

Decacarbonylbis(methylcyclopentadienyl)-tetrahydro-diiridiumdimolybdenum and decacarbonylbis(tetramethylcyclopentadienyl)-tetrahydro-diiridiumdimolybdenum dichloromethane hemisolvate

Nigel T. Lucas and Mark G. Humphrey*

Department of Chemistry, Australian National University, Canberra ACT 0200, Australia

Correspondence e-mail: mark.humphrey@anu.edu.au

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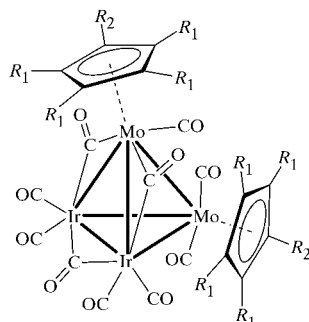
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The two title compounds, $[\text{Mo}_2\text{Ir}_2(\text{C}_6\text{H}_7)_2(\text{CO})_{10}]$ and $[\text{Mo}_2\text{Ir}_2(\text{C}_9\text{H}_{13})_2(\text{CO})_{10}] \cdot 0.5\text{CH}_2\text{Cl}_2$, respectively, or collectively $[\text{Mo}_2\text{Ir}_2(\mu\text{-CO})_3(\text{CO})_7(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2]$ ($n = 1$ or 4), have a pseudo-tetrahedral Mo_2Ir_2 core geometry, an $\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n$ group ligating each Mo atom, bridging carbonyls spanning the edges of an MoIr_2 face and seven terminally bound carbonyl groups.

Comment

The title compounds, tri- μ -carbonyl-1:3 $\kappa^2\text{C}$;1:4 $\kappa^2\text{C}$;3:4 $\kappa^2\text{C}$ -heptacarbonyl-1 κC ,2 $\kappa^2\text{C}$,3 $\kappa^2\text{C}$,4 $\kappa^2\text{C}$ -bis[1,2(η^5)-methylcyclopentadienyl]-tetrahydro-diiridiumdimolybdenum, (I), and tri- μ -carbonyl-1:3 $\kappa^2\text{C}$;1:4 $\kappa^2\text{C}$;3:4 $\kappa^2\text{C}$ -heptacarbonyl-1 κC ,2 $\kappa^2\text{C}$,



(I) $R_1 = \text{H}; R_2 = \text{Me}$

(II) $R_1 = \text{Me}; R_2 = \text{H}, 0.5\text{CH}_2\text{Cl}_2$

3 $\kappa^2\text{C}$,4 $\kappa^2\text{C}$ -bis[1,2(η^5)-tetramethylcyclopentadienyl]-tetrahydro-diiridiumdimolybdenum dichloromethane hemisolvate, (II), have been prepared as part of a general study of tetrahedral mixed group-6–Ir cluster complexes (Lee *et al.*, 1993; Waterman *et al.*, 1996, 1998, 1999; Waterman & Humphrey, 1999; Lucas *et al.*, 2001). Alkylcyclopentadienyl ligands

provide flexibility in tuning the electronic and/or steric properties of a complex, which should modify the physical properties and derivative chemistry. The chemistry of the cyclopentadienyl analogue of (I) and (II) has been examined in depth. The title compounds have been prepared to broaden this study and their structures are presented here.

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. Both complexes possess pseudo-tetrahedral core geometry and a general ligand disposition of the cyclopentadienyl analogue $[\text{Mo}_2\text{Ir}_2(\mu\text{-CO})_3(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)_2]$, (III) (Lucas *et al.*, 1997), with the sole exception that, in (II),

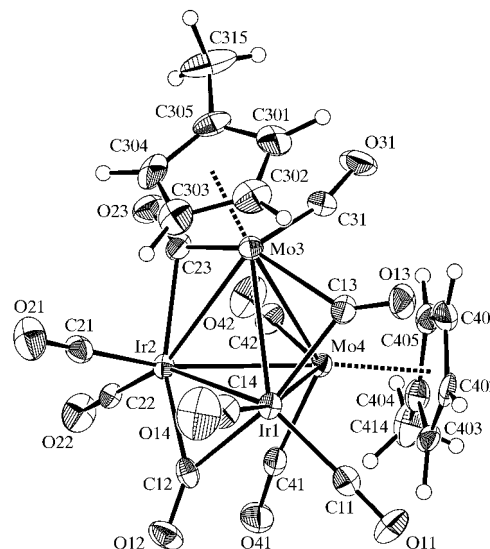


Figure 1

A view of the molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms are represented as spheres of arbitrary radii.

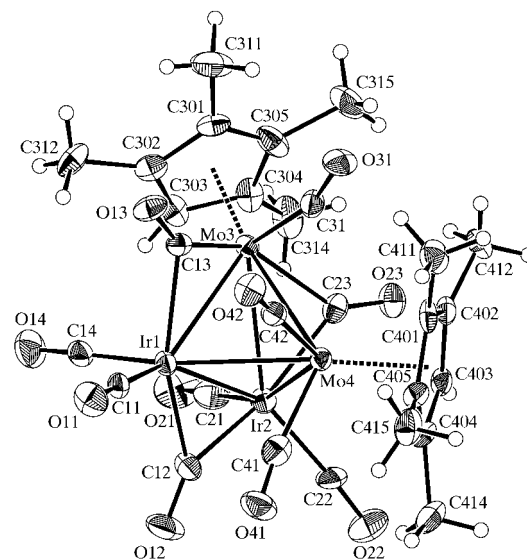


Figure 2

A view of the molecular structure of (II) showing 30% probability displacement ellipsoids. H atoms are represented as spheres of arbitrary radii. The disordered solvent molecule is not shown.

the ligands at Mo4 are rotated *ca* 60° about the metal. The tetramethylcyclopentadienyl group in (II) is thus *trans* to the Ir1—Mo4 bond, rather than *trans* to the Ir2—Mo4 bond, as in (I) and (III).

The core Ir—Ir, Mo—Mo and Ir—Mo bond distances for (I), (II) and (III) show a slight lengthening on increasing the methyl substitution of the cyclopentadienyl ring. In all three structures, the longest Ir—Mo bond is always *trans* to the η^5 -C₅H_{5-n}Me_n group on Mo4, and the shortest Ir—Mo bond is the other non-bridged Ir—Mo4 vector. As the number of methyl groups increases, the carbonyls bridging the Ir1/Ir2—Mo3 bonds become unsymmetrically disposed, moving closer to the Mo atoms. This suggests that electronic factors (the need to redistribute electron density from the increasingly electron-rich Mo atoms) dominate over steric considerations (the need to alleviate the increasing steric pressure from the bulky cyclopentadienyl ligands). The same electronic factors probably explain the presence of semi-bridging interactions for the three Mo-bound carbonyl groups (C31/O31, C41/O41 and C42/O42), which again probably help redistribution of electron density to the other metal atoms.

Experimental

The syntheses of (I) and (II) were carried out according to the literature procedure of Lucas *et al.* (2002). Crystals were obtained by slow diffusion of methanol for (I) or ethanol for (II) into dichloro-methane solutions of the complexes at 276 K.

Compound (I)

Crystal data

[Mo ₂ Ir ₂ (C ₆ H ₇) ₂ (CO) ₁₀]	$D_x = 2.719 \text{ Mg m}^{-3}$
$M_r = 1014.67$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 9.890 (1) \text{ \AA}$	$\theta = 15.9\text{--}18.9^\circ$
$b = 16.563 (1) \text{ \AA}$	$\mu = 11.78 \text{ mm}^{-1}$
$c = 15.135 (2) \text{ \AA}$	$T = 296.2 \text{ K}$
$\beta = 91.67 (1)^\circ$	Prism, red-brown
$V = 2478.2 (4) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.2 \text{ mm}$
$Z = 4$	

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

Ir1—Ir2	2.6896 (6)	Ir2—C12	2.12 (1)
Ir1—Mo3	2.871 (1)	Ir2—C21	1.88 (1)
Ir1—Mo4	2.832 (1)	Ir2—C22	1.89 (1)
Ir2—Mo3	2.8456 (9)	Ir2—C23	2.18 (1)
Ir2—Mo4	2.8744 (9)	Mo3—C13	2.16 (1)
Mo3—Mo4	3.100 (1)	Mo3—C23	2.11 (1)
Ir1—C11	1.90 (1)	Mo3—C31	1.95 (1)
Ir1—C12	2.07 (1)	Mo4—C41	1.99 (1)
Ir1—C13	2.16 (1)	Mo4—C42	2.00 (1)
Ir1—C14	1.90 (1)		
Ir2—Ir1—Mo3	61.46 (2)	Ir2—Mo3—Mo4	57.63 (2)
Ir2—Ir1—Mo4	62.68 (2)	Ir1—Mo4—Ir2	56.24 (2)
Mo3—Ir1—Mo4	65.85 (3)	Ir1—Mo4—Mo3	57.67 (3)
Ir1—Ir2—Mo3	62.40 (2)	Ir2—Mo4—Mo3	56.74 (2)
Ir1—Ir2—Mo4	61.09 (2)	Mo3—C31—O31	166 (1)
Mo3—Ir2—Mo4	65.63 (3)	Mo4—C41—O41	172 (1)
Ir1—Mo3—Ir2	56.13 (2)	Mo4—C42—O42	171 (1)
Ir1—Mo3—Mo4	56.48 (2)		

Table 2

Short-contact geometry (\AA) for (I).

Ir2...C41	2.95 (1)	Mo4...C31	2.93 (1)
Ir2...C42	3.12 (1)	Mo4...C13	3.06 (1)

Data collection

Rigaku AFC-6S diffractometer	$R_{\text{int}} = 0.025$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 11$
$T_{\text{min}} = 0.047$, $T_{\text{max}} = 0.095$	$k = 0 \rightarrow 19$
4826 measured reflections	$l = -18 \rightarrow 18$
4376 independent reflections	3 standard reflections every 150 reflections
3501 reflections with $I > 2\sigma(I)$	intensity decay: negligible

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R = 0.033$	$\Delta\rho_{\text{max}} = 2.25 \text{ e \AA}^{-3}$
$wR = 0.038$	$\Delta\rho_{\text{min}} = -1.41 \text{ e \AA}^{-3}$
$S = 1.84$	Extinction correction: Zachariasen (1967)
3501 reflections	Extinction coefficient: $2.4 (1) \times 10^{-7}$
326 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o) + 0.0001 F_o ^2]$	

Compound (II)

Crystal data

[Mo ₂ Ir ₂ (C ₉ H ₁₃) ₂ (CO) ₁₀].0.5CH ₂ Cl ₂	Mo $K\alpha$ radiation
$M_r = 1134.28$	Cell parameters from 22 reflections
Orthorhombic, $Fdd2$	$\theta = 18.9\text{--}23.2^\circ$
$a = 38.199 (4) \text{ \AA}$	$\mu = 9.18 \text{ mm}^{-1}$
$b = 36.135 (5) \text{ \AA}$	$T = 296.2 \text{ K}$
$c = 9.303 (4) \text{ \AA}$	Plate, red-brown
$V = 12\,842 (4) \text{ \AA}^3$	$0.39 \times 0.18 \times 0.08 \text{ mm}$
$Z = 16$	
$D_x = 2.347 \text{ Mg m}^{-3}$	

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

Ir1—Ir2	2.6738 (7)	Ir2—C12	2.06 (1)
Ir1—Mo3	2.875 (1)	Ir2—C21	1.91 (1)
Ir1—Mo4	2.8926 (9)	Ir2—C22	1.91 (1)
Ir2—Mo3	2.880 (1)	Ir2—C23	2.14 (1)
Ir2—Mo4	2.8600 (9)	Mo3—C13	2.08 (1)
Mo3—Mo4	3.113 (1)	Mo3—C23	2.16 (1)
Ir1—C11	1.90 (1)	Mo3—C31	1.95 (1)
Ir1—C12	2.12 (1)	Mo4—C41	1.95 (1)
Ir1—C13	2.20 (1)	Mo4—C42	1.97 (1)
Ir1—C14	1.86 (1)		
Ir2—Ir1—Mo3	62.41 (2)	Ir2—Mo3—Mo4	56.85 (2)
Ir2—Ir1—Mo4	61.69 (2)	Ir1—Mo4—Ir2	55.39 (2)
Mo3—Ir1—Mo4	65.32 (3)	Ir1—Mo4—Mo3	57.07 (2)
Ir1—Ir2—Mo3	62.22 (2)	Ir2—Mo4—Mo3	57.48 (2)
Ir1—Ir2—Mo4	62.92 (2)	Mo3—C31—O31	162 (1)
Mo3—Ir2—Mo4	65.67 (3)	Mo4—C41—O41	170 (1)
Ir1—Mo3—Ir2	55.37 (2)	Mo4—C42—O42	174.9 (9)
Ir1—Mo3—Mo4	57.61 (2)		

Table 4

Short-contact geometry (\AA) for (II).

Ir1...C41	2.88 (1)	Mo4...C31	2.88 (1)
Ir1...C42	3.11 (1)	Mo4...C23	2.99 (1)

Data collection

Rigaku AFC-6S diffractometer	$R_{\text{int}} = 0.061$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$h = -49 \rightarrow 49$
$T_{\text{min}} = 0.205$, $T_{\text{max}} = 0.480$	$k = -46 \rightarrow 46$
15 709 measured reflections	$l = 0 \rightarrow 12$
3901 independent reflections	3 standard reflections
2937 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: negligible

Refinement

Refinement on F	H-atom parameters constrained
$R = 0.023$	$w = 1/[\sigma^2(F_o) + 0.0001 F_o ^2]$
$wR = 0.023$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.82$	$\Delta\rho_{\text{max}} = 0.96 \text{ e } \text{\AA}^{-3}$
2937 reflections	$\Delta\rho_{\text{min}} = -0.71 \text{ e } \text{\AA}^{-3}$
386 parameters	

Residual electron density in a region of space adjacent to the cluster molecule of (II) was attributed to solvent of crystallization, with the two largest peaks modelled as the Cl atoms of a dichloromethane molecule, which refined to an occupancy of 0.5. However, the C atom could not be located, suggesting disordering of the solvent molecule over numerous sites about the Cl1–Cl2 axis. For the same reason, the H atoms of the dichloromethane were also omitted. In a separate refinement of (II), the Flack (1983) parameter refined to -0.003 (6), establishing that the correct absolute structure of this racemic compound had been chosen. The cyclopentadienyl ring and methyl H atoms of both (I) and (II) were placed in calculated positions ($C-H = 0.95 \text{ \AA}$). The orientations of the methyl H atoms were determined from difference Fourier maps.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1125). Services for accessing these data are described at the back of the journal.

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