metal-organic papers

Undecacarbonyl(pyridine-κN)-tetrahedro-tetrairidium(4Ir—Ir)

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.018 Å
R factor = 0.037
wR factor = 0.090
Data-to-parameter ratio = 13.4

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

The title compound, $[Ir_4(C_5H_5N)(CO)_{11}]$, shows a tetrahedral Ir_4 core in which each Ir atom is linked to three other Ir atoms and three terminal carbonyl groups, except for one Ir atom, which carries two carbonyl ligands and one N-coordinated pyridine molecule. An intricate set of C—H···π hydrogen bonds stabilizes the crystal packing, where the π-systems are those of the C≡O bonds of the carbonyl ligands.

Comment

Among the examples of metal carbonyl clusters which disproportionate on reaction with pyridine, $Co_2(CO)_8$ (Fachinetti *et al.*, 1986), $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ (Fachinetti *et al.*, 1994) are notable. By contrast, the cluster $Ir_4(CO)_{12}$ (Churchill & Hutchinson, 1978), with no bridging carbonyl ligands, is not susceptible to disproportionation as its structure is distinct from that of $Rh_4(CO)_{12}$, which has nine terminal carbonyls and three edge-bridging carbonyl ligands with an average Rh—Rh bond length of 2.73 Å (Wei, 1969). In the Rh cluster the bridging carbonyls allow flexibility that is not observed in the Ir analogue (Dickson, 1983). It is this structural feature that might explain the robustness of the Ir cluster, with the attendant stronger Ir—Ir bonds, to substitution reactions with pyridine. Accordingly, we have used $Ir_4(CO)_{12}$ as a precursor in water gas-shift reactions in which the metal framework is anticipated to be non-susceptible to rearrangement under these conditions (Pardey *et al.*, 2002). We report here the crystal structure of (I), which resulted from reaction of the $Ir_4(CO)_{12}$ and pyridine.

(I)
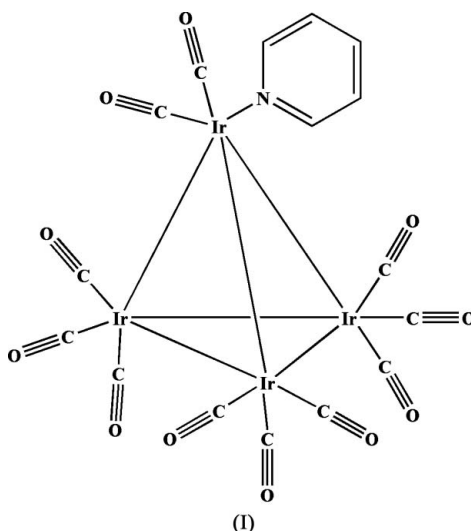
The cluster (I) (Fig. 1 and Table 1) maintains its tetrahedral Ir_4 core. Each octahedral Ir centre is attached to three other Ir
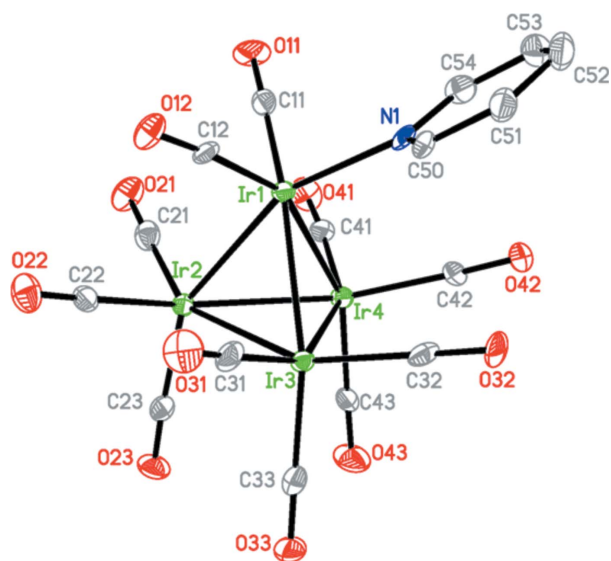
Figure 1
Molecular structure of (I). Anisotropic displacement parameters are shown at the 35% probability level. H atoms have been omitted.
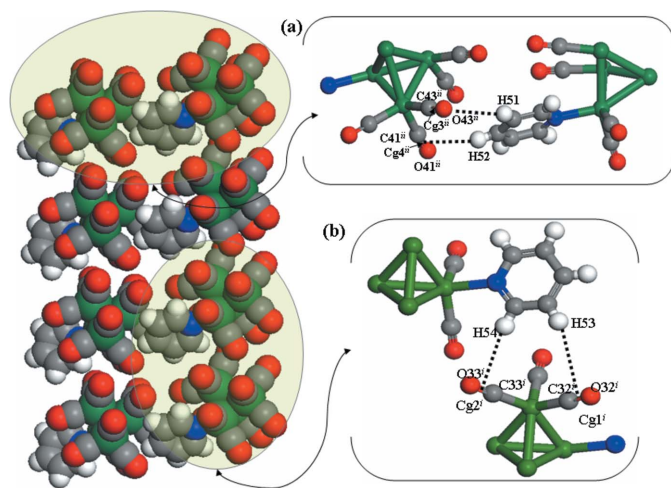

Figure 2
View of the parallel columns extending along the *a* axis observed in the crystal structure of (I). The assembly is sustained by C—H···π interactions (dashed lines, insets) in which the acceptors are the π-electron clouds of the carbonyl groups. *Cg* symbols correspond to the centroids of the carbonyl ligands. Inset (*a*) shows the interactions responsible for the columnar connection in the *bc* plane. Inset (*b*) indicates the interactions along the columns. Geometric parameters: H53···$Cg1^{i}$ = 3.47 Å, C53—H53···$Cg1^{i}$ = 154°; H54···$Cg2^{i}$ = 3.00 Å, C54—H54···$Cg2^{i}$ = 164°; H51···$Cg3^{ii}$ = 3.28 Å, C51—H51···$Cg3^{ii}$ = 132°; H52···$Cg4^{ii}$ = 2.74 Å, C52—H52···$Cg4^{ii}$ = 148°. [Symmetry codes: (i) $1 + x, y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

atoms and three carbonyl groups, except for atom Ir1, which is bound to only two carbonyl ligands with the third site occupied by the pyridine N atom. In order to avoid close intramolecular contacts, the plane of the pyridine ligand is forced to adopt a parallel position with respect to the C32/O32 and C42/O42 carbonyl groups. This is reflected in the angle of 166.7 (2)° formed between the Ir1—N1 bond and the vector normal to the mean plane defined by atoms Ir1, Ir3 and Ir4. The Ir—Ir distances lie in the narrow range 2.6529 (6)–

2.7024 (5) Å. The lower limit corresponds to the Ir1—Ir2 bond located *transoid* to the Ir—N bond [N1—Ir1—Ir2 = 157.78 (19)°].

The crystal packing is controlled by an intricate pattern of C—H···π hydrogen bonds where the acceptors correspond to the π-electron density located in C≡O bonds of the carbonyl groups. A columnar array, Fig. 2, aligned along the *a* axis is stabilized by such intermolecular interactions. Similar C—H···π hydrogen bonds link these columns in the *bc* plane *via* a head-to-head configuration (Fig. 2). Geometric parameters defining these interactions are included in the caption to Fig. 2.

Experimental

$Ir_4(CO)_{12}$ (0.5 g) was refluxed overnight with an excess of pyridine under nitrogen. After 2 h, the colour of the solution changed from yellow to dark brown. Some of this solution (2 ml) was transferred to an NMR tube, avoiding air contact. The tube was sealed and *n*-pentane (0.5 ml) added. Red crystals of the title compound were formed after 2 d. Complex (I) was previously synthesized by Ros *et al.* (2005) using a different starting material.

Crystal data

$[Ir_4(C_5H_5N)(CO)_{11}]$	$D_x = 3.540$ Mg m^{-3}
$M_r = 1156.01$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6184
$a = 8.5042$ (1) Å	reflections
$b = 13.1544$ (2) Å	$\theta = 2.1$–27.8°
$c = 19.8188$ (4) Å	$\mu = 24.52$ mm^{-1}
$\beta = 101.9766$ (7)°	$T = 150$ (2) K
$V = 2168.82$ (6) Å^3	Irregular block, red
$Z = 4$	$0.30 \times 0.15 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer	3422 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.092$
Absorption correction: multi-scan	$\theta_{max} = 25.1°$
(*SHELXTL*; Sheldrick, 2001)	$h = -10 \rightarrow 10$
$T_{min} = 0.271$, $T_{max} = 0.385$	$k = -15 \rightarrow 15$
18728 measured reflections	$l = -23 \rightarrow 23$
3866 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 5.447P]$
$wR(F^2) = 0.090$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
3866 reflections	$\Delta\rho_{max} = 2.27$ e Å^{-3}
289 parameters	$\Delta\rho_{min} = -2.42$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Ir1—Ir2	2.6529 (6)	Ir2—Ir3	2.6836 (6)
Ir1—Ir3	2.6842 (5)	Ir2—Ir4	2.6883 (5)
Ir1—Ir4	2.6906 (5)	Ir3—Ir4	2.7024 (5)
Ir1—N1	2.193 (10)		

All H atoms were included in calculated positions in the riding-model approximation, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The 26 highest residual electron density peaks (2.27–1.06 e Å^{-3}) are located close to Ir atoms in the range 0.96–1.77 Å. The deepest hole is also located near to an Ir atom (0.77 Å from Ir4).

Data collection: *DENZO–SCALEPACK* (Otwinowski & Minor, 1997); cell refinement: *DENZO–SCALEPACK*; data reduction: *DENZO–SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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