Undecacarbonyl(methylcyclopentadienyl)-*tetrahedro*-triiridiummolybdenum, undecacarbonyl(tetramethylcyclopentadienyl)-*tetrahedro*-triiridiummolybdenum and undecacarbonyl(pentamethylcyclopentadienyl)-*tetrahedro*-triiridiummolybdenum

Nigel T. Lucas, Ian R. Whittall and Mark G. Humphrey*

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

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

The three title compounds tri-μ-carbonyl-1:2κ^2C;1:3κ^2-C;2:3κ^2C-octacarbonyl-1κC,2κ^2C,3κ^2C,4κ^3C-η^5-methylcyclopentadienyl-*tetrahedro*-triiridiummolybdenum(3 *Ir—Ir*)(3 *Ir—Mo*), tri-μ-carbonyl-1:2κ^2C;1:3κ^2C;2:3κ^2C-octacarbonyl-1κC, 2κ^2C,3κ^2C,4κ^3C-η^5-tetramethylcyclopentadienyl-*tetrahedro*-triiridiummolybdenum(3 *Ir—Ir*)(3 *Ir—Mo*) and tri-μ-carbonyl-1:2κ^2C;1:3κ^2C;2:3κ^2C-octacarbonyl-1κC,2κ^2C,3κ^2C,-4κ^3C-η^5-pentamethylcyclopentadienyl-*tetrahedro*-triiridiummolybdenum(3 *Ir—Ir*)(3 *Ir—Mo*), [MoIr$_3$(η^5-C$_5$H$_{5-n}$Me$_n$)-(μ-CO)$_3$(CO)$_8$], where n = 1, 4 or 5, have a pseudotetrahedral MoIr$_3$ core geometry, with a η^5-C$_5$H$_{5-n}$Me$_n$ group ligating the Mo atom, bridging carbonyls spanning the edges of an MoIr$_2$ face, and eight terminally bound carbonyls.

Comment

The title compounds, (I), (II) and (III), have been prepared as part of a general study of tetrahedral mixed-group Ir$_6$ 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 physical properties and derivative chemistry. The chemistry of the cyclopentadienyl analogues of (I), (II) and (III) have been examined in depth; the title compounds have been prepared to broaden this study.

Complexes (I), (II) and (III), shown in Figs. 1, 2 and 3, respectively, all possess pseudo-tetrahedral core geometry and a general ligand disposition of the cyclopentadienyl-ligated analogue [MoIr$_3$(μ-CO)$_3$(CO)$_8$(η^5-C$_5$H$_5$)] (Churchill *et al.*,

1986). A second crystal form of (III) has been identified recently (Lucas *et al.*, 2002); metrical differences to the form

(I) R_1=H; R_2=Me
(II) R_1=Me; R_2=H
(III) R_1=R$_2$=Me
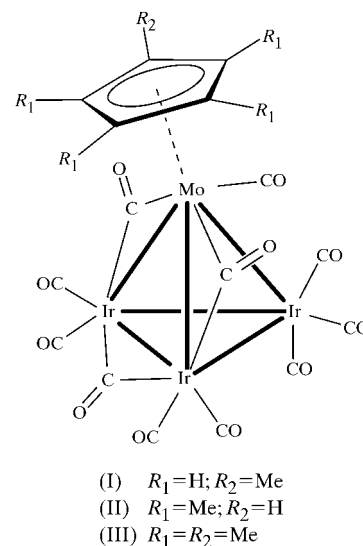
reported herein are minor [Ir1—Ir3 2.705 (1) *versus* 2.7172 (6) Å in (III); Ir1—Mo4 2.869 (2) *versus* 2.860 (1) Å in (III)]. Core Ir—Ir and Mo—Ir bond distances for (I)–(III) fall in the ranges 2.6802 (8)–2.7172 (6) and 2.832 (1)–2.907 (1) Å, respectively, with no systematic trends on increasing alkylcyclopentadienyl ligand bulk and electron-donating characteristics. Within each structure, the non-bridged Ir3—Mo4 bond [2.897 (1)–2.907 (1) Å] is significantly longer than the other two carbonyl-bridged Ir—Mo bonds [2.832 (1)–2.867 (1) Å] and the angles subtended at Mo4 [55.75 (3)–57.02 (3)°] are significantly smaller than those at the iridium vertices [59.58 (2)–63.14 (3)°]. The alkylcyclopentadienyl groups are inclined toward the MoIr$_2$ faces spanned by the bridging carbonyls and are *trans* to the long Ir3—Mo4 bond. Curtis and co-workers have defined an asymmetry parameter
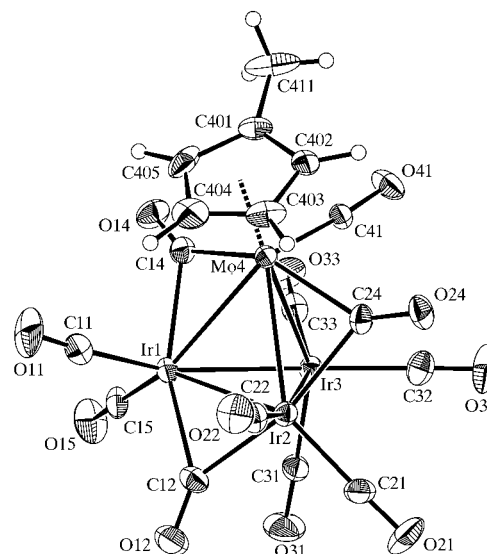

Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms are represented as spheres of arbitrary radii.
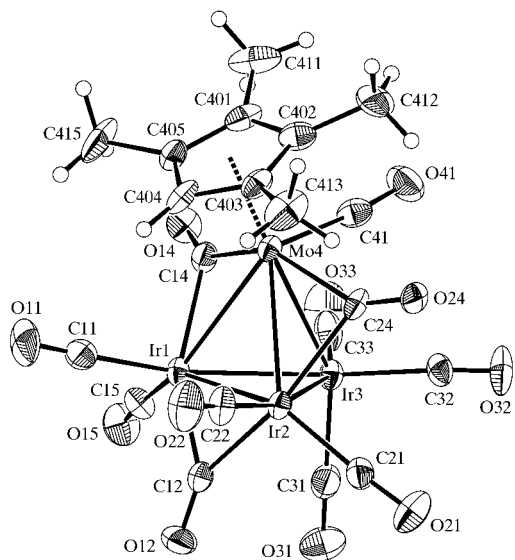
metal-organic compounds

Figure 2
The molecular structure of (II) showing 30% probability displacement ellipsoids. H atoms are represented as spheres of arbitrary radii.

α to evaluate semi-bridging character (Klingler *et al.*, 1978; Curtis *et al.*, 1980), with values of α between 0.1 and 0.6 corresponding to semi-bridging. The Mo4-bound CO(41) carbonyl is semi-bridging with Ir3 [Mo4—C41—O41 169 (1)–173 (1)$^\circ$ and Ir3$\cdots$C41 2.79 (1)–2.87 (1) Å; α = 0.43–0.48]. Increasing the number of methyl groups in the cyclopentadienyl ligand [in proceeding from (I) to (II) and thence (III)] results in increasingly unsymmetrical carbonyls bridging the Ir—Mo bonds. Bridging carbonyls are more efficient at removing electron density from metal centres, and the decreasing Mo—CO distances on increasing both steric bulk and electron-donating properties of the alkylcyclopentadienyl ligands suggests that electronic factors dominate over steric considerations for this ligand disposition.
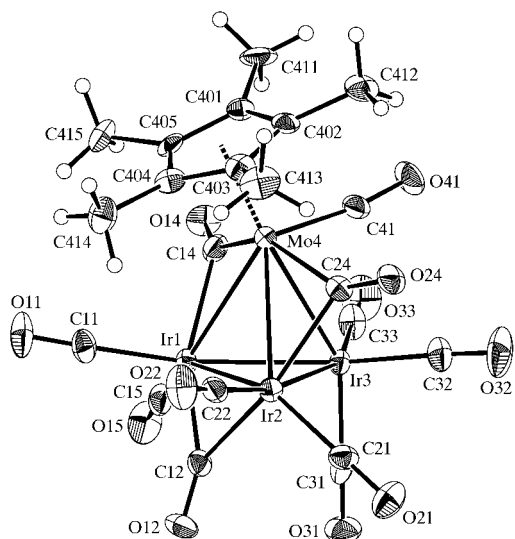

Figure 3
The molecular structure of (III) showing 30% probability displacement ellipsoids. H atoms are represented as spheres of arbitrary radii.

Experimental

The syntheses of (I), (II) and (III) 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) and (III), into dichloromethane solutions of the complexes at 276 K.

Compound (I)

Crystal data

[MoIr$_3$(C$_6$H$_7$)(CO)$_{11}$]	Mo $K\alpha$ radiation
$M_r = 1059.84$	Cell parameters from 23
Orthorhombic, *Pbca*	reflections
$a = 12.287$ (4) Å	$\theta = 2.8$–17.4°
$b = 14.352$ (4) Å	$\mu = 18.93$ mm^{-1}
$c = 24.719$ (3) Å	$T = 296.2$ K
$V = 4359$ (2) Å^3	Plate, orange
$Z = 8$	$0.30 \times 0.25 \times 0.10$ mm
$D_x = 3.230$ Mg m^{-3}	

Data collection

Rigaku AFC-6S diffractometer	$\theta_{max} = 25^\circ$
ω–2θ scans	$h = 0 \rightarrow 14$
Absorption correction: ψ scan	$k = 0 \rightarrow 17$
(North *et al.*, 1968)	$l = 0 \rightarrow 29$
$T_{min} = 0.006$, $T_{max} = 0.151$	3 standard reflections
4329 measured reflections	every 150 reflections
3850 independent reflections	intensity decay: 6.7%
2961 reflections with $I > 1.5\sigma(I)$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.034$	$\Delta\rho_{max} = 1.16$ e Å^{-3}
$wR = 0.034$	$\Delta\rho_{min} = -1.21$ e Å^{-3}
$S = 1.55$	Extinction correction: Zachariasen
2961 reflections	(1967)
290 parameters	Extinction coefficient:
H-atom parameters not refined	2.10 (4) $\times 10^{-7}$
$w = 1/[\sigma^2(F_o) + 0.0001|F_o|^2]$	

Compound (II)

Crystal data

[MoIr$_3$(C$_9$H$_{13}$)(CO)$_{11}$]	Mo $K\alpha$ radiation
$M_r = 1101.92$	Cell parameters from 18
Orthorhombic, *Pbca*	reflections
$a = 11.543$ (5) Å	$\theta = 10.1$–14.8°
$b = 17.198$ (9) Å	$\mu = 16.38$ mm^{-1}
$c = 25.382$ (6) Å	$T = 296.2$ K
$V = 5039$ (3) Å^3	Prism, orange
$Z = 8$	$0.40 \times 0.20 \times 0.20$ mm
$D_x = 2.905$ Mg m^{-3}	

Data collection

Rigaku AFC-6S diffractometer	$\theta_{max} = 25.1^\circ$
ω–2θ scans	$h = 0 \rightarrow 13$
Absorption correction: ψ scan	$k = 0 \rightarrow 20$
(North *et al.*, 1968)	$l = 0 \rightarrow 30$
$T_{min} = 0.023$, $T_{max} = 0.048$	3 standard reflections
4985 measured reflections	every 150 reflections
4459 independent reflections	intensity decay: 8.7%
3219 reflections with $I > 1.5\sigma(I)$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
$R = 0.038$	$\Delta\rho_{max} = 1.33$ e Å^{-3}
$wR = 0.034$	$\Delta\rho_{min} = -1.21$ e Å^{-3}
$S = 1.31$	Extinction correction: Zachariasen
3219 reflections	(1967)
317 parameters	Extinction coefficient:
H-atom parameters not refined	1.62 (3) $\times 10^{-7}$
$w = 1/[\sigma^2(F_o) + 0.0001|F_o|^2]$	

Compound (III)

Crystal data

[MoIr$_3$(C$_{10}$H$_{15}$)(CO)$_{11}$]
M_r = 1115.94
Monoclinic, Pn
a = 10.922 (3) Å
b = 10.226 (2) Å
c = 11.725 (2) Å
β = 104.64 (2)°
V = 1267.1 (5) Å^3
Z = 2

D_x = 2.925 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25
   reflections
θ = 15.2–18.2°
μ = 16.29 mm^{-1}
T = 296.2 K
Prism, orange
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-6S diffractometer
ω–2θ scans
Absorption correction: ψ scan
   (North et al., 1968)
   T_{min} = 0.025, T_{max} = 0.038
2512 measured reflections
2372 independent reflections
2326 reflections with $I > \sigma(I)$

R_{int} = 0.064
θ_{max} = 25°
h = 0 → 13
k = 0 → 12
l = −13 → 13
3 standard reflections
   every 150 reflections
   intensity decay: −0.8%

Refinement

Refinement on F
R = 0.019
wR = 0.022
S = 1.39
2326 reflections
324 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0001|F_o|^2]$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.84 e Å^{-3}
$\Delta\rho_{min}$ = −0.95 e Å^{-3}
Extinction correction: Zachariasen
   (1967)
Extinction coefficient:
   4.2 (2) × 10^{-7}

The cyclopentadienyl-ring and methyl H atoms were placed in calculated positions (C—H = 0.95 Å); the orientations of the methyl group H atoms were determined from Fourier difference maps. The absolute configuration for (III) was determined by comparison of the R factors for each of the two configurations when refined to convergence. The largest residual peaks were found close to Ir atoms [1.11 Å from Ir2 in (I), 1.34 Å from Ir1 in (II) and 1.16 Å from Ir2 in (III)].

For compounds (I), (II) and (III), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992–1997); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR*92 (Altomare et al., 1993) for compound (I) and *PATTY* in *DIRDIF*92 (Beurskens et al., 1992) for compounds (II) and (III); program(s) used to refine structure: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1356). Services for accessing these data are described at the back of the journal.

Table 1
A comparison of selected geometry (Å, °).

	(I)	(II)	(III)
Ir1—Ir2	2.7061 (8)	2.6802 (8)	2.7011 (6)
Ir1—Ir3	2.6993 (6)	2.7014 (8)	2.7172 (6)
Ir2—Ir3	2.692 (1)	2.694 (1)	2.7070 (6)
Ir1—Mo4	2.832 (1)	2.858 (1)	2.860 (1)
Ir2—Mo4	2.837 (1)	2.853 (1)	2.867 (1)
Ir3—Mo4	2.897 (1)	2.907 (1)	2.905 (1)
Ir1—C11	1.93 (1)	1.90 (2)	1.89 (1)
Ir1—C12	2.13 (1)	2.11 (1)	2.10 (1)
Ir1—C14	2.20 (1)	2.16 (1)	2.19 (1)
Ir1—C15	1.91 (1)	1.86 (1)	1.89 (1)
Ir2—C12	2.11 (1)	2.08 (1)	2.13 (1)
Ir2—C21	1.88 (1)	1.89 (1)	1.86 (1)
Ir2—C22	1.88 (1)	1.89 (1)	1.87 (1)
Ir2—C24	2.15 (1)	2.21 (1)	2.19 (1)
Ir3—C31	1.90 (1)	1.89 (2)	1.87 (2)
Ir3—C32	1.93 (1)	1.93 (1)	1.92 (1)
Ir3—C33	1.95 (1)	1.94 (2)	1.93 (1)
Ir3···C41	2.82 (1)	2.87 (1)	2.79 (1)
Mo4—C14	2.17 (1)	2.11 (1)	2.12 (1)
Mo4—C24	2.16 (1)	2.14 (1)	2.12 (1)
Mo4—C41	1.95 (1)	1.94 (1)	1.95 (1)
Ir2—Ir1—Ir3	60.06 (3)	59.73 (2)	59.95 (2)
Ir2—Ir1—Mo4	61.93 (3)	61.58 (3)	61.99 (3)
Ir3—Ir1—Mo4	62.97 (3)	63.12 (3)	62.72 (2)
Ir1—Ir2—Ir3	60.36 (2)	60.01 (2)	60.32 (2)
Ir1—Ir2—Mo4	62.09 (3)	61.40 (3)	61.72 (2)
Ir3—Ir2—Mo4	63.12 (3)	63.14 (3)	62.74 (2)
Ir1—Ir3—Ir2	59.58 (2)	60.26 (2)	59.73 (2)
Ir1—Ir3—Mo4	61.14 (3)	60.68 (2)	61.04 (2)
Ir2—Ir3—Mo4	61.12 (3)	60.88 (3)	61.32 (3)
Ir1—Mo4—Ir2	55.98 (3)	57.02 (3)	56.29 (2)
Ir1—Mo4—Ir3	55.89 (2)	56.20 (2)	56.24 (2)
Ir2—Mo4—Ir3	55.75 (3)	55.98 (3)	55.94 (2)

References

Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *DIRDIF*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Churchill, M. R., Li, Y.-J., Shapley, J. R., Foose, D. S. & Uchiyama, W. S. (1986). *J. Organomet. Chem.* **312**, 121–131.

Curtis, M. D., Han, K. R. & Butler, W. M. (1980). *Inorg. Chem.* **19**, 2096–2101.

Klingler, J. C., Butler, W. M. & Curtis, M. D. (1978). *J. Am. Chem. Soc.* **100**, 5034–5039.

Lee, J., Humphrey, M. G., Hockless, D. C. R., Skelton, B. W. & White, A. H. (1993). *Organometallics*, **12**, 3468–3473.

Lucas, N. T., Blitz, J. P., Petrie, S., Stranger, R., Humphrey, M. G., Heath, G. A. & Otieno-Alego, V. (2002). In preparation.

Lucas, N. T., Humphrey, M. G. & Rae, A. D. (2001). *Macromolecules*, **34**, 6188–6195.

Molecular Structure Corporation (1985). *TEXSAN*. Version 1.8. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1992–1997). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Waterman, S. M. & Humphrey, M. G. (1999). *Organometallics*, **18**, 3116–3127.

Waterman, S. M., Humphrey, M. G., Lee, J., Ball, G. E. & Hockless, D. C. R. (1999). *Organometallics*, **18**, 2440–2451.

Waterman, S. M., Humphrey, M. G., Tolhurst, V.-A., Bruce, M. I., Low, P. J. & Hockless, D. C. R. (1998). *Organometallics*, **17**, 5789–5795.

Waterman, S. M., Humphrey, M. G., Tolhurst, V.-A., Skelton, B. W., White, A. H. & Hockless, D. C. R. (1996). *Organometallics*, **15**, 934–940.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.