  trigonal-bipyramidal cluster, with two Ru atoms occupying axial sites. In the iron complexes, the shorter Fe-N bonds necessitate a correspondingly shorter  $\text{N}\cdots\text{N}$ , 2.301 (6) Å in the case of (4).

The geometry of the phenyl rings is normal, and the CO groups are essentially linear, with C-O 1.124 (3)–1.145 (3) Å and Fe-C-O 174.2 (2)–178.6 (2)°.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles for the ligands have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39698 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

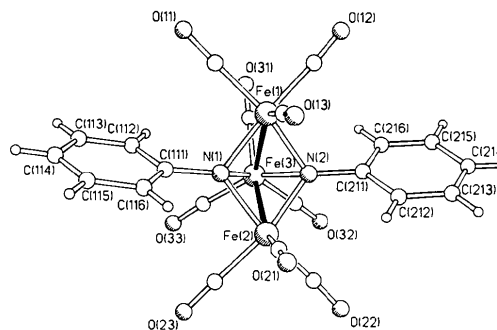


Fig. 1. Molecular structure of (4), showing the atom-labelling scheme. Carbonyl C atoms take the same numbers as the corresponding O atoms; H atoms take the same numbers as the corresponding phenyl C atoms.

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## Di-2-pyridyl Ketone 2-Pyridylhydrazone, $\text{C}_{16}\text{H}_{13}\text{N}_5$

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**Abstract.**  $M_r = 275.34$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.9213$  (13),  $b = 10.603$  (3),  $c = 16.499$  (2) Å,  $V = 1386$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.304$  (10),  $D_x = 1.320$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.91$  cm<sup>-1</sup>,  $F(000) =$

2304.2,  $T = 295$  K,  $R_w = 0.039$  for 1751 independent reflections. One pyridyl ring of the dipyridyl ketone group is coplanar with the 2-pyridylhydrazone moiety. The planarity results from the hydrogen bond formed

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