Mono- and bis-(acetylacetonato) complexes of arene–ruthenium(II) and arene–osmium(II): variation of the binding mode of η^1-acetylacetonate with the nature of the arene

Martin A. Bennett, Thomas R.B. Mitchell, Mark R. Stevens, and Anthony C. Willis

Abstract: The mono(acetylacetonato) complexes [MCl(*O*,*O*′-acac)(η^6-arene)] (M = Ru, Os, arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; M = Os, arene = 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$), which are formed from [MCl_2(η^6-arene)]$_2$ and thallium or sodium acetylacetonate, react with thallium acetylacetonate to give bis(acetylacetonato) complexes [M(*O*,*O*′-acac)(η^1-acac)(η^6-arene)]. The η^1-acac ligand is bound through the γ-carbon atom for M = Ru, Os, arene = C_6H_6; M = Os, arene = 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$ and through a keto-oxygen atom for M = Ru, Os, arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6, the difference being attributed to a combination of steric and electronic effects. Cationic ruthenium(II) derivatives [Ru(L)(*O*,*O*′-acac)(η^6-arene)]$^+$ (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; L = DMSO, MeCN, py, PPh_3) and [Ru(CO)(*O*,*O*′-acac)(η^6-arene)]$^+$ (arene = 1,3,5-$C_6H_3Me_3$,C_6Me_6), and neutral osmium(II) η^1-acetato derivatives [Os(η^1-OAc)(*O*,*O*′-acac)(η^6-arene)] (arene = C_6H_6, 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$, 1,3,5-$C_6H_3Me_3$, C_6Me_6) are also described. The molecular structures of the following complexes have been determined by X-ray crystallography: [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)], triclinic, space group $P\bar{1}$ (No. 2), a = 9.922(2), b = 9.974(2), and c = 11.001(2) Å, α = 68.33(1), β = 64.18(1), and γ = 62.38(1)°, V = 849.0(3) Å^3, Z = 2; [Os(*O*,*O*′-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)], monoclinic, space group $C2/c$ (No. 15), a = 16.032(4), b = 11.989(3), and c = 21.562(7) Å, β = 108.91(2)°, V = 3921(2) Å, Z = 8; [Os(η^1-OAc)(*O*,*O*′-acac)(η^6-C_6H_6)], triclinic, space group $P\bar{1}$ (No. 2), a = 8.368(4), b = 8.402(4), and c = 11.008(4) Å, α = 71.68(3), β = 69.35(3), and γ = 69.77(3)°, V = 663.0(6) Å^3, Z = 2.

Key words: arene–ruthenium, arene–osmium, acetylacetone, crystal structures.

Résumé : Les complexes mono(acétylacétonato) [MCl(*O*,*O*′-acac)(η^6-arène)] (M = Ru, Os, arène = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; M = Os, arène = 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$), qui se forment par réaction de [MCl_2(η^6-arène)]$_2$ avec l'acétylacétonate de thallium ou de sodium, réagissent avec l'acétylacétonate de thallium pour donner des complexes bis(acétylacétonato) [M(*O*,*O*′-acac)(η^1-acac)(η^6-arène)]. Le ligand η^1 est lié par le carbone γ dans les cas où M = Ru, Os, arène = C_6H_6; M = Os, arène = 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$ et par l'atome d'oxygène de la cétone lorsque M = Ru, Os, arène = 1,3,5-$C_6H_3Me_3$, C_6Me_6; on attribue les différences à une combinaison d'effets stériques et électroniques. On décrit aussi les dérivés cationiques du ruthénium [Ru(L)(*O*,*O*′-acac)(η^6-arène)]$^+$ (arène = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; L = DMSO; MeCN; py, PPh_3) et [Ru(CO)(*O*,*O*′-acac)(η^6-arène)]$^+$ (arène = 1,3,5-$C_6H_3Me_3$, C_6Me_6) et les dérivés neutres η^1-acétato de l'osmium(II) [Os(η^1-OAc)(*O*,*O*′-acac)(η^6-arène)] (arène = C_6H_6, 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$, 1,3,5-$C_6H_3Me_3$, C_6Me_6). Les structures moléculaires des complexes suivants ont été déterminées par diffraction des rayons X: [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)], triclinique, groupe d'espace $P\bar{1}$ (No. 2), avec a = 9,922(2), b = 9,974(2) et c = 11,001(2) Å, α = 68,33(1), β = 64,18(1) et γ = 62,38(1)°, V = 849,0(3) Å^3 et Z = 2; [Os(*O*,*O*′-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)], monoclinique, groupe d'espace $C2/c$ (No. 15), avec a = 16,032(4), b = 11,989(3) et c = 21,562(7) Å, β = 108,91(2), V = 3921(2) Å^3 et Z = 8; [Os(η^1-OAc)(*O*,*O*′-acac)(η^6-C_6H_6)], triclinique, groupe d'espace $P\bar{1}$ (No. 2), avec a = 8,368(4), b = 8,402(4) et c = 11,008(4) Å, α = 71,68(3), β = 69,35(3) et γ = 69,77(3)°, V = 663,0(6) Å^3 et Z = 2.

Mots clés : arène–ruthénium, arène–osmium, acétylacétone, structures cristallines.

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This paper is dedicated to Brian James on the occasion of his 65th birthday, and in recognition of his many contributions to organometallic chemistry, coordination chemistry, and homogeneous catalysis.

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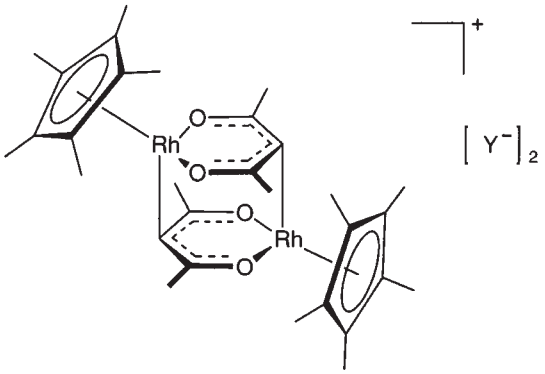
Introduction

Although the acac anion $(CH_3COCHCOCH_3)^-$ (see *List of abbreviations*),[2] and the mono-anions of other β-dicarbonyl compounds, usually behave as bidentate chelate *O*,*O*′-donors to transition metal ions, the more electronegative elements towards the end of the 4*d*- and 5*d*-series, especially Hg(II), Au(I), Au(III), Pt(II), Pd(II), Pt(IV), and Ir(III), display a pronounced tendency to bind to the γ-carbon atom of acetylacetonate ion (Fig. 1) (1–3). There are fewer examples of this behaviour in the coordination chemistry of rhodium, ruthenium, and osmium, which form stable chelate complexes such as [M(*O*,*O*′-acac)$_3$]. Starting from the η^5-pentamethylcyclopentadienyl complexes $[MCl_2(\eta^5\text{-}C_5Me_5)]_2$ (M = Rh, Ir), Maitlis et al. (4) have prepared [MCl(*O*,*O*′-acac)(η^5-C_5Me_5)], [Ir(*O*,*O*′-acac)(η^1-*C*-acac)(η^5-C_5Me_5)], and $[Rh_2(\mu\text{-}O,O',C\text{-acac})_2(\eta^5\text{-}C_5Me_5)_2]Y_2$ (Y = BF_4, PF_6) (**1**); in **1** each acac anion is bound as an *O*,*O*′-bidentate ligand to one rhodium atom and as a γ-*C*-donor to the other. Some



1, Y = BF_4, PF_6

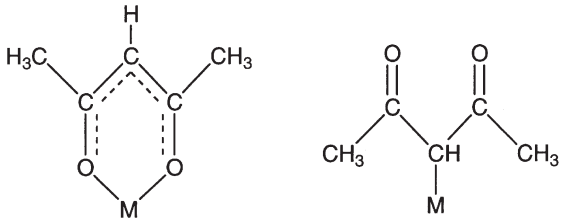
analogous compounds are known in the isoelectronic η^6-*p*-cymene–ruthenium(II) and –osmium(II) systems. The complexes [MCl(*O*,*O*′-acac)(η^6-cym)] have been obtained by reaction of $[MCl_2(\eta^6\text{-cym})]_2$ with acetylacetone and base (5, 6), and [Os(*O*,*O*′-acac)(η^1-*C*-acac) (η^6-cym)] is formed by treatment of the *tert*-butylimido compound [Os(N-*t*-Bu) (η^6-cym)] with acetylacetone (6). We report here the preparation and structural characterization of a wider range of (η^6-arene)ruthenium(II) and (η^6-arene)osmium(II) acetylacetonato complexes, and show that the mode of binding of a second acetylacetonate anion to the [M(*O*,*O*′-acac)(η^6-arene)] moiety depends on the nature of the arene.

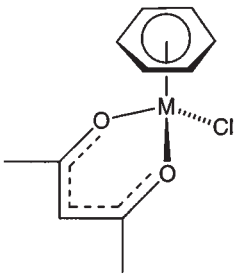
Results and discussion

Mono(acetylacetonato) complexes

Chloro(acetylacetonato) complexes of arene–ruthenium(II) or arene–osmium(II) of general formula [MCl(acac)(η^6-arene)] (M = Ru, Os; arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; M = Os, arene = 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$) have been prepared in yields of 60–80% by reaction of 1 mol of the dichloride dimers $[MCl_2(\eta^6\text{-arene})]_2$ with 2 mol of thallium acetylacetonate or sodium acetylacetonate in dichloromethane or dichloromethane–methanol at room temperature. The ruthenium compounds can also be obtained, in generally lower yield, by heating $[RuCl_2(\eta^6\text{-arene})]_2$ with acetylacetone in DMF in the presence of anhyd Na_2CO_3 for 2–10 min at 100°C; longer periods or higher temperatures cause the formation of $[Ru(acac)_3]$. The complexes are orange or yellow, air-stable, microcrystalline solids that are very soluble in chloroform, dichloromethane, or methanol and are poorly soluble in benzene or ether. Molecular weight determinations in dichloromethane confirm that the ruthenium compounds are monomeric. Selected spectroscopic data are collected in Tables 1 and 2. In addition to the expected resonances in the region of δ 5 arising from the protons of the complexed arene, the ^{1}H NMR spectra show a 1H singlet at δ 4.9–5.1 and a 6H singlet at δ ca. 1.9 due to the γ-proton and the methyl protons of the acac group, respectively. The IR spectra show a pair of strong bands at ca. 1570 and 1510 cm^{-1}, which are assignable to coupled ν(C=O) + ν(C=C) modes of the bidentate *O*,*O*′-acetylacetonate (1–3, 7). Thus, the data are in agreement with the half-sandwich formulation **2**, similar to that proposed for the *p*-cymene–ruthenium and –osmium analogues (5, 6).

Fig. 1. Common binding modes of acetylacetonate to metal ions.





M = Ru, Os; arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6
M = Os; arene = 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$

2

In a similar manner, we have also made the corresponding hexafluoroacetylacetonato complexes [RuCl(η^6-arene)(*O*,*O*′-hfacac)] (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$,C_6Me_6), whose

[2] Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub_e.shtml. Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

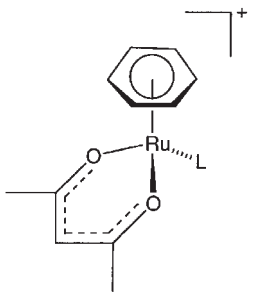
Table 1. ^{1}H NMR data and characteristic IR bands for Ru(acac)(η^6-arene) and Ru(hfacac)(η^6-arene) complexes.

	^{1}H NMR (δ)					
Complex	Solvent	acac-*Me*	acac-γ-*H*	Arene ring-*H*	Arene ring-*Me*	IR[a]
[RuCl(*O*,*O*′-acac)(η^6-C_6H_6)]	$CDCl_3$	1.97 (s, 6H)	5.16 (s, 1H)	5.61 (s, 6H)		1572, 1525
[RuCl(*O*,*O*′-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	$CDCl_3$	1.98 (s, 6H)	5.15 (s, 1H)	4.84 (s, 3H)	2.12 (s, 9H)	1583, 1516
[RuCl(*O*,*O*′-acac)(η^6-C_6Me_6)]	$CDCl_3$	1.92 (s, 6H)	4.94 (s, 1H)		1.97 (s, 18H)	1584, 1513
[Ru(*O*,*O*′-acac)(dmso)(η^6-C_6H_6)]BF_4	CD_2Cl_2	2.04 (s, 6H)	5.28 (s, 1H)	5.77 (s, 6H)		1555, 1519
[Ru(*O*,*O*′-acac)(dmso)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	$CDCl_3$	2.10 (s, 6H)	5.27 (s, 1H)	4.98 (s, 3H)	2.06 (s, 9H)	1565, 1523
[Ru(*O*,*O*′-acac)(dmso)(η^6-C_6Me_6)]BF_4	$CDCl_3$	2.04 (s, 6H)	5.27 (s, 1H)		2.01 (s, 18H)	1562, 1520
[Ru(*O*,*O*′-acac)(NCMe)(η^6-C_6H_6)]BF_4	CD_2Cl_2	2.00 (s, 6H)	5.21 (s, 1H)	5.20 (s, 6H)		1569, 1514
[Ru(*O*,*O*′-acac)(NCMe)(η^6-C_6Me_6)]BF_4	$CDCl_3$	2.01 (s, 6H)	5.13 (s, 1H)		2.05 (s, 18H)	1569, 1518
[Ru(*O*,*O*′-acac)(py)(η^6-C_6H_6)]BF_4	$CDCl_3$	1.92 (s, 6H)	4.96 (s, 1H)	5.75 (s, 6H)		nm
[Ru(*O*,*O*′-acac)(py)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	$CDCl_3$	1.93 (s, 6H)	4.96 (s, 1H)	5.01 (s, 3H)	1.95 (s, 9H)	nm
[Ru(*O*,*O*′-acac)(py)(η^6-C_6Me_6)]BF_4	$CDCl_3$	1.96 (s, 6H)	4.90 (s, 1H)		1.96 (s, 18H)	nm
[Ru(*O*,*O*′-acac)(CO)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	$CDCl_3$	2.03 (s, 6H)	5.42 (s, 1H)	5.63 (s, 3H)	2.23 (s, 9H)	1580, 1519
[Ru(*O*,*O*′-acac)(CO)(η^6-C_6Me_6)]BF_4	$CDCl_3$	2.04 (s, 6H)	5.41 (s, 1H)		2.16 (s, 18H)	1566, 1522
[Ru(*O*,*O*′-acac)(PPh_3)(η^6-C_6H_6)]BF_4	$CDCl_3$	1.66 (s, 6H)	4.71 (s, 1H)	5.59 (s, 6H)		nm
[Ru(*O*,*O*′-acac)(PPh_3)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	$CDCl_3$	1.67 (s, 6H)	4.71 (s, 1H)	4.91 (s, 6H)	1.84 (s, 9H)	nm
[Ru(*O*,*O*′-acac)(PPh_3)(η^6-C_6Me_6)]BF_4	$CDCl_3$	1.73 (s, 6H)	4.60 (s, 1H)		1.73 (s, 18H)	nm
[RuCl(*O*,*O*′-hfacac)(PPh_3)(η^6-C_6H_6)]	$CDCl_3$		5.85 (s, 1H)	5.77 (s, 6H)		1628, 1605 (m), 1558
[RuCl(*O*,*O*′-hfacac)(η^6-1,3,5-$C_6H_3Me_3$)]	$CDCl_3$		5.85 (s, 1H)	4.84 (s, 3H)	2.12 (s, 9H)	1629, 1584 (m), 1554
[RuCl(*O*,*O*′-hfacac)(η^6-C_6Me_6)]	$CDCl_3$		5.79 (s, 1H)		2.06 (s, 18H)	1624, 1574 (m), 1547

[a]ν(C=O), ν(C=C) of acac (KBr, cm^{-1}); bands are very strong except where indicated; nm = not measured.

IR spectra show strong ν(C=O), ν(C=C) bands in the region of 1630–1550 cm^{-1} typical of bidentate *O*,*O*′-coordination of hfacac (7–9). The far-IR spectra of the [RuCl(acac)(η^6-arene)] and [RuCl(hfacac)(η^6-arene)] complexes contain a medium-intensity band at ca. 280 cm^{-1} that may be assigned to ν(RuCl).

Treatment of the [RuCl(*O*,*O*′-acac)(η^6-arene)] complexes with $AgBF_4$ or $AgPF_6$ in an acetone solution containing neutral ligands (L = dimethylsulfoxide (DMSO), acetonitrile, pyridine (py), triphenylphosphine) generates cationic complexes [Ru(L)(*O*,*O*′-acac)(η^6-arene)]$^+$, which can be isolated in good yield as their BF_4 or PF_6 salts. The IR spectra all show the characteristic pair of bands at ca. 1570 and 1510 cm^{-1} due to bidentate, O-bonded acac. The spectroscopic data (Table 1) are consistent with the half-sandwich structure **3**. In the solid state, the IR spectra of the DMSO complexes



L = DMSO, MeCN, py, PPh_3;
arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6
L = CO; arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6

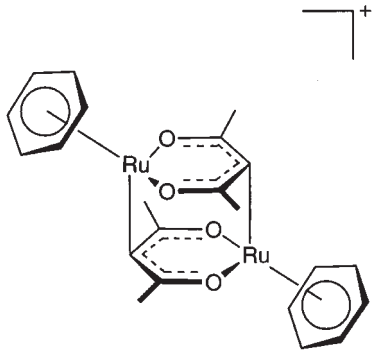
3

Table 2. ^{1}H NMR data and characteristic IR bands for Os(η^6-arene)(acac) complexes.

Complex	^{1}H NMR (δ)[a] Solvent	acac-*Me*	acac-γ-*H*	Arene ring-*H*	Arene ring-*Me*	IR[b]
[OsCl(*O*,*O*′-acac)(η^6-C_6H_6)]	C_6D_6	1.90 (s, 6H)	5.28 (s, 1H)	5.42 (s, 6H)		1570, 1527
[OsCl(*O*,*O*′-acac)(η^6-1,2-$C_6H_4Me_2$)]	C_6D_6	1.87 (s, 6H)	5.25 (s, 1H)	5.39 (m, 2H), 5.46 (m, 2H)	1.89 (s, 6H)	1579, 1520
	$CDCl_3$	1.99 (s, 6H)	5.35 (s, 1H)	5.84 (m, 2H), 5.93 (m, 2H)	2.14 (s, 6H)	
[OsCl(*O*,*O*′-acac)(η^6-1,2,3-$C_6H_3Me_3$)]	C_6D_6	1.87 (s, 6H)	5.23 (s, 1H)	5.29 (d, 2H), 5.53 (t, *J* = 5, 1H)	1.76 (s, 3H), 1.95 (s, 6H)	1578, 1516
	CD_2Cl_2	1.94 (s, 6H)	5.30 (s, 1H)	5.68 (d, 2H), 5.87 (t, *J* = 5, 1H)	1.95 (s, 3H), 2.10 (s, 6H)	
[OsCl(*O*,*O*′-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	C_6D_6	1.88 (s, 6H)	5.26 (s, 1H)	5.00 (s, 3H)	2.02 (s, 9H)	1580, 1520
	$CDCl_3$	1.98 (s, 6H)	5.35 (s, 1H)	5.46 (s, 3H)	2.17 (s, 9H)	
[OsCl(*O*,*O*′-acac)(η^6-C_6Me_6)]	C_6D_6	1.83 (s, 6H)	5.14 (s, 1H)		1.91 (s, 18H)	1580, 1518
	$CDCl_3$	1.95 (s, 6H)	5.22 (s, 1H)		2.03 (s, 18H)	
[Os(OAc)(*O*,*O*′-acac)(η^6-C_6H_6)][c]	C_6D_6	1.87 (s, 6H)	5.23 (s, 1H)	5.72 (s, 6H)		1625,[d] 1580, 1525
[Os(OAc)(*O*,*O*′-acac)(η^6-1,2-$C_6H_4Me_2$)][e]	C_6D_6	1.85 (s, 6H)	5.19 (s, 1H)	5.79 (m, 2H), 6.06 (m, 2H)	1.83 (s, 6H)	1631,[d] 1581, 1519
[Os(OAc)(*O*,*O*′-acac)(η^6-1,2,3-$C_6H_3Me_3$)][e]	C_6D_6	1.89 (s, 6H)	5.14 (s, 1H)	5.78 (d, 2H), 6.50 (t, *J* = 5, 1H)	1.65 (s, 3H), 1.83 (s, 6H)	1634,[d] 1579, 1522
[Os(OAc)(*O*,*O*′-acac)(η^6-1,3,5-$C_6H_3Me_3$)][e]	C_6D_6	1.83 (s, 6H)	5.11 (s, 1H)	5.29 (s, 3H)	2.08 (s, 9H)	1626,[d] 1576, 1530
[Os(OAc)(*O*,*O*′-acac)(η^6-C_6Me_6)][f]	C_6D_6	1.84 (s, 6H)	5.06 (s, 1H)		2.01 (s, 18H)	1635,[d] 1575, 1524

[a]Coupling constants (*J*) in Hz.
[b]ν(C=O), ν(C=C) of acac (KBr, cm^{-1}); bands are very strong.
[c]δ 2.37 (s, 3H, C*H*$_3$CO$_2$).
[d]ν(C=O) of acetate.
[e]δ 2.38 (s, 3H, C*H*$_3$CO$_2$).
[f]δ 2.35 (s, 3H, C*H*$_3$CO$_2$).

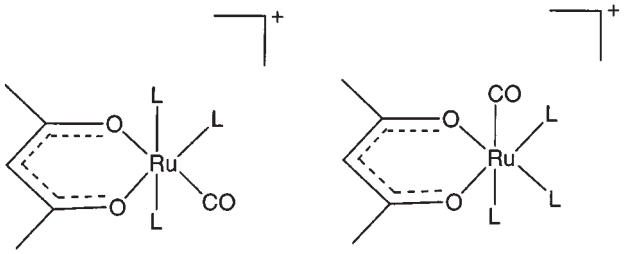
contain a band at ca. 1120 cm^{-1}, which is assigned to ν(S=O) of S-bonded DMSO (10*a*). The region 950–1100 cm^{-1} where ν(S=O) of O-bonded DMSO is expected to appear is masked by an intense ν(BF) absorption of the BF_4 anion, but the spectrum of [Ru(DMSO)(*O*,*O*′-acac)(η^6-C_6H_6)]PF_6 showed no band attributable to ν(S=O) of O-bonded DMSO. However, the IR spectrum of [Ru(DMSO)(*O*,*O*′-acac)(η^6-C_6H_6)]PF_6 in CD_2Cl_2 contains a strong band at 1055 cm^{-1} due to free DMSO, in addition to the band at 1112 cm^{-1} due to S-coordinated DMSO, showing that this ligand is readily lost from the coordination sphere. The ^{1}H NMR spectra of the DMSO complexes in CD_2Cl_2 show a 6H singlet at δ 2.6 due to *Me*$_2$SO, the chemical shift being similar to that of free DMSO (δ 2.53), and addition of DMSO to the solution shifts the resonance towards that of free DMSO; hence, there is rapid exchange on the NMR timescale between free and coordinated DMSO. This conclusion was confirmed by adding DMSO-d_6 (6 mol) to [Ru(*O*,*O*′-acac) (DMSO)(η^6-C_6H_6)] in CH_2Cl_2; the ^{1}H NMR spectrum of the recovered complex showed the presence of only about one-sixth of the original DMSO methyl protons. Since the observations imply the existence of the coordinatively unsaturated or solvent-stabilized species [Ru(*O*,*O*′-acac)(η^6-arene)]$^+$, we treated the [RuCl(*O*,*O*′-acac)(η^6-arene)] complexes with $AgBF_4$ or $AgPF_6$ in acetone. Silver chloride is precipitated, and yellow solutions are formed that presumably contain [Ru(acetone)(*O*,*O*′-acac)(η^6-arene)]$^+$. Addition of ether precipitates yellow powders that are insoluble in chloroform, dichloromethane, or methanol and do not redissolve in acetone. They do dissolve in acetonitrile or DMSO-d_6 to generate solutions of the appropriate cations [Ru(L)(*O*,*O*′-acac)(η^6-arene)]$^+$ (L = MeCN, DMSO-d_6), as shown by ^{1}H NMR spectroscopy. Elemental analyses of the yellow solids were not completely satisfactory, but the presence of a strong ν(C=O) band at 1620 cm^{-1} in the IR spectra suggests that the complexes are the (η^6-arene)ruthenium(II) analogues (**4**) of the binuclear Rh(η^5-C_5Me_5) complex **1**, containing bridging *O*,*O*′,*C*-acac groups.



4

Cationic carbonyl complexes [Ru(CO)(*O*,*O*′-acac)(η^6-arene)]$^+$ (arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6) can be isolated as their BF_4

salts by bubbling CO through the yellow solutions containing [Ru(acetone)(*O*,*O*′-acac)(η^6-arene)]$^+$. The mesitylene complex is unstable in chloroform over a period of hours and decomposes slowly in air. The IR spectra show an intense ν(CO) band at ca. 2030–2050 cm^{-1}. Attempts to prepare ethylene analogues were unsuccessful. Under the same conditions, CO displaces benzene from solutions of [Ru(L)(*O*,*O*′-acac)(η^6-C_6H_6)]BF_4 (L = Me_2CO, MeCN) to give an intractable brown oil. Addition of ether to an acetonitrile solution gave a low yield of a pale yellow crystalline salt formulated as [Ru(*O*,*O*′-acac)(CO)$(MeCN)_3$]BF_4 on the basis of spectroscopic data. In addition to the usual resonances of coordinated acac there are two singlets in a 2:1 ratio in the ^{1}H NMR spectrum at δ ca. 2.5 corresponding to the methyl protons of coordinated acetonitrile. The IR spectrum contains a pair of weak bands in the region of 2300 cm^{-1} arising from ν(CN) of coordinated acetonitrile, a strong ν(CO) band at 1982 cm^{-1}, and the usual pair of *O*,*O*′-acac bands at ca. 1570 and 1510 cm^{-1}. These data are consistent with either of the octahedral structures **5a** or **5b** in which the acetonitrile ligands adopt a *mer* or *fac* arrangement about ruthenium, respectively.



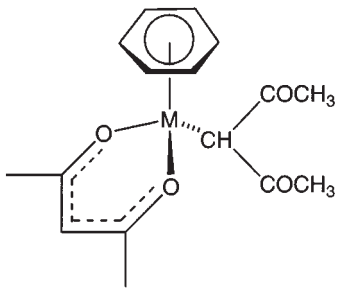
5a **5b**

Chloride ion can also be abstracted from the osmium complexes [OsCl(*O*,*O*′-acac)(η^6-arene)], which react with silver acetate to give the acetato complexes [Os(η^1-OAc)(*O*,*O*′-acac)(η^6-arene)]. Their IR spectra (Table 2) show, in addition to the usual *O*,*O*′-acac bands at ca. 1580 and 1520 cm^{-1}, a strong ν(C=O) absorption at ca. 1630 cm^{-1} characteristic of either monodentate or asymmetric bidentate acetate (10b); the ^{1}H NMR spectra show the expected 3H singlet at δ ca. 1.9. The structure of the η^6-benzene complex has been confirmed by X-ray crystallography (see below).

Bis(acetylacetonato) complexes

The [RuCl(*O*,*O*′-acac)(η^6-arene)] complexes react with an equimolar quantity of Tl(acac) in methanol at –20°C to give orange-red (benzene) or yellow (mesitylene, hexamethylbenzene) microcrystalline solids of formula [Ru$(acac)_2$(η^6-arene)]. Attempts to prepare analogous bis(hfacac) complexes were unsuccessful. The benzene complex decomposes both as a solid and in solution, and satisfactory elemental analyses could not be obtained. The mesitylene and hexamethylbenzene complexes are stable for short periods in the solid state at room temperature, but they also decompose in solution at room temperature over periods ranging from minutes in chloroform to several days in methanol. The corresponding thermally more stable osmium compounds [Os$(acac)_2$(η^6-arene)] (arene = C_6H_6, 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$, 1,3,5-$C_6H_3Me_3$, C_6Me_6) are obtained similarly from [OsCl(*O*,*O*′-acac)(η^6-arene)], and the benzene compound can also be isolated from the reaction of [$OsCl_2$(η^6-C_6H_6)]$_2$ with Tl(acac) in a 1:4 mol ratio in methanol. At a late stage of the study, during attempts to grow single crystals of [Os$(acac)_2$(η^6-C_6H_6)], we realized that the η^1-acetato complexes [Os(η^1-O_2CMe)(*O*,*O*′-acac)(η^6-arene)] are formed as byproducts in these reactions; these complexes have been prepared independently and have been fully characterized (see above). We have not established whether the byproducts arose from adventitious thallium acetate impurity in the sample of Tl(acac), or more likely, from a catalyzed process similar to the known base-promoted decomposition of acetylacetonate ion to acetate ion (11). In most cases the less soluble acetato complexes could be separated from the bis(acetylacetonato) complexes by fractional crystallization.

The key spectroscopic data for the [M$(acac)_2$(η^6-arene)] complexes are collected in Table 3. For the ruthenium compound [Ru$(acac)_2$(η^6-C_6H_6)], and for the osmium compounds [Os$(acac)_2$(η^6-arene)] (arene = C_6H_6, 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$), these data indicate a structure (**6**) in which one acac group is still bidentate (*O*,*O*′) while the other is bound as a monodentate ligand through the γ-carbon atom.



M = Ru, Os; arene = C_6H_6
M = Os; arene = 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$

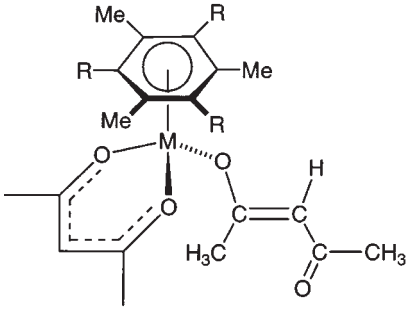
6

Thus, the solid state and solution IR spectra show two pairs of strong bands in the ν(C=O), ν(C=C) region, one due to *O*,*O*′-acac at ca. 1580 and 1520 cm^{-1}, the other at 1650–1680 and 1620 cm^{-1} assignable to $CH(COMe)_2$ (7). Correspondingly, the ^{1}H NMR spectra contain a singlet acac methyl resonance at δ 1.9–2.3 (6H) and a γ-CH resonance at δ 4.3–4.7 assignable to C-bonded acac, in addition to a methyl resonance at δ ca. 1.8 (6H) and a γ-CH resonance at ca. δ 5.2 due to *O*,*O*′-acac. In contrast, although the ^{1}H NMR spectra of [M$(acac)_2$(η^6-arene)] (M = Ru, Os; arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6) contain resonances typical of *O*,*O*′-acac, the η^1- acac group in each case gives rise to two methyl singlets at δ ca. 2.5 and 3.0, and a γ-CH singlet at δ ca. 5.0, consistent with binding through a keto-oxygen atom (structure **7**). The IR spectra show two pairs of strong bands in the ν(C=O), ν(C=C) region, one due to *O*,*O*′-acac at ca. 1580 and 1520 cm^{-1}, the other at ca. 1620 and 1500 cm^{-1}. The bands in the second pair clearly differ from those due to η^1-C-bonded acac and are similar to those reported for the structurally characterized compound [Rh(η^1-*O*-acac)(CO){P(*i*Pr)$_3$}$_2$] (1613 (w), 1515 (m) cm^{-1})) (12). However, the bands reported for *trans*-[Pt(η^1-*O*-acac)$_2$(PEt_3)$_2$] and

Table 3. ^{1}H NMR data and characteristic IR bands for M(acac)$_2$(η^6-arene) complexes (M = Ru, Os).

Complex	^{1}H NMR (δ) Solvent	acac-*Me*	acac-γ-*H*	Arene ring-*H*	Arene ring-*Me*	IR[a]
[Ru(*O,O′*-acac)(η^1-*C*-acac)(η^6-C_6H_6)]	C_6D_6	1.77 (s, 6H) (*O,O′*); 2.06 (s, 6 H) (η^1-*C*)	5.04 (s, 1H) (*O,O′*); 3.35 (s, 1 H) (η^1-*C*)	4.71 (s, 6H)		1574, 1520 (*O,O′*); 1672, 1623 (m) (η^1-*C*)
	CD_2Cl_2	1.83 (s, 6H) (*O,O′*); 1.98 (s, 6H) (η^1-*C*)	5.60 (s, 1H) (*O,O′*); 3.12 (s, 1 H) (η^1-*C*)	5.26 (s, 6H)		
[Ru(*O,O′*-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	CD_2Cl_2	1.89 (s, 6H) (*O,O′*); 1.91 (s, 3H), 2.17 (s, 3H) (η^1-*O*)	5.43 (s, 1H) (*O,O′*); 4.97 (s, 1H) (η^1-O)	4.77 (s, 3H)	2.08 (s, 9H)	1579, 1525 (*O,O′*); 1616 (m), 1500 (η^1-*O*)
[Ru(*O,O′*-acac)(η^1-*O*-acac)(η^6-C_6Me_6)]	CD_2Cl_2	1.89 (s, 6H) (*O,O′*); 1.84 (s, 3H), 2.14 (s, 3H) (η^1-*O*)	5.14 (s, 1H) (*O,O′*); 4.94 (s, 1H) (η^1-*O*)		1.96 (s, 18H)	1582, 1519 (*O,O′*); 1613 (m), 1489 (η^1-*C*)
[Os(*O,O′*-acac)(η^1-*C*-acac)(η^6-C_6H_6)]	C_6D_6	1.88 (s, 6H) (*O,O′*)	5.27 (s, 1H) (*O,O′*); 4.64 (s, 1H) (η^1-*C*)	5.22 (s, 6H)		1570, 1520 (*O,O′*); 1678, 1631 (m) (η^1-*C*)
		2.28 (s, 6H) (η^1-*C*)				1583, 1523 (*O,O′*); 1678 1650 (sh), 1633 (η^1-*C*)[b]
[Os(*O,O′*-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)]	C_6D_6	1.84 (s, 6H) (*O,O′*); 2.29 (s, 6H) (η^1-*C*)	5.22 (s, 1H) (*O,O′*); 4.69 (s, 1H) (η^1-*C*)	5.23 (m, 2H), 5.38 (m, 2H)	1.57 (s, 6H)	1573, 1520 (*O,O′*); 1646, 1630 (η^1-*C*)
	CD_2Cl_2	1.90 (s, 6H) (*O,O′*); 1.94 (s, 6H) (η^1-*C*)	5.42 (s, 1H) (*O,O′*); 4.30 (s, 1H) (η^1-*C*)	5.33 (s, 2H), 5.47 (s, 2H)	1.88 (s, 6H)	1581, 1523 (*O,O′*); 1675, 1650 (sh), 1632 (η^1-C)[b]
[Os(*O,O′*-acac)(η^1-*C*-acac)(η^6-1,2,3-$C_6H_3Me_3$)]	C_6D_6	1.82 (s, 6H) (*O,O′*)	5.17 (s, 1H) (*O,O′*); 4.73 (s, 1H) (η^1-*C*)	4.87 (d, 2H), 6.08 (t, 1H)	1.48 (s, 3H), 1.58 (s, 6H)	1575, 1527 (*O,O′*); 1646, 1626 (m) (η^1-*C*)
		2.34 (s, 6H) (η^1-*C*)				1581, 1522 (*O,O′*); 1673. 1631 (η^1-*C*)[b]
[Os(*O,O′*-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	C_6D_6	1.77 (s, 6H) (*O,O′*); 2.47 (s, 3H), 3.05 (s, 3H) (η^1-*O*)	5.85 (s, 1H) (*O,O′*); 5.05 (s, 1H) (η^1-*C*)	4.95 (s, 3H)	1.95 (s, 9H)	1576, 1531 (*O,O′*); 1618 (m), 1502 (η^1-*C*)
	CD_2Cl_2	1.89 (s, 6H) (*O,O′*); 1.93 (s, 3H), 2.23 (s, 3H) (η^1-*O*)	5.46 (s, 1H) (*O,O′*); 5.23 (s, 1H) (η^1-*O*)	5.41 (s, 3H)	2.16 (s, 9H)	1582, 1524 (*O,O′*); 1617 (w), 1503 (η^1-*O*)[b]
[Os(*O,O′*-acac)(η^1-*O*-acac)(η^6-C_6Me_6)]	C_6D_6	1.76 (s, 6H) (*O,O′*)	5.52 (s, 1H) (*O,O′*); 5.00 (s, 1H) (η^1-*O*)		1.84 (s, 18H)	1580, 1526 (*O,O′*); 1624 (m), 1499 (η^1-*O*)
		2.46 (s, 3H), 2.99 (s, 3H) (η^1-*O*)				1579, 1523 (*O,O′*); 1620 (w), 1502 (η^1-*O*)[b]

[a] ν(C=O), ν(C=C) of acac (KBr, cm^{-1}); bands are strong or very strong except where indicated.
[b] In CH_2Cl_2.



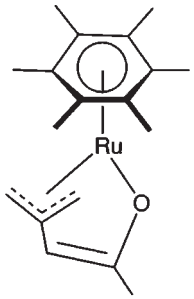
M = Ru, Os; R = H, Me

7

trans-[Pt(η^1-*O*-acac)$_2$($C_5H_{10}NH)_2$] appear at somewhat different frequencies, namely 1650 (s) and 1605 (m) cm^{-1} (13) and 1621 (vs) and 1583 (w) cm^{-1} (14), respectively, so that conclusions based on IR data must be treated with caution. Nevertheless, the proposed structures have been confirmed by single crystal X-ray diffraction studies (see below).

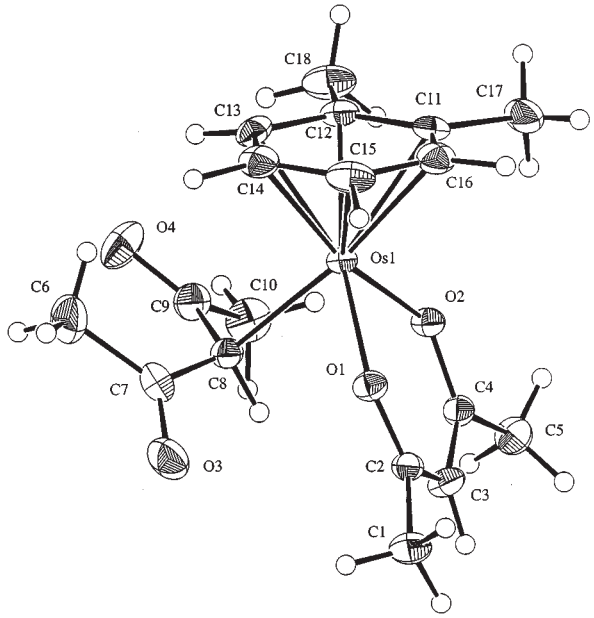
Although the ^{1}H NMR spectrum of [Ru(acac)$_2$(η^6-C_6Me_6)] in coordinating solvents such as acetone and acetonitrile is similar to that in $CDCl_3$ or CD_2Cl_2, the behaviour in methanol is different and suggestive of selective protonation of the acac ligands. At 28°C in methanol-d_4 there is one broad resonance at δ ca. 1.97 arising from the methyl protons of both acac ligands; the methine protons exchange rapidly with residual protons in the solvent and appear as a singlet at δ 4.77 (2H). It should be noted that the methine proton of [RuCl(acac)(η^6-C_6Me_6)] undergoes a similar but slower process at room temperature, complete exchange requiring ca. 100 h. At 7°C the ^{1}H NMR spectrum of [Ru(acac)$_2$(η^6-C_6Me_6)] in methanol-d_4 contains two broad methyl singlets of approximately equal intensity at δ 1.93 and ca. 2.01, the latter being partly obscured by the C_6Me_6 singlet. At this temperature, protonation of the monodentate ligand and subsequent rapid exchange between coordinated and uncoordinated acetylacetone averages the methyl environments of the enolate ligand, whereas at 28°C this process is rapid for both acac ligands. Only at –3°C in methanol-d_4 do the expected three acac methyl singlets appear.

The acac methyl protons of [Ru(acac)$_2$(η^6-C_6Me_6)] exchange completely with CH_3OD over a period of 3 days at room temperature, and the IR spectrum of the resulting deuterated complex shows characteristic shifts of the ν(C=O), ν(C=C) bands to ca. 1560 and 1480 cm^{-1} (15). A plausible intermediate in this process is **8**, which contains



8

Fig. 2. Molecular structure of [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)] with selected atom labeling. Thermal ellipsoids in the ORTEP plot show 30% probability levels.



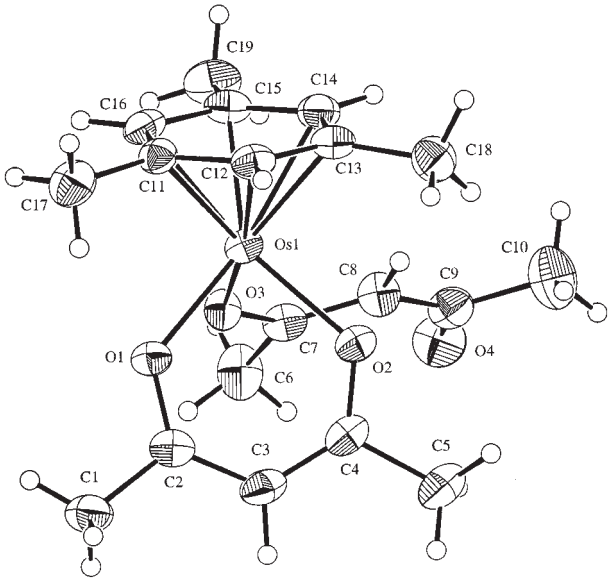
η^3-acetylacetonate dianion derived by deprotonation of the intermediate [Ru(*O*,*O*′-acac) (solvent)(η^6-C_6Me_6)]$^+$. Examples of this mode of coordination are known for palladium(II) (16) and platinum(II) (17).

Structures determined by X-ray crystallography

The molecular structures of [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)], [Os(*O*,*O*′-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)], and [Os(η^1-OAc)(*O*,*O*′-acac)(η^6-C_6H_6)] are shown in Figs. 2–4, respectively, with atom labeling. They confirm the conclusions drawn above on the basis of spectroscopic data. Selected bond lengths and angles of these three compounds are listed in Tables 4–6, respectively.

All three compounds contain an almost planar η^6-arene ring attached to an osmium atom that is coordinated trigonally by a bidentate *O*,*O*′-bonded acac and a monodentate ligand. In the first compound, the η^1-acac group is bound through carbon atom C(8), the Os(1)–C(8) vector approximately eclipsing one of the Os–C(arene) vectors (Os(1)–C(13)). The orientation of the η^6-arene ring places its two methyl groups well away from the $COCH_3$ substituents of the η^1-acac group. The C=O groups of η^1-acac adopt a mutually *anti*-orientation, and their bond lengths are as expected (1.221(5), 1.235(5) Å). The Os(1)—C(8) bond length (2.233(4) Å) is slightly but significantly greater than the limited number of reported Os(II)—CH_3 and Os(II)—C sp^3 distances, which fall in the range of 2.17–2.21 Å (18–21). In the second compound, the η^1-acac group is bound through one of the keto-oxygen atoms, i.e., it acts as a η^1-enolate; the Os—O vectors of the trigonal array almost eclipse the methyl-bearing carbon atoms of the η^6-arene ring. The Os—O(η^1-acac) distance (2.099(5) Å) is just significantly greater than the Os—O (*O*,*O*′-acac) distances (2.078(5), 2.072(5) Å). The geometry and metrical parameters of the enolate fragment are similar to those observed in the acetylacetonato derivatives *trans*-[Rh(η^1-*O*-acac)(CO)L_2] (L = P(*i*Pr)$_3$, PCy_3) (12, 22),

Fig. 3. Molecular structure of [Os(*O,O′*-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)] with selected atom labeling. Thermal ellipsoids in the ORTEP plot show 30% probability levels.



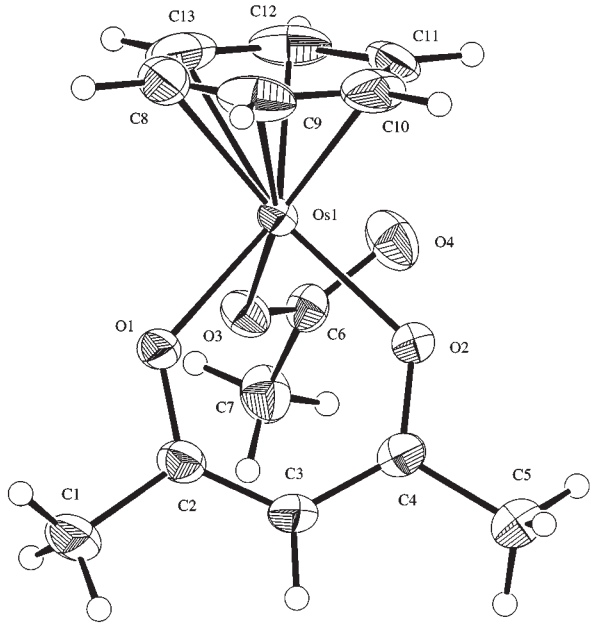
[$Cr(CO)_5${$PPh(\eta^1$-*O*-acac$)_2$}] (23), and [$Mn(\eta^5$-$C_5H_5)(CO)_2${$PPh_2(\eta^1$-*O*-acac)}] (24), and in the trifluoroacetylacetonato complex [Pd(*O,O′*-tfac)(η^1-*O*-tfac){P(*o*-tolyl)$_3$}] (25); the enolate group is almost planar, the Os-O and $COCH_3$ groups are mutually *trans* about the C—C bond, and the C=C and C=O groups are mutually *cis*. As expected, the C—O bond length of the bound enolate (1.301(9) Å) is greater than that of the uncoordinated C=O group (1.23(1) Å). The structure of [Os(η^1-OAc)(*O,O′*-acac)(η^6-C_6H_6)] confirms that the acetato group is monodentate, the Os—O bond length (2.077(3) Å) being similar to those to the *O,O′*-acac unit (2.074(3), 2.064(3) Å). In contrast to the two structures discussed above, the Os—O vectors of the trigonal array do not eclipse the arene carbon atoms.

Experimental

General procedures

All experiments were performed under an inert atmosphere with use of Schlenk techniques, and all solvents were dried and degassed by standard methods before use. ^{1}H NMR spectra were measured on Varian HA-100 or Jeol MH-100 spectrometers at 100 MHz or on Varian Gemini 300-BB or VXR-300 spectrometers at 300 MHz. Chemical shifts (δ) are in ppm referenced to residual proton signals of the solvent; coupling constants (*J*) are in Hz. IR spectra in the range 4000–400 cm^{-1} were recorded as KBr discs or Nujol™ mulls, or as CH_2Cl_2 solutions in 0.1 mm pathlength cells, on PerkinElmer PE 457 or 683 spectrometers. IR spectra in the range 450–150 cm^{-1} were measured as polythene discs on a PerkinElmer FT-1800 instrument. Electron impact (EI) mass spectra at 70 eV were measured on AEI–MS 902 or VG Micromass 7070 F spectrometers. ^{1}H NMR and selected IR data are collected in Tables 1–3; elemental analyses, which were carried out in-house, are listed in Tables 7 and 8.

Fig. 4. Molecular structure of [Os(*O,O′*-acac)(η^1-O_2CMe)(η^6-C_6H_6)] with selected atom labeling. Thermal ellipsoids in the ORTEP plot show 30% probability levels.



Starting materials

Hydrated ruthenium chloride and osmium tetraoxide were obtained from Johnson Matthey, U.K. The acetylacetonates of sodium and thallium were prepared by literature procedures (34, 35). Most of the [$MCl_2(\eta^6$-arene)]$_2$ complexes were made by reaction of the appropriate cyclohexa-1,3-diene or cyclohexa-1,4-diene with hydrated $RuCl_3$ or Na_2OsCl_6 in refluxing ethanol (27–29). The previously unknown compound [$OsCl_2$ (η^6-1,2,3-$C_6H_3Me_3$)]$_2$ was made in this way as orange microcrystals in 67% yield from Na_2OsCl_6 and a mixture of dihydro-isomers obtained by Li–NH_3 reduction of the arene. Anal. calcd. for $C_9H_{12}Cl_2Os$: C 28.35, H 3.2; found: C 27.8, H 2.8. The hexamethylbenzene complexes [$MCl_2(\eta^6$-$C_6Me_6)]_2$ were prepared by fusion of the corresponding *p*-cymene complexes with an excess of hexamethylbenzene (19, 30, 31). Since cyclohexa-1,3-diene undergoes extensive polymerization on heating with osmium chlorides, we prepared [$OsI_2(\eta^6$-$C_6H_6)]_2$ (32), converted it into the bis(acetate) by treatment with AgOAc for 2 days, and treated the bis(acetate) with conc. HCl to give [$OsCl_2(\eta^2$-$C_6H_6)]_2$ (33).

Preparations

*[RuCl(*O,O′*-acac)(η^6-arene)]*

(*i*) A mixture of [$RuCl_2(\eta^6$-$C_6H_6)]_2$ (200 mg, 0.40 mmol) and Tl(acac) (244 mg, 0.80 mmol) suspended in dichloromethane (15 mL) was stirred for 2 h and then filtered through Celite™ to remove the precipitated TlCl. The orange crystalline product [RuCl(*O,O′*-acac)(η^6-C_6H_6)], which formed on cooling the filtrate, was separated by filtration, washed with ether, and dried in vacuo. The yield was 165 mg (66%). Similarly prepared from [$RuCl_2(\eta^6$-1,3,5-$C_6H_3Me_3)]_2$ or [$RuCl_2(\eta^6$-$C_6Me_6)]_2$ and Tl(acac) with periods of stirring of 2 h and 10 min, respectively, were

Table 4. Selected bond distances and angles in [Os(*O,O′*-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)].

Bond distances (Å)			
Os(1)—O(1)	2.076(2)	Os(1)—O(2)	2.078(2)
Os(1)—C(8)	2.233(4)	Os(1)—C(11)	2.207(4)
Os(1)—C(12)	2.195(3)	Os(1)—C(13)	2.156(3)
Os(1)—C(14)	2.189(4)	Os(1)—C(15)	2.177(4)
Os(1)—C(16)	2.218(4)	O(1)—C(2)	1.289(4)
O(2)—C(4)	1.277(4)	O(3)—C(7)	1.221(5)
O(4)—C(9)	1.235(5)	C(1)—C(2)	1.503(5)
C(2)—C(3)	1.388(5)	C(3)—C(4)	1.389(5)
C(4)—C(5)	1.506(5)	C(6)—C(7)	1.511(6)
C(7)—C(8)	1.481(6)	C(8)—C(9)	1.483(5)
C(9)—C(10)	1.495(6)	C—C(arom)	1.405(6)–1.431(6)
C(arom)—CH_3	1.508(6), 1.509(6)		
Bond angles (°)			
O(1)-Os(1)-O(2)	86.82(9)	O(1)-Os(1)-C(8)	83.6(1)
O(2)-Os(1)-C(8)	83.0(1)	O(1)-C(2)-C(1)	114.8(3)
O(1)-C(2)-C(3)	125.7(3)	C(2)-C(3)-C(4)	125.7(3)
O(2)-C(4)-C(3)	125.4(3)	O(2)-C(4)-C(5)	115.1(3)
Os(1)-O(1)-C(2)	126.8(2)	Os(1)-O(2)-C(4)	127.5(2)
Os(1)-C(8)-C(7)	108.7(3)	Os(1)-C(8)-C(9)	107.7(3)
C(7)-C(8)-C(9)	120.2(3)	C(6)-C(7)-C(8)	120.7(4)
O(3)-C(7)-C(8)	120.8(4)	O(4)-C(9)-C(8)	124.4(4)
O(4)-C(9)-C(10)	119.2(4)	C(8)-C(9)-C(10)	116.4(3)

Table 5. Selected bond distances and angles in [Os(*O,O′*-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)].

Bond distances (Å)			
Os(1)—O(1)	2.078(5)	Os(1)—O(2)	2.072(5)
Os(1)—O(3)	2.099(5)	Os(1)—C(11)	2.175(8)
Os(1)—C(12)	2.172(8)	Os(1)—C(13)	2.173(8)
Os(1)—C(14)	2.172(8)	Os(1)—C(15)	2.159(8)
Os(1)—C(16)	2.178(8)	O(1)—C(2)	1.278(9)
O(2)—C(4)	1.282(9)	O(3)—C(7)	1.301(9)
O(4)—C(9)	1.23(1)	C(1)—C(2)	1.50(1)
C(2)—C(3)	1.40(1)	C(3)—C(4)	1.37(1)
C(4)—C(5)	1.51(1)	C(6)—C(7)	1.50(1)
C(7)—C(8)	1.36(1)	C(8)—C(9)	1.43(1)
C(9)—C(10)	1.51(1)	C—C(arom)	1.39(1)–1.45(1)
C(arom)—CH_3	1.49(1)–1.51(1)		
Bond angles (°)			
O(1)-Os(1)-O(2)	87.2(2)	O(1)-Os(1)-O(3)	78.4(2)
O(2)-Os(1)-O(3)	83.5(2)	O(1)-C(2)-C(1)	114.7(8)
O(1)-C(2)-C(3)	126.0(8)	C(2)-C(3)-C(4)	125.1(8)
O(2)-C(4)-C(3)	126.7(8)	O(2)-C(4)-C(5)	113.2(8)
C(1)-C(2)-C(3)	119.3(8)	C(3)-C(4)-C(5)	120.1(8)
Os(1)-O(1)-C(2)	126.2(6)	Os(1)-O(2)-C(4)	125.4(6)
Os(1)-O(3)-C(7)	128.8(5)	O(3)-C(7)-C(8)	125.9(7)
C(6)-C(7)-C(8)	122.5(8)	C(7)-C(8)-C(9)	128.4(8)
O(4)-C(9)-C(8)	127.4(9)	O(4)-C(9)-C(10)	116.6(8)
C(8)-C(9)-C(10)	116.0(8)		

Table 6. Selected bond distances and angles in [Os(η^1-OAc)(*O,O′*-acac)(η^6-C_6H_6)].

Bond distances (Å)			
Os(1)—O(1)	2.074(3)	Os(1)—O(2)	2.064(3)
Os(1)—O(3)	2.077(3)	Os(1)—C(8)	2.135(7)
Os(1)—C(9)	2.131(7)	Os(1)—C(10)	2.126(6)
Os(1)—C(11)	2.148(6)	Os(1)—C(12)	2.128(6)
Os(1)—C(13)	2.152(7)	O(1)—C(2)	1.282(6)
O(2)—C(4)	1.272(6)	O(3)—C(6)	1.283(6)
O(4)—C(6)	1.219(6)	C(1)—C(2)	1.501(7)
C(2)—C(3)	1.368(8)	C(3)—C(4)	1.390(8)
C(4)—C(5)	1.489(8)	C(6)—C(7)	1.503(8)
C(7)—C(8)	1.481(6)	C(8)—C(9)	1.483(5)
C—C(arom)	1.32(1)–1.46(1)		
Bond angles (°)			
O(1)-Os(1)-O(2)	87.4(1)	O(1)-Os(1)-O(3)	77.9(1)
O(2)-Os(1)-O(3)	82.4(1)	Os(1)-O(1)-C(2)	126.9(3)
Os(1)-O(2)-C(4)	127.2(3)	Os(1)-O(3)-C(6)	126.1(3)
O(1)-C(2)-C(1)	114.7(5)	O(1)-C(2)-C(3)	125.0(5)
C(1)-C(2)-C(3)	120.2(5)	C(2)-C(3)-C(4)	127.1(5)
O(2)-C(4)-C(3)	125.3(5)	O(2)-C(4)-C(5)	114.8(5)
C(3)-C(4)-C(5)	119.8(5)	O(3)-C(6)-O(4)	126.1(5)
O(3)-C(6)-C(7)	113.2(5)		

[RuCl(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)] (81%) and [RuCl(*O,O′*-acac)(η^6-C_6Me_6)] (82%).

(*ii*) A suspension of [$RuCl_2$(η^6-C_6H_6)]$_2$ (200 mg, 0.40 mmol) and Na(acac) (99 mg, 0.81 mmol) in dichloromethane–methanol (1:1) (15 mL) was stirred for 2 h at room temperature. The solution was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane and the solution was filtered. Addition of ether to the filtrate and cooling gave orange crystals of the product, which were separated by filtration, washed with ether, and dried in vacuo. The yield was 150 mg (60%). The complexes [RuCl(*O,O′*-acac)(η^6-arene)] (arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6) were prepared similarly, with periods of stirring of 2 h and 15 min, respectively, in yields of 60 and 85%, respectively.

(*iii*) A mixture of [$RuCl_2$(η^6-C_6H_6)]$_2$ (200 mg, 0.40 mmol) and an excess of anhyd Na_2CO_3 (1 g) was suspended in DMF (5 mL) and stirred for 10 min at 100°C. The solution was filtered and methanol was added to the filtrate. The orange crystals that separated on cooling were washed with ether and dried in vacuo. The yield was 65 mg (26%).

Similarly prepared were [RuCl(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)] (63%) and [RuCl(*O,O′*-acac)(η^6-C_6Me_6)] (29%), the mixture being heated for only 2 min in the latter case.

*[RuCl(*O,O′*-hfacac)(η^6-arene)]*

(*i*) A solution of Tl(hfacac) (197 mg, 0.48 mmol) in dichloromethane (20 mL) was cooled to 0°C and treated with [$RuCl_2$(η^6-C_6H_6)]$_2$ (200 mg, 0.40 mmol). The suspension was stirred for 1 min and filtered at 0°C. Addition of ether to the filtrate gave [RuCl(*O,O′*-hfacac)(η^6-C_6H_6)] as an orange crystalline solid, which was separated by filtration, washed with ether, and dried in vacuo. The yield was 135 mg (67%). The complex [RuCl(*O,O′*-hfacac)(η^6-1,3,5-$C_6H_3Me_3$)] was

Table 7. Elemental analyses for Ru(acac)(η^6-arene) complexes.

	%C		%H		%Other	
Complex	Calcd.	Found	Calcd.	Found	Calcd.	Found
[RuCl(*O,O′*-acac)(η^6-C_6H_6)][a]	42.0	42.15	4.5	4.4	11.3 (Cl)	12.0 (Cl)
[RuCl(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)][b]	47.2	47.6	5.7	5.6	9.9 (Cl)	9.8 (Cl)
[RuCl(*O,O′*-acac)(η^6-C_6Me_6)][c]	51.3	51.25	6.3	6.3	8.9 (Cl)	8.7 (Cl)
[RuCl(*O,O′*-hfacac)(η^6-C_6H_6)]	31.3	31.6	1.7	1.7	8.4 (Cl)	8.7 (Cl)
[RuCl(*O,O′*-hfacac)(η^6-1,3,5-$C_6H_3Me_3$)]	36.3	35.5	2.8	3.1	7.6 (Cl)	8.1 (Cl)
[RuCl(*O,O′*-hfacac)(η^6-C_6Me_6)]	40.4	40.2	3.8	4.1	7.0 (Cl)	7.25 (Cl)
[Ru(*O,O′*-acac)(dmso)(η^6-C_6H_6)]BF_4	35.2	34.9	4.3	4.3	7.0 (S)	7.2 (S)
[Ru(*O,O′*-acac)(dmso)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	39.6	39.1	5.2	5.35	6.6 (S)	6.3 (S)
[Ru(*O,O′*-acac)(dmso)(η^6-C_6Me_6)]BF_4	43.3	43.4	5.9	5.9	6.1 (S)	5.7 (S)
[Ru(*O,O′*-acac)(MeCN)(η^6-C_6H_6)]BF_4	38.4	38.2	4.0	4.2	3.45 (N)	3.0 (N)
[Ru(*O,O′*-acac)(MeCN)(η^6-C_6Me_6)]BF_4	46.5	46.8	5.8	5.9	2.9 (N)	2.8 (N)
[Ru(*O,O′*-acac)(py)(η^6-C_6H_6)]BF_4	43.3	43.3	4.1	4.2	3.15 (N)	3.0 (N)
[Ru(*O,O′*-acac)(py)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	46.9	46.7	5.0	5.1	2.9 (N)	2.9 (N)
[Ru(*O,O′*-acac)(py)(η^6-C_6Me_6)]BF_4	50.0	49.8	5.7	5.9	2.65 (N)	2.5 (N)
[Ru(*O,O′*-acac)(CO)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	41.4	41.4	4.4	4.2		
[Ru(*O,O′*-acac)(CO)(η^6-C_6Me_6)]BF_4	45.3	45.2	5.3	5.3		
[Ru(*O,O′*-acac)(PPh_3)(η^6-C_6H_6)]BF_4	55.5	56.0	4.5	4.9		
[Ru(*O,O′*-acac)(PPh_3)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	57.4	57.3	5.1	5.2		
[Ru(*O,O′*-acac)(PPh_3)(η^6-C_6Me_6)]BF_4	59.1	59.1	5.7	5.7		
[Ru(*O,O′*-acac)(η^6-C_6H_6)]$_n$(BF_4)$_n$	36.4	36.2	4.8	3.2		
[Ru(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)]$_n$(BF_4)$_n$	42.5	41.3	5.0	4.8		
[Ru(*O,O′*-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	54.4	53.1	6.3	6.2		
[Ru(*O,O′*-acac)(η^1-*O*-acac)(η^6-C_6Me_6)][d]	57.25	56.5	7.0	7.2		

[a]MW calcd.: 315; found: 300 (osmometry in CH_2Cl_2).
[b]MW calcd.: 356; found: 364 (osmometry in CH_2Cl_2).
[c]%Ru calcd.: 25.4; found: 25.4. MW calcd.: 398; found: 392 (osmometry in CH_2Cl_2).
[d]%Ru calcd.: 21.9; found: 21.8. MW calcd.: 461; found: 407.

prepared similarly from [RuCl(η^6-1,3,5-$C_6H_3Me_3$)]$_2$ and Tl(hfacac).

(*ii*) A solution of [$RuCl_2$(η^6-C_6Me_6)]$_2$ (150 mg, 0.22 mmol) in dichloromethane (15 mL) was stirred for 1 min with Tl(hfacac) (185mg, 0.45 mmol) at room temperature and then filtered. The filtrate was evaporated to ca. half the volume and ether was added to give [RuCl(*O,O′*-hfacac)(η^6-C_6Me_6)] as a red crystalline solid. The yield was 143 mg (63%).

*[Ru(*O,O′*-acac)(η^6-arene)(L)]BF_4 (L = DMSO, MeCN, py, PPh_3)*

Equimolar quantities of [RuCl(*O,O′*-acac)(η^6-arene)] and $AgBF_4$ were stirred in acetone at room temperature for 5 min. The solution was filtered through Celite™, the filtrate was treated with an equimolar quantity of ligand L, and the solution stirred for 1 h. Evaporation to ca. half the volume and addition of ether gave the products as yellow microcrystalline solids, which could be recrystallized from dichloromethane–ether. Yields were 40–80%. L = DMSO: arene = C_6H_6: IR (KBr, cm^{-1}): 1124 (s) (S=O). ^{1}H NMR ($CDCl_3$) δ: 2.66 (s, *Me*$_2$SO). Arene = 1,3,5-$C_6H_3Me_3$: IR (KBr, cm^{-1}): 1123 (s) (S=O). ^{1}H NMR ($CDCl_3$) δ: 2.64 (s, *Me*$_2$SO). Arene = C_6Me_6: IR (KBr, cm^{-1}): 1124 (s) (S=O). ^{1}H NMR ($CDCl_3$) δ: 2.57 (s, *Me*$_2$SO). L = MeCN: arene = C_6H_6: IR (KBr, cm^{-1}): 2295 (w) (CN). ^{1}H NMR (CD_2Cl_2) δ: 2.32 (s, *Me*CN). Arene = C_6Me_6: IR (KBr, cm^{-1}): 2290 (w) (CN). ^{1}H NMR ($CDCl_3$) δ: 2.42 (s, *Me*CN). L = py: arene = C_6H_6: ^{1}H NMR ($CDCl_3$) δ: 7.44 (m, 2H), 7.84 (m, 1H), 8.47 (m, 2H) (py). Arene = 1,3,5-$C_6H_3Me_3$: ^{1}H NMR ($CDCl_3$) δ: 7.49 (m, 2H), 7.87 (m, 1H), 8.50 (m, 2H) (py). Arene = C_6Me_6: ^{1}H NMR ($CDCl_3$) δ: 7.52 (m, 2H), 7.88 (m, 1H), 8.14 (m, 2H) (py).

*[Ru(*O,O′*-acac)(η^6-arene)(CO]BF_4*

A solution of $AgBF_4$ (55 mg, 0.28 mmol) in acetone (15 mL) was saturated with CO and treated with [RuCl(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)] (100 mg, 0.28 mmol). The solution was stirred for 5 min while CO was bubbled into it, then filtered, and evaporated under reduced pressure to ca. 5 mL volume. Addition of ether caused the product, [RuCl(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)(CO)]BF_4, to form as a yellow microcrystalline solid, which was separated by filtration, washed with ether, and dried in vacuo. The yield was 50 mg (41%). IR (KBr, cm^{-1}): 2045 (vs) (CO). A similar procedure was used to prepare [RuCl(*O,O′*-acac)(η^6-C_6Me_6)(CO)]BF_4 from [RuCl(*O,O′*-acac)(η^6-C_6Me_6)]. Evaporation to dryness of the filtered acetone solution gave an oil, which was dissolved in the minimum volume of dichloromethane. Addition of ether gave the product as a pale yellow solid in 45% yield. IR (KBr, cm^{-1}): 2026 (vs) (CO).

[Ru(acac)(arene)]$_n$(BF_4)$_n$

To a solution of $AgBF_4$ (64 mg, 0.33 mmol) in acetone (15 mL) was added [RuCl(*O,O′*-acac)(η^6-C_6H_6)] (100 mg, 0.32 mmol). The mixture was stirred for 15 min and filtered. Evaporation of the filtrate to ca. 5 mL volume and addition of ether gave [Ru(acac)(η^6-C_6H_6)]$_n$(BF_4)$_n$ as a pale yellow

Table 8. Elemental analyses for Os(acac)(η^6-arene) complexes.

	%C		%H	
Complex	Calcd.	Found	Calcd.	Found
[OsCl(*O,O′*-acac)(η^6-C_6H_6)]	32.8	32.0	3.2	3.2
[OsCl(*O,O′*-acac)(η^6-1,2-$C_6H_4Me_2$)][a]	36.2	36.0	4.0	3.9
[OsCl(*O,O′*-acac)(η^6-1,2,3-$C_6H_3Me_3$)]	37.8	37.5	4.3	3.95
[OsCl(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	37.8	38.1	4.3	4.5
[OsCl(*O,O′*-acac)(η^6-C_6Me_6)]	41.9	42.5	5.2	5.6
[Os(η^1-O_2CMe)(*O,O′*-acac)(η^6-C_6H_6)]	36.6	37.2	3.8	4.4
[Os(η^1-O_2CMe)(*O,O′*-acac)(η^6-1,2-$C_6H_4Me_2$)]	39.6	40.3	4.4	4.7
[Os(η^1-O_2CMe)(*O,O′*-acac)(η^6-1,2,3-$C_6H_3Me_3$)]	41.0	40.4	4.7	5.1
[Os(η^1-O_2CMe)(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	41.0	40.6	4.7	5.0
[Os(η^1-O_2CMe)(*O,O′*-acac)(η^6-C_6Me_6)]	44.7	44.6	5.5	5.4
[Os(*O,O′*-acac)(η^1-*C*-acac)(η^6-C_6H_6)]	41.2	40.8	4.3	4.1
[Os(*O,O′*-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)]	43.7	43.3	4.9	4.7
[Os(*O,O′*-acac)(η^1-*C*-acac)(η^6-1,2,3-$C_6H_3Me_3$)]	44.9	43.9	5.15	4.9
[Os(*O,O′*-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	44.9	43.1	5.15	5.7
[Os(*O,O′*-acac)(η^1-O-acac)(η^6-C_6Me_6)]	48.0	46.7	5.9	5.7

[a]%Cl calcd.: 8.2; found: 8.2.

powder, which was separated by filtration and washed with ether. The yield was 30 mg (26%). IR (KBr, cm^{-1}): 1620 (vs) (C=O)–(C=C). The mesitylene analogue was prepared similarly in 31% yield. IR (KBr, cm^{-1}): 1620 (vs) (C=O), (C=C).

*[Ru(*O,O′*-acac)(CO)(MeCN)$_3$]BF$_4$*

Carbon monoxide was bubbled into a solution of [Ru(*O,O′*-acac)(η^6-C_6H_6) (MeCN)] BF_4 (100 mg, 0.24 mmol) in acetone (15 mL) for 5 min. The solution was filtered and the filtrate evaporated under reduced pressure to give a brown oil. This was dissolved in acetonitrile and to the filtered solution was added ether dropwise to precipitate [Ru(*O,O′*-acac)(CO)$(MeCN)_3$]BF_4 (20mg, 18%) as a pale yellow solid. IR(KBr, cm^{-1}): 2300 (vw) (CN), 1980 (vs) (CO), 1570 (vs) (C=O), (C=C) of acac. ^{1}H NMR ($CDCl_3$) δ: 2.00 (s, 6H, acac-CH_3), 2.51 (s, 3H), 2.54 (s, 6H, MeCN), 5.31 (s, 1H, acac-γ-C*H*). Anal. calcd. for $C_{12}H_{16}BF_4N_3O_3Ru$: C 32.9, H 3.8, N 9.6; found: C 32.9, H 3.7, N 9.6.

*[OsCl(*O,O′*-acac)(η^6-arene)]*

(*i*) A mixture of [$OsCl_2$(η^6-1,3,5-$C_6H_3Me_3$)]$_2$ (200 mg, 0.26 mmol) and Tl(acac) (160 mg, 0.53 mmol) was stirred in dichloromethane (10 mL) for 2 h at room temperature. The yellow solution was separated from the precipitated TlCl by decantation and filtered through Celite™. The solution was concentrated in vacuo and ether was added. Cooling in dry ice – acetone gave [OsCl(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)] as a yellow-brown solid (176 mg, 75%). Evaporation of the supernatant liquid gave more yellow-brown solid, which was shown by ^{1}H NMR spectroscopy to be an approximately 1:1 mixture of [OsCl(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)] and the acetato complex [Os(η^1-O_2CMe)(*O,O′*-acac)(η^6-1,3,5-$C_6H_3Me_3$)].

The complexes [OsCl(*O,O′*-acac)(η^6-arene)] (arene = 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$, and C_6Me_6) were prepared similarly from the corresponding [$OsCl_2$(η^6-arene)]$_2$ complexes in yields of 83, 74, and 73%, respectively.

(*ii*) The benzene complex can be made from [$OsCl_2$(η^6-C_6H_6)]$_2$ and Na(acac) as described for the ruthenium analogue (1(*ii*)) or as follows.

Addition of a few drops of acetyl chloride to a solution of [Os(*O,O′*-acac)(η^1-*C*-arene) (η^6-C_6H_6)](125 mg, 0.27 mmol) (see below) in methanol (4 mL) caused a precipitate to form immediately. The solvent was removed in vacuo and the residue was extracted with dichloromethane. The extract was filtered through Celite™, concentrated under reduced pressure, and cooled to give [OsCl(*O,O′*-acac)(η^6-C_6H_6)] (73 mg, 67%) in two crops.

*[Os(*η^1-O$_2$CMe*)(*O,O′*-acac)(*η^6-arene*)]*

A suspension of [OsCl(*O,O′*-acac)(η^6-C_6H_6)] (48 mg, 0.12 mmol) and silver acetate (21 mg, 0.13 mmol) in benzene (10 mL) was stirred overnight. The yellow solution was separated by decantation from the precipitated AgCl, filtered through Celite™, and evaporated to dryness. The resulting yellow solid [Os(η^1-O_2CMe)(*O,O′*-acac)(η^6-C_6H_6)] (47 mg, 92%) was spectroscopically and analytically pure.

The corresponding complexes containing 1,2-$C_6H_4Me_2$, 1,2,3-$C_6H_3Me_3$, 1,3,5-$C_6H_3Me_3$, and C_6Me_6 were prepared similarly in yields of 71, 95, 59, and 95%, respectively.

*[Ru(acac)$_2$(*η^6-arene*)]*

A mixture of [RuCl(*O,O′*-acac)(η^6-C_6H_6)] (200 mg, 0.64 mmol) and Tl(acac) (190 mg, 0.63 mmol) was stirred in methanol (10 mL) at –20°C for 2 h. The solution was evaporated to dryness, the residue was extracted with ether, and the extract was filtered, the temperature being kept below 0°C at all times. The filtrate was concentrated under reduced pressure to give [Ru(*O,O′*-acac)(η^1-*C*-acac)(η^6-C_6H_6)] as a microcrystalline red solid, which darkened when warmed to room temperature. The yield was 120 mg (51%).

The complexes [Ru(*O,O′*-acac)(η^1-*O*-acac)(η^6-arene)] (arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6) were prepared similarly from [RuCl(*O,O′*-acac)(η^6-arene)] in yields of 40 and 60%, respectively.

Table 9. Crystallographic data collection parameters for (η^6-arene)osmium complexes.

Complex	[Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)]	[Os(*O*,*O*′-acac)(η^1-*O*-acac)(η^6-1,3,5-$C_6H_3Me_3$)]	[Os(η^1-OAc)(*O*,*O*′-acac)(η^6-C_6H_6)]
Formula	$C_{18}H_{24}O_4Os$	$C_{19}H_{26}O_4Os$	$C_{13}H_{16}O_4Os$
FW	494.59	508.61	426.47
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	9.922(2)	16.032(4)	8.368(4)
b (Å)	9.974(2)	11.989(3)	8.402(4)
c (Å)	11.001(2)	21.562(7)	11.008(4)
α (°)	68.33(1)		71.68(3)
β (°)	64.18(1)	108.91(2)	69.35(3)
γ (°)	62.38 (1)		69.77(3)
V (Å^3)	849.0(3)	3921(2)	663.0(6)
Z	2	8	2
$\rho_{calcd.}$ (g cm^{-3})	1.935	1.723	2.133
Crystal size (mm)	0.38 × 0.37 × 0.08	0.25 × 0.20 × 0.17	0.40 × 0.23 × 0.04
Temperature (K)	296 ± 1	296 ± 1	296 ± 1
F (000)	480.00	1984.00	404.00
Colour, habit	Yellow, plate	Yellow, multifaceted	Orange, wedge
μ (cm^{-1})	75.22 (Mo Kα)	65.18 (Mo Kα)	96.01 (Mo Kα)
Diffractometer	Philips PW 1100/20	Philips PW 1100/20	Philips PW 1100/20
Data collection method	ω–2θ	ω–2θ	ω–2θ
ω-Scan width (°)	1.20 + 0.35 tan θ	1.0 + 0.35 tan θ	1.20 + 0.34 tan θ
2θ limits (°)	60.0	55.0	55.2
Total unique reflections	4949	4721	3064
Total observed reflections[a]	4508	2717	2738
Max/min transmission factor[b]	0.104–0.578	0.318–0.436	0.127–0.582
No. of parameters	281	217	164
Largest difference peak and hole (e Å^{-3})	1.73, –1.17	0.56, –1.63	0.85, –0.72
R[c]	0.023	0.032	0.023
R_w[c]	0.026	0.034	0.027
GoF[d]	1.54	1.53	1.50

[a] $I > 3\sigma(I)$.
[b] Analytical absorption correction.
[c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma\{w(|F_o| - |F_c|)\}/\Sigma(w|F_o|)^2]^{1/2}$.
[d] $\{\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)\}^{1/2}$, where N_o = number of observations, N_v = number of variables.

[Os(acac)$_2$(η^6-arene)]

(*i*) A mixture of [OsCl$_2$(η^6-C_6H_6)]$_2$ (100 mg, 0.15 mmol) and Tl(acac) (179 mg, 0.59 mmol) in methanol (10 mL) was stirred for 2 h. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane. The extracts were filtered through Celite™ and again evaporated to dryness. The residue was extracted with ether (ca. 20 mL) and the ether solution passed down a short column of Celite™. Concentration and cooling gave two crops (34 mg in total) of a yellow solid containing [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-C_6H_6)] contaminated by the acetato complex [Os(η^1-O_2CMe)(*O*,*O*′-acac)(η^6-C_6H_6)] (ca. 10–15%) as shown by ^{1}H NMR spectroscopy. An X-ray quality crystal of the latter was obtained by evaporation of the ether solution. A crystalline, spectroscopically and analytically pure sample of [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-C_6H_6)] was obtained by diffusion of pentane into a dichloromethane solution.

(*ii*) A mixture of [OsCl(*O*,*O*′-acac)(η^6-1,2-$C_6H_4Me_2$)] (130 mg, 0.30 mmol) and Tl(acac) (95 mg, 0.31 mmol) in methanol (10 mL) was stirred for 2 h giving a yellow solution and a colourless precipitate. The methanol was removed in vacuo and the residue was extracted with ether and filtered through Celite™. Concentration of the filtrate and cooling gave a yellow solid containing mainly [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)], as shown by ^{1}H NMR spectroscopy. The yield was 82 mg (55%). Evaporation of the supernatant liquid gave a further 34 mg of less pure product. Yellow-brown X-ray quality crystals of [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-1,2-$C_6H_4Me_2$)] were obtained by diffusion of hexane into a benzene solution of the first solid; these crystals also gave satisfactory microanalytical data. EI-MS (70 eV) *m*/*z* : 496.1 (M$^+$, based on ^{192}Os), 397 ([M – acac]$^+$).

(*iii*) Similarly prepared from OsCl(*O*,*O*′-acac)(η^6-1,2,3-$C_6H_3Me_3$)] (123 mg, 0.28 mmol) and Tl(acac) (85 mg, 0.28 mmol) in methanol, after extraction with dichloromethane (10 mL), was crude [Os(*O*,*O*′-acac)(η^1-*C*-acac)(η^6-1,2,3-$C_6H_3Me_3$)] (127 mg, 89%). Purification was carried out by extraction with ether as described above.

(*iv*) Reaction of [OsCl(*O*,*O*′-acac)(η^6-1,3,5-$C_6H_3Me_3$)] (150 mg, 0.34 mmol) with Tl(acac) (103 mg, 0.34 mmol) in

Table 10. Positional parameters and isotropic thermal parameters for non-hydrogen atoms of [Os(*O*,*O′*-acac)(η¹-*C*-acac)(η⁶-1,2-$C_6H_4Me_2$)].

Atom	*x*	*y*	z	B_{eq}[a]
Os(1)	0.18151(1)	0.29901(1)	0.29616(1)	2.147(2)
O(1)	0.0834(2)	0.5387(2)	0.2434(2)	2.66(4)
O(2)	0.2262(2)	0.3002(2)	0.0929(2)	2.58(3)
O(3)	0.3610(3)	0.5716(3)	0.2550(3)	4.90(7)
O(4)	0.6139(3)	0.0977(3)	0.2733(3)	5.25(6)
C(1)	0.0263(4)	0.7945(3)	0.1137(4)	3.79(7)
C(2)	0.0971(3)	0.6232(3)	0.1205(3)	2.53(4)
C(3)	0.1658(4)	0.5690(3)	–0.0004(3)	3.10(5)
C(4)	0.2185(3)	0.4161(3)	–0.0087(3)	2.60(5)
C(5)	0.2720(4)	0.3779(4)	–0.1467(3)	3.46(6)
C(6)	0.4659(5)	0.3523(5)	0.4125(5)	5.3(1)
C(7)	0.4089(4)	0.4306(4)	0.2879(4)	3.66(6)
C(8)	0.4134(3)	0.3380(3)	0.2066(3)	2.93(5)
C(9)	0.5454(4)	0.1867(4)	0.1873(4)	3.59(6)
C(10)	0.5934(4)	0.1407(4)	0.0553(4)	4.40(7)
C(11)	0.0695(4)	0.1278(3)	0.3566(3)	3.20(6)
C(12)	0.2231(4)	0.0511(3)	0.3749(3)	2.99(5)
C(13)	0.2572(4)	0.1076(4)	0.4562(3)	3.21(6)
C(14)	0.1433(5)	0.2344(4)	0.5184(3)	3.59(6)
C(15)	–0.0062(4)	0.3093(4)	0.4961(3)	3.81(6)
C(16)	–0.0450(4)	0.2542(4)	0.4196(4)	3.50(6)
C(17)	0.0315(6)	0.0780(5)	0.2650(4)	4.8(1)
C(18)	0.3515(5)	–0.0832(4)	0.3089(4)	4.65(8)

[a] $B_{eq} = 8\pi^2/3\{U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha\}$.

Table 11. Positional parameters and isotropic thermal parameters for non-hydrogen atoms of [Os(*O*,*O′*-acac)(η¹-*O*-acac)(η⁶-1,3,5-$C_6H_3Me_3$)].

Atom	*x*	*y*	*z*	B_{eq}[a]
Os(1)	0.19613(2)	–0.00494(3)	0.07174(1)	3.272(6)
O(1)	0.1366(4)	0.1412(4)	0.0270(3)	3.7(1)
O(2)	0.3051(3)	0.0912(4)	0.1204(3)	3.9(1)
O(3)	0.1456(3)	0.0597(4)	0.1427(3)	3.8(1)
O(4)	0.2731(5)	0.0444(5)	0.3525(3)	6.3(2)
C(1)	0.1030(6)	0.3303(7)	0.0065(4)	5.1(2)
C(2)	0.1626(6)	0.2405(7)	0.0447(4)	4.2(2)
C(3)	0.2398(6)	0.2700(7)	0.0949(5)	4.7(2)
C(4)	0.3048(6)	0.1972(7)	0.1282(4)	4.1(2)
C(5)	0.3877(6)	0.2402(8)	0.1782(5)	5.8(3)
C(6)	0.1229(6)	0.1159(9)	0.2389(5)	6.1(3)
C(7)	0.1809(6)	0.0591(6)	0.2062(4)	3.9(2)
C(8)	0.2600(6)	0.0126(7)	0.2407(4)	4.5(2)
C(9)	0.3027(6)	0.0113(8)	0.3100(4)	4.9(2)
C(10)	0.3951(7)	–0.037(1)	0.3333(5)	7.3(3)
C(11)	0.1396(5)	–0.0884(6)	–0.0222(4)	3.7(2)
C(12)	0.2331(6)	–0.0928(6)	0.0035(4)	4.0(2)
C(13)	0.2842(6)	–0.1326(6)	0.0573(4)	4.2(2)
C(14)	0.2417(6)	–0.1736(6)	0.1006(4)	4.4(2)
C(15)	0.1507(6)	–0.1695(6)	0.0859(4)	4.2(2)
C(16)	0.0976(6)	–0.1284(6)	0.0219(5)	4.2(2)
C(17)	0.0858(6)	–0.0386(8)	–0.0861(4)	5.5(2)
C(18)	0.3836(6)	–0.1249(8)	0.0787(5)	5.7(3)
C(19)	0.1055(7)	–0.2042(8)	0.1340(5)	6.0(3)

[a] B_{eq} defined as in Table 10.

methanol (10 mL) and work-up as described for the *o*-xylene preparation gave 150 mg (88%) of crude [Os(*O*,*O′*-acac)(η¹-*O*-acac)(η⁶-1,3,5-$C_6H_3Me_3$)] contaminated with the acetato complex. Yellow X-ray quality crystals of the former were obtained by diffusion of hexane into a benzene solution.

(*v*) Reaction of [OsCl(*O*,*O′*-acac)(η⁶-C_6Me_6)] (94 mg, 0.19 mmol) with Tl(acac) (60 mg, 0.20 mmol) in methanol (10 mL) and work-up as described above gave [Os(*O*,*O′*-acac)(η¹-*O*-acac)(η⁶-C_6Me_6)] (38 mg, 36%), which was ca. 90% pure, although ^{1}H NMR spectroscopy and elemental analyses indicated the presence of some of the acetato complex.

Molecular structure determinations

Crystals of [Os(*O*,*O′*-acac)(η¹-*C*-acac)(η⁶-1,2-$C_6H_4Me_2$)] and [Os(*O*,*O′*-acac)(η¹-*O*-acac)(η⁶-1,3,5-$C_6H_3Me_3$)] suitable for X-ray diffraction studies were obtained by vapour diffusion of hexane into benzene solutions. Crystals of [Os(*O*,*O′*-acac)(η¹-OAc)(η⁶-C_6H_6)] were obtained fortuitously from an ether solution of the crude η¹-*C*-acac complex. The crystal data and parameters for data collection are summarized in Table 9. The structures were solved by heavy atom Patterson methods (36) and expanded by use of Fourier techniques (37). Non-hydrogen atoms were refined anisotropically. Most of the hydrogen atoms were located in the difference electron density maps and the positions used to generate all the hydrogen atoms, assuming idealized geometry. For the *o*-xylene complex, the positional parameters for the hydrogen atoms were refined, the isotropic *B*-values being held fixed and tight restraints being imposed on distances and angles for the methyl groups only. For the mesitylene and benzene complexes, the hydrogen atoms were periodically recalculated but

Table 12. Positional parameters and isotropic thermal parameters for non-hydrogen atoms of [Os(*O*,*O′*-acac)(η¹-O_2CMe)(η⁶-C_6H_6)].

Atom	*x*	*y*	*z*	B_{eq}[a]
Os(1)	0.18666(2)	0.08777(2)	0.23193(2)	2.743(4)
O(1)	–0.0167(4)	0.2837(4)	0.3121(4)	3.53(7)
O(2)	0.2701(5)	0.2798(4)	0.0746(3)	3.61(7)
O(3)	0.3100(5)	0.1704(5)	0.3257(4)	3.77(8)
O(4)	0.5922(5)	0.0402(6)	0.2379(5)	5.2(1)
C(1)	–0.1831(9)	0.5568(8)	0.3596(7)	5.7(2)
C(2)	–0.0321(7)	0.4477(6)	0.2725(6)	3.8(1)
C(3)	0.0726(9)	0.5251(7)	0.1585(6)	4.8(1)
C(4)	0.2120(8)	0.4433(6)	0.0651(5)	3.9(1)
C(5)	0.2991(9)	0.5496(8)	–0.0612(6)	5.3(1)
C(6)	0.4775(7)	0.1353(7)	0.3078(5)	3.5(1)
C(7)	0.5256(8)	0.2229(9)	0.3847(6)	4.9(2)
C(8)	0.022(1)	–0.086(1)	0.326(1)	7.3(2)
C(9)	0.024(1)	–0.0307(9)	0.197(1)	6.4(2)
C(10)	0.183(2)	–0.0470(9)	0.0991(7)	7.4(2)
C(11)	0.346(1)	–0.127(1)	0.139(1)	7.7(2)
C(12)	0.327(1)	–0.1789(8)	0.275(1)	6.6(2)
C(13)	0.171(2)	–0.1610(9)	0.3631(8)	7.6(3)

[a] B_{eq} defined as in Table 10.

not refined. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weights w given by $w = |\sigma^2(F_o)|^{-1}$. The software packages used were Xtal (38) for data reduction and teXsan (39) for structure solution, refinement, and graphics. Neutral atom scattering factors were taken from ref. 40. Anomalous dispersion effects were included in F_{calc} (41); values of $\Delta f'$ and $\Delta f''$ and of mass attenuation coefficients were taken from standard compilations (42, 43). Selected bond distances and angles are given in Tables 4–6, atomic coordinates are listed in Tables 10–12.

Crystal data, complete tables of bond distances and angles, atomic coordinates, anisotropic thermal parameters for the non-hydrogen atoms, non-bonded contacts, and selected least-squares planes have been deposited.[2]

Conclusion

In this work, we have shown that the [M(*O*,*O*′-acac)(η^6-arene)] (M = Ru, Os) fragments are capable of binding a range of ligands containing nitrogen, phosphorus, oxygen, and sulfur donor atoms. The mode of binding of a second acac group depends on the nature of the arene. The fact that the preferred binding mode changes from η^1-*C* to η^1-*O* in going from 1,2,3- to 1,3,5-$C_6H_3Me_3$ suggests that there is a delicate balance, possibly mediated by a steric effect. The more symmetrical arrangement of ring methyl groups could give rise to an unavoidable steric repulsion between them and the $COCH_3$ groups of a η^1-*C*-acac group, thus favouring coordination of the sterically less demanding η^1-*O*- enolate form. However, on this basis alone, it is difficult to see why η^1-*C*-bonding should be favoured for the isoelectronic complexes of rhodium(III) and iridium(III) [M(*O*,*O*′-acac)(η^1-*C*-acac)(η^5-C_5Me_5)] (4), since the estimated average cone angles of Rh^{III}-C_5Me_5 and Ru^{II}-$C_6H_3Me_3$ are likely to be very similar (ca. 188°) (26). Another possibility is that, since the charge separation in an arene–metal bond in the sense (arene)(δ^+)–metal(δ^-) is probably greater than that in its isoelectronic C_5Me_5–metal counterpart, the negative charge on the metal may be better accommodated by the more electronegative oxygen atom of an O-bound enolate.

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List of Abbreviations

acac = acetylacetonate, 2,4-pentanedionato, $CH_3COCHCOCH_3$; tfacac = trifluoroacetylacetonato, 1,1,1-trifluoro-2,4-pentanedionato, $CF_3COCHCOCH_3$; hfacac = hexafluoroacetylacetonato, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato, $CF_3COCHCOCF_3$; cym = *p*-cymene, 1,4-$MeC_6H_4CHMe_2$; DMSO = dimethylsulfoxide; py = pyridine.