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Tricarbonyl[η^4-2-phenyl-4-(3-phenylallylidene)-4*H*-oxazol-5-one]iron(0)

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The title compound, [Fe($C_{18}H_{13}NO_2$)(CO)$_3$], is produced by the reaction of $Fe_2(CO)_9$ with an azlactone obtained from hippuric acid and cinnamaldehyde. Although, in principle, various coordination sites are possible in the ligand, the 1,3-butadiene subunit exclusively binds to the transition metal in an η^4-fashion. The crystal structure is stabilized by intermolecular interactions between the O atoms of the lactone and terminal carbon monoxide ligands and various CH groups.

Key indicators

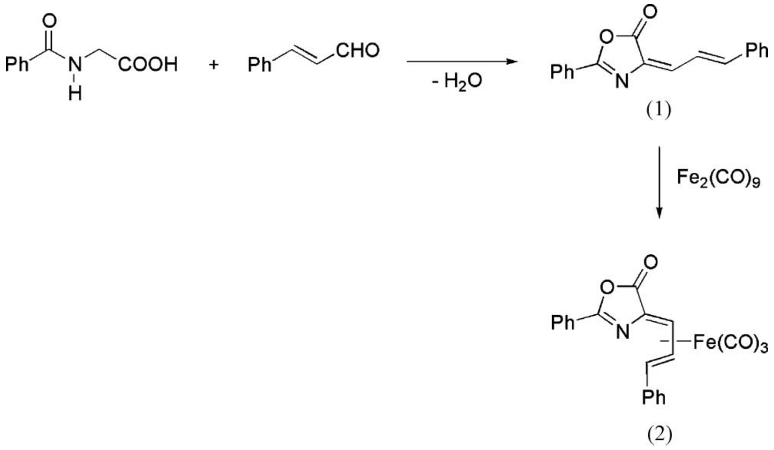
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.097
Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

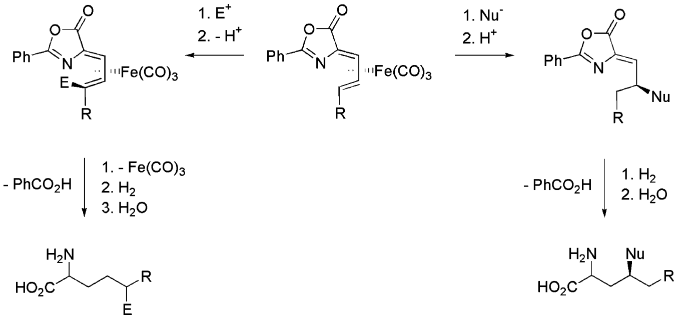
Comment

Butadiene–iron–tricarbonyl complexes exhibit a remarkable stability and are therefore suitable for use in a number of reactions at the coordinated diene function. The irontricarbonyl group thus activates the butadiene towards nucleophiles and electrophiles, and might also be used as a stereodirecting group, because the coordination of the irontricarbonyl fragment to a prochiral butadiene derivative protects the *Re* or *Si* side of the ligand from being attacked by the nucleophile or electrophile (Gree, 1989; Cox & Ley, 1998; Semmelhack, 2002).

The reaction of hippuric acid with cinnamaldehyde produces the azlactone (1) in good yields. Compound (1) shows a number of potential coordination sites for transition metals since it exhibits a 2-aza-1,3-butadiene, a 1-oxa-1,3-butadiene and a 1,3-butadiene subunit. The reaction of (1) with $Fe_2(CO)_9$ leads to the formation of (2), in which the Fe atom is coordinated by the 1,3-butadiene subunit of the ligand.



Since azlactones may be converted into α-amino acids by hydrogenation and subsequent hydrolysis, stereoselective transformations of irontricarbonyl complexes such as (2) might be used for the synthesis of non-natural α-amino acids (see scheme below).



The molecular structure of the title compound, (2), is presented in Fig. 1; the most important bond lengths and angles are summarized in Table 1. The Fe atom shows a distorted square-pyramidal coordination environment, with two of the carbon monoxide ligands and the centroids of the C9—C10 and C11—C12 bonds forming the base, and the third carbon monoxide ligand representing the apex of the pyramid. The distinction between a square-pyramidal and a trigonal–bipyramidal coordination mode of a transition metal may be made according to Addison *et al.* (1984).

According to other structurally characterized (diene)-Fe(CO)$_3$ derivatives, the butadiene ligand in (2) adopts an *s-cis* configuration. An *s-trans* configuration of dienes coordinated to transition metals is much less common and has been reported for Cp$_2M$ (M = Zr and Hf) and CpMo(NO) moieties (Erker *et al.*, 1985; Yasuda *et al.*, 1985; Hunter *et al.*, 1985, 1986). Nevertheless, the corresponding (*s-trans*-butadiene)-Fe(CO)$_3$ has recently been observed by time-resolved IR spectroscopy and has been calculated by high-level DFT methods (Bachler *et al.*, 2003).

The bond lengths in the butadiene group of (2) are influenced by the coordination of the irontricarbonyl group, so that the former double bonds (C9—C10 and C11—C12) are elongated whereas the central C—C single bond is quite short. The bonds in the azlactone system are almost unaffected by the coordination of the Fe atom, the C8—N1 and C9—N1 bonds showing values typical for C—N bonds adjacent to a carbonyl group or an olefinic substituent, respectively. Correspondingly, the N1—C7 bond clearly is best described as a C═N double bond.

The substituents at C9 and C12 are not coplanar with the butadiene ligand systems for steric as well as for electronic reasons, as has frequently been observed for butadiene and 1-azabutadiene irontricarbonyl complexes, and in accordance with theoretical investigations on several derivatives (Marr & Rockett, 1982; Adams *et al.*, 1988; Imhof *et al.*, 1999; Gonzalez-Blanco & Branchadell 1997; Gonzalez-Blanco *et al.* 1999; Mills & Robinson, 1963). The butadiene system C9═C10—C11═C12 shows a *Z*,*E* configuration together with an *s-cis* configuration with respect to the C10—C11 bond. In contrast, the free ligand most probably adopts an *E*,*E* configuration of the double bonds together with an *s-trans* configuration of the central C—C bond.

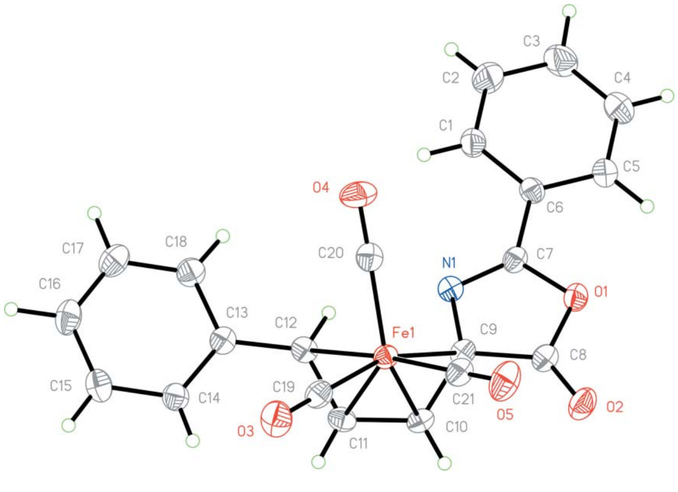


Figure 1
Molecular structure of (2). Displacement ellipsoids are drawn at the 40% probability level.

The crystal structure of (2) is depicted in Fig. 2 and is determined by rather weak C—H—O interactions (Desiraju & Steiner, 1999). A dimeric substructure is built up by the interaction of an aromatic C—H bond in the phenyl substituent of the lactone group with the carbonyl O atom of the lactone ring of a neighbouring molecule and *vice versa*. This also leads to a very weak interaction between another aromatic C—H bond and the O atom in the lactone ring. These dimeric subunits are connected into infinite double chains by the interaction of an aromatic C—H bond of the phenyl group of the allylidene chain with a terminal carbon monoxide ligand (Fig. 2).

Experimental

2-Phenyl-4-(3-phenylallylidene)-4*H*-oxazol-5-one, (1), was prepared by the reaction of hippuric acid (4.60 g, 25.6 mmol) with cinnamaldehyde (3.38 g) in anhydrous ethanol (50 ml). Upon heating the yellow suspension to 343 K, it turned red as all the material dissolved. Cooling to room temperature led to the isolation of (1) (yield 5.7 g, 81.2%) as a yellow microcrystalline precipitate. ^{1}H NMR (CDCl$_3$, 298 K, p.p.m.): δ 7.04–7.24 (*m*, 2H), 7.36–7.74 (*m*, 9H), 8.03–8.14 (*m*, 2H); ^{13}C MNR (CDCl$_3$, 298 K, p.p.m.): δ 123.4, 125.7, 127.8, 128.0, 128.1, 128.9, 130.0, 132.9, 133.1, 134.0, 135.9, 143.9, 162.3, 166.7. In addition, the ^{13}C NMR spectrum of (1) shows the presence of a minor component, most probably an isomer of (1) with a *Z* configuration of the C9═C10 double bond. Treatment of Fe$_2$(CO)$_9$ (500 mg, 1.38 mmol) with an equimolar amount of (1) (380 mg) in anhydrous *n*-heptane (20 ml) led to the formation of a yellow suspension that turned red as the mixture was warmed to 323 K and all the material dissolved. After 45 min, all volatile material had been evaporated *in vacuo* and the resulting oily residue was chromatographed using silica gel. An orange band containing (2) was eluted using a mixture of light petroleum (b.p. 313–333 K) and CH$_2$Cl$_2$ (2:1) as eluant (yield 170 mg, 29.6%). Recrystallization of (2) was performed from a mixture of light petroleum (b.p. 313–333 K) and CH$_2$Cl$_2$ (3:1) at 253 K, leading to the precipitation of (2) as orange crystals. ^{1}H NMR (CDCl$_3$, 298 K, p.p.m.): 5.25 (*d*, 1H, $^3J_{\rm HH}$ = 10.1 Hz), 5.83 (*d*, 1H, $^3J_{\rm HH}$ = 5.1 Hz), 6.35 (*dd*, 1H, $^3J_{\rm HH}$ = 5.1 Hz, $^3J_{\rm HH}$ = 10.1 Hz), 7.23–7.53 (*m*, 8H), 7.93 (*m*, 2H); ^{13}C NMR ($CDCl_3$, 298 K, p.p.m.): 68.1, 77.3, 78.4, 88.5, 126.4, 126.9, 127.1, 127.8, 128.9, 129.0, 132.2, 138.3, 159.8, 176.4, no resonances representing the terminal carbon monoxide ligands were detectable; MS (EI) [m/z, %]: 415 (M^+, 2), 387 ($M^+ - CO$, 17), 359 ($M^+ - 2\,CO$, 20), 331 ($M^+ - 3\,CO$, 100), 275 [$M^+ - Fe(CO)_3$, 71].

Crystal data

$[Fe(C_{18}H_{13}NO_2)(CO)_3]$
$M_r = 415.17$
Triclinic, $P\overline{1}$
$a = 8.8352\ (4)$ Å
$b = 10.0584\ (7)$ Å
$c = 11.4944\ (8)$ Å
$\alpha = 71.20\ (3)^\circ$
$\beta = 88.61\ (4)^\circ$
$\gamma = 69.86\ (4)^\circ$
$V = 903.5\ (3)$ Å^3
$Z = 2$
$D_x = 1.526$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3311 reflections
$\theta = 1.9–27.5^\circ$
$\mu = 0.87$ mm^{-1}
$T = 173\ (2)$ K
Block, orange
0.2 × 0.2 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: none
6679 measured reflections
4041 independent reflections
3311 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\rm max} = 27.5^\circ$
$h = -10 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.097$
$S = 1.04$
4041 reflections
305 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.1046P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—C20	1.809 (2)	N1—C9	1.432 (2)
Fe1—C10	2.034 (2)	C8—O2	1.199 (2)
Fe1—C11	2.088 (2)	C8—O1	1.385 (3)
Fe1—C9	2.125 (2)	C8—C9	1.482 (3)
Fe1—C12	2.211 (2)	C9—C10	1.433 (3)
C6—C7	1.463 (3)	C10—C11	1.398 (3)
C7—N1	1.275 (3)	C11—C12	1.413 (3)
C7—O1	1.394 (2)		
C10—Fe1—C11	39.62 (8)	O1—C8—C9	105.98 (16)
C10—Fe1—C9	40.23 (8)	C8—O1—C7	105.23 (15)
C11—Fe1—C9	71.56 (9)	N1—C9—C10	127.69 (18)
C10—Fe1—C12	69.54 (8)	N1—C9—C8	106.43 (17)
C11—Fe1—C12	38.25 (8)	C10—C9—C8	117.39 (18)
C9—Fe1—C12	81.29 (8)	C11—C10—C9	120.95 (19)
N1—C7—O1	116.43 (18)	C10—C11—C12	119.24 (19)
C7—N1—C9	105.78 (16)	C11—C12—C13	124.06 (19)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$\cdots$O2$^{\rm i}$	0.92 (3)	2.70 (3)	3.520 (3)	150 (2)
C17—H17$\cdots$O3$^{\rm ii}$	0.96 (3)	2.67 (3)	3.442 (3)	138 (2)

Symmetry codes: (i) $-x, -y+1, -z-1$; (ii) $x-1, y, z$.

All H atoms were detected in a difference Fourier map and were refined without any constraints.

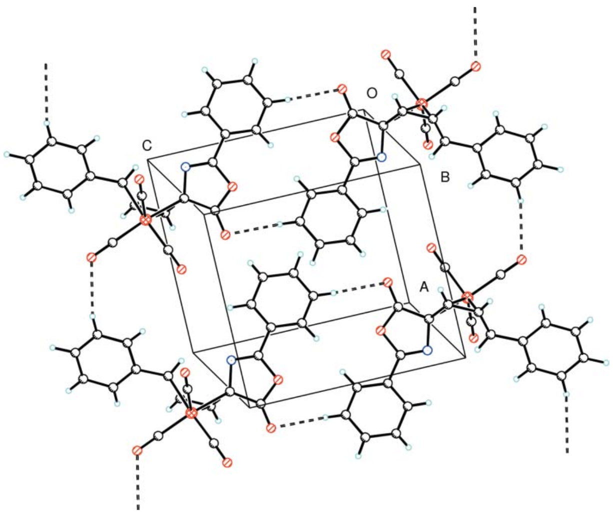


Figure 2
Packing diagram of (2); dashed lines indicate hydrogen bonds.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *XP*.

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