

Synthesis and crystal structures of the distorted pentagonal bipyramidal seven-coordinate acetylacetonate complexes $[M(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ ($M = \text{Mo}$ or W)

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Abstract

Equimolar quantities of $[M_2(\text{CO})_3(\text{PEt}_3)_2]$ ($M = \text{Mo}$ or W) and $\text{Na}[\text{acac}]$ react in a $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2/\text{EtOH}$ mixture at room temperature to give high yields of the seven-coordinate complexes $[M(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ (**1** and **2**). The crystal structures of **1** and **2**, while not isomorphous, show similar seven-coordination geometries with the acetylacetonate ligand coordinating in a bidentate manner. The geometry around these complexes can best be described as distorted pentagonal bipyramidal with one carbonyl and iodine in the axial positions and the acetylacetonate ligand, two phosphine ligands and one carbonyl group in equatorial positions. Spectroscopic data for **1** and **2** are reported. © 1997 Elsevier Science S.A.

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1. Introduction

Although a large number of six- and seven-coordinate complexes of molybdenum(II) and tungsten(II) containing dithiocarbamates and related ligands have been described [1–11], hitherto very few analogous complexes containing bidentate anionic oxygen donor ligands such as acetylacetonate have been reported. In 1986, Riera et al. [12] described the preparation and characterisation of the seven-coordinate complexes $[\text{MoBr}(\text{XOCR})(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{X} = \text{O}$, $\text{R} = \text{H}$, Me , Ph , CCl_3 ; $\text{X} = \text{S}$, $\text{R} = \text{Me}$, Ph). Similarly, in the same year Templeton et al. [13] described the reactions of $[\text{MCl}_2(\text{CO})_3\text{L}_2]$ ($M = \text{Mo}$ or W ; $\text{L} = \text{PEt}_3$ or PPh_3) with $\text{Na}[\text{O}^-\text{O}]$ ($\text{O}^-\text{O} = \text{acetylacetonate}$ or hexafluoroacetylacetonate, hfacac) to give the seven-coordinate complexes $[\text{MCl}(\text{O}^-\text{O})(\text{CO})_2\text{L}_2]$. Brisdon et al. [14] have reported the crystal structures of

$[\text{MoBr}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ and $[(\text{WBr}(\text{CO})_2(\text{PMe}_2\text{Ph})_2)_2(\mu\text{-C}_2\text{O}_4)]$, while Batschelet et al. have described the preparation [15] and crystal structures [16] of the seven-coordinate 5,7-dichloro-8-quinolato complexes $[\text{WCl}(\text{dcq})(\text{CO})_3(\text{PPh}_3)]$ ($\text{dcq} = 5,7\text{-dichloro-8-quinolato}$), $[\text{W}(\text{dcq})_2(\text{CO})_2(\text{PPh}_3)]$ and $[\text{WCl}(\text{dcq})(\text{CO})_2(\text{PPh}_3)]$. The importance of preparing this type of complex is highlighted since the active site of the nitrogenase enzyme has been shown [17–19] to have a bidentate anionic oxygen homocitrate ligand attached to a molybdenum centre.

In 1991, we described [20] the synthesis and characterisation of a series of iodo-seven-coordinate complexes of the types $[\text{MI}(\text{O}^-\text{O})(\text{CO})_3(\text{PPh}_3)]$ ($M = \text{Mo}$ or W ; $\text{O}^-\text{O} = \text{acac}$, hfacac or $\text{benzoylacetylacetonate}$ (bzacac)) and $[\text{MI}(\text{O}^-\text{O})(\text{CO})_2(\text{PPh}_3)_2]$ ($M = \text{Mo}$ or W ; $\text{O}^-\text{O} = \text{acac}$, hfacac or bzacac), however we could not obtain suitable single crystals for X-ray crystallography on any of these complexes. We describe in this paper how, in order to obtain suitable single crystals for X-ray crystallography, we used the reactions of the considerably more soluble complexes

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$[\text{Ml}_2(\text{CO})_3(\text{PEt}_3)_2]$ ($\text{M} = \text{Mo}$ or W) [21], with one equivalent of $\text{Na}[\text{acac}]$ to give the crystalline complexes $[\text{Ml}(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ which have been crystallographically characterised.

2. Results and discussion

The reactions of $[\text{Ml}_2(\text{CO})_3(\text{PEt}_3)_2]$ ($\text{M} = \text{Mo}$ or W) with one equivalent of $\text{Na}[\text{acac}]$ gave the new seven-coordinate complexes $[\text{Ml}(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ (**1**) ($\text{M} = \text{Mo}$ or W) in high yield. The complexes have been characterised by elemental analysis, IR spectroscopy and ^1H NMR spectroscopy (see Section 3). Both complexes are red-orange in colour and are very soluble in chlorinated solvents such as dichloromethane. The complexes are both relatively air-stable in the solid state and can be handled in air for several minutes without any discernable decomposition.

The IR spectra of **1** and **2** show two strong carbonyl bands in CH_2Cl_2 solution and in the solid state, consistent with the single *cis*-dicarbonyl isomer, observed by X-ray crystallography (see Section 3.2). Carbonyl stretches for the bound acetylacetonate ligand are observed at ca. 1550 cm^{-1} , lower frequency, compared to the uncoordinated group.

Suitable crystals of complexes **1** and **2** for X-ray structure determination have been grown as described in Section 3; the structures are shown in Figs. 1 and 2 with the atomic numbering schemes. The crystal data and selected bond lengths and angles can be found in Tables 1 and 2, respectively.

The two molecular structures, though not isomorphous, are very similar as is shown by the dimensions in the metal coordination sphere listed in Table 2. Because of the similar sizes of the metal ions, there is very little difference in the bond lengths and in addition the angles subtended at the metal are very similar, the maximum difference in an equivalent angle being 7.5° , the significant differences are in the positions of the ethyl groups.

The geometry of the coordination sphere is highly distorted but can be described as a pentagonal bipyramid with approximate mirror symmetry passing through the metal, two axial atoms C(100) and I(2) and one equatorial atom C(200). The remainder of the equatorial plane contains the two phosphine ligands and the two oxygen atoms of the acetylacetonate ligand. The geometries are therefore very different from those observed in the four seven-coordinate structures mentioned above; namely $[\text{MoBr}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ [14], $[\text{WBr}(\text{CO})_2(\text{PMe}_2\text{Ph})_2]_2(\mu\text{-C}_2\text{O}_4)$ [14],

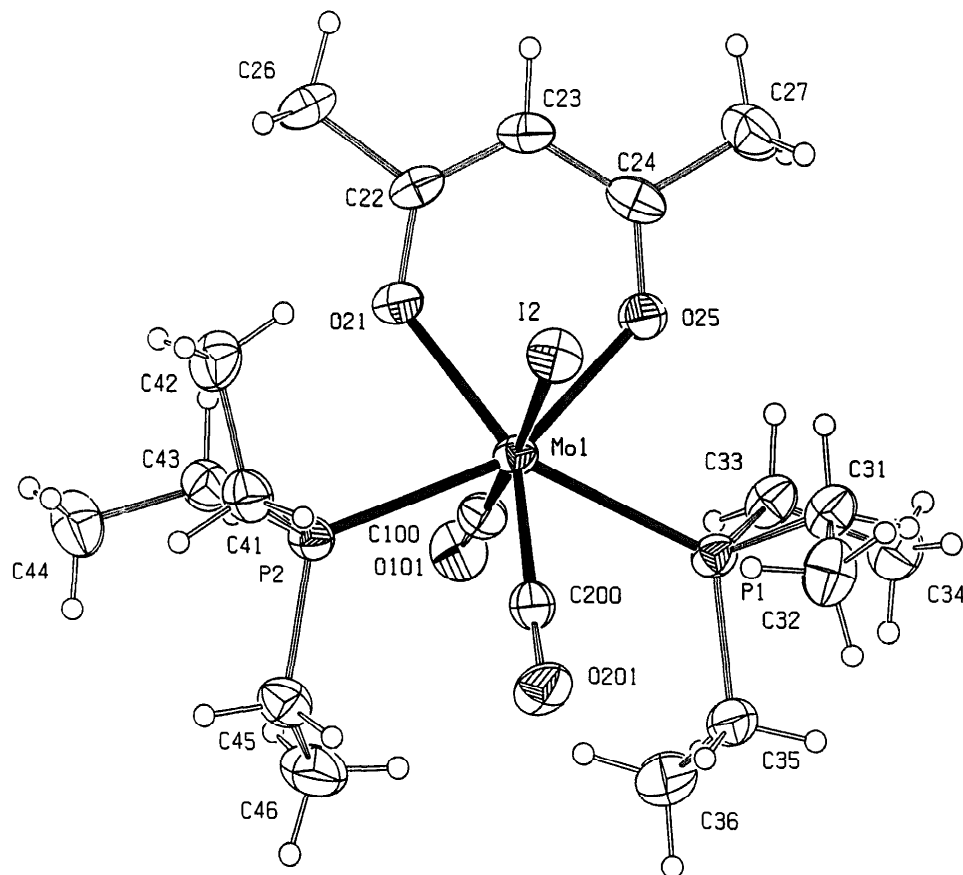


Fig. 1. X-ray crystal structure of the complex $[\text{Mo}(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ (**1**). Thermal ellipsoids shown at 30% probability. Hydrogen atoms included with small arbitrary radii.

[WCl(dcq)(CO)₃(PPh₃)] [16] and [W(dcq)₂(CO)₂(PPh₃)] [16] which have geometries intermediate between the capped trigonal prism and the capped octahedron though most structures conform more to the former with the bidentate O–O ligand in the capped face and coplanar with two other donor atoms. These present structures are therefore unique with the acac ligand in the equatorial plane of a pentagonal bipyramid.

While the C(100)–M–I(2) axial angle is close to 180° the remaining angles are far from ideal and axial–M–equatorial angles range from 76 to 103°. It seems likely that the major cause of the distortion arises from the chelate angle in the acetylacetonate which is 80.7 (3) in (1) and 81.7 (6) in (2), greater than the ideal 72° in the equatorial plane.

The ¹H NMR spectra of complexes 1 and 2 are consistent with the structures shown in Figs. 1 and 2. The ¹³C{¹H} NMR (CD₂Cl₂, 25°C) spectra of complexes 1 and 2 are very similar, suggesting very closely related structures in solution. The molybdenum complex 1 shows a carbonyl resonance at 237 ppm which corre-

sponds to the *cis*-carbonyl ligands. This suggests the two carbonyl ligands are equivalent in solution at ambient temperatures.

3. Experimental details

Both new preparations were carried out at room temperature under a stream of dry nitrogen using standard vacuum/Schlenk line techniques. The complexes [M₂(CO)₃(PEt₃)₂] were prepared as previously described [21]. All chemicals were purchased from commercial sources.

Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). IR spectra were recorded both as thin CH₂Cl₂ films between NaCl plates or in the solid state as KBr discs on a Perkin-Elmer 1600 series FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a JEOL FX 270 NMR spectrometer (all NMR spectra were referenced to SiMe₄).

Table 1
Crystal data and structure refinement for 1 and 2

Compound	Mo(CO) ₂ (acac)(PEt ₃) ₂ I	W(CO) ₂ (acac)(PEt ₃) ₂ I
Empirical formula	C ₁₉ H ₃₇ IMoO ₄ P ₂	C ₁₉ H ₃₇ IWO ₄ P ₂
Formula weight	614.27	702.18
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions		
<i>a</i> (Å)	12.707(13)	16.749(14)
<i>b</i> (Å)	15.691(14)	10.499(11)
<i>c</i> (Å)	13.623(14)	16.793(14)
β (deg)	103.46(1)	117.07(1)
Volume (Å) ³	2642	2630
<i>Z</i>	4	4
Density (calculated) (mg/m ³)	1.545	1.774
Absorption coefficient (mm ⁻¹)	1.805	5.708
<i>F</i> (000)	1232	1360
Crystal size (mm)	0.32 × 0.25 × 0.25	0.25 × 0.25 × 0.35
θ range for data collection (deg)	2.36 to 25.10	2.33 to 25.20
Index ranges	0 ≤ <i>h</i> ≤ 15 –18 ≤ <i>k</i> ≤ 18 –16 ≤ <i>l</i> ≤ 15	–20 ≤ <i>h</i> ≤ 19 0 ≤ <i>k</i> ≤ 11 –17 ≤ <i>l</i> ≤ 18
Reflections collected	8250	6263
Independent reflections [<i>R</i> (int)]	4587 [0.0635]	3768 [0.1019]
Weighing Scheme (<i>a</i> , <i>b</i>) ^a	0.165, 0.000	0.247, 0.000
Data/restraints/parameters	4582/0/253	3768/0/253
Goodness-of-fit on <i>F</i> ²	1.023	0.978
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] <i>R</i> 1	0.0736	0.0935
<i>wR</i> 2	0.1862	0.2576
<i>R</i> indices (all data) <i>R</i> 1	0.0977	0.1822
<i>wR</i> 2	0.2064	0.3131
Extinction coefficient	0.027(2)	0.002(1)
Largest diff. peak and hole (e Å ⁻³)	3.173 –1.976	2.959 –3.179

^aWeighting scheme $w = 1/(\sigma^2(F^2) + (aP)^2 + bP)$, where $P = (F^2 + 2F_c^2)/3$.

Table 2
Bond lengths [Å] and angles [deg] for **1** and **2**

	(1) M = Mo	(2) M = W
M(1)–C(100)	1.950(11)	1.94(3)
M(1)–C(200)	1.994(10)	1.96(3)
M(1)–O(21)	2.158(6)	2.14(2)
M(1)–O(25)	2.161(6)	2.15(2)
M(1)–P(1)	2.541(2)	2.524(7)
M(1)–P(2)	2.543(3)	2.564(7)
M(1)–I(2)	3.005(1)	3.029(3)
C(100)–M(1)–C(200)	102.8(4)	100.4(10)
C(100)–M(1)–O(21)	93.8(3)	101.3(7)
C(200)–M(1)–O(21)	139.2(3)	134.4(8)
C(100)–M(1)–O(25)	100.2(3)	101.0(8)
C(200)–M(1)–O(25)	131.2(4)	131.9(9)
O(21)–M(1)–O(25)	80.3(2)	81.7(6)
C(100)–M(1)–P(1)	79.9(3)	75.6(6)
C(200)–M(1)–P(1)	71.0(3)	72.4(7)
O(21)–M(1)–P(1)	149.4(2)	152.2(5)
O(25)–M(1)–P(1)	71.5(2)	72.0(5)
C(100)–M(1)–P(2)	80.7(3)	78.1(6)
C(200)–M(1)–P(2)	71.6(3)	73.9(7)
O(21)–M(1)–P(2)	74.8(2)	72.2(4)
O(25)–M(1)–P(2)	155.1(2)	153.0(5)
P(1)–M(1)–P(2)	132.43(8)	132.0(2)
C(100)–M(1)–I(2)	176.8(3)	177.1(5)
C(200)–M(1)–I(2)	78.5(3)	77.7(8)
O(21)–M(1)–I(2)	83.4(2)	81.5(5)
O(25)–M(1)–I(2)	80.9(2)	78.9(6)
P(1)–M(1)–I(2)	103.24(6)	101.7(2)
P(2)–M(1)–I(2)	97.02(6)	103.3(2)

3.1. $[\text{Mo}(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ (**1**), $[\text{W}(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ (**2**)

To acetylacetone (0.18 cm³, 1.76 mmol) in dry Et₂O (5 cm³) was added NaH (0.04 g 1.76 mmol) and the mixture stirred for 5 min. The solvent was removed in vacuo and the resulting sodium salt was dissolved in CH₂Cl₂ (10 cm³) and EtOH (10 cm³). To a stirred suspension of $[\text{Wl}_2(\text{CO})_3(\text{NCMe})_2]$ (1.07 g, 1.77 mmol) in dry degassed Et₂O (50 cm³) under a stream of dry nitrogen was added 1.0 M triethyl phosphine in THF (3.53 cm³, 3.53 mmol). The resulting yellow solution was stirred for 5 min and filtered. To the filtered solution was added the previously prepared solution of Na[acac] and the mixture stirred for further 18 h, after which the solvents were removed in vacuo. The product was dissolved in Et₂O (20 cm³) and CH₂Cl₂ (10 cm³) and the solution was filtered twice to remove NaI. The solvent was reduced to a minimum and cooled to 0°C affording red-orange crystals of $[\text{Wl}(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ (**2**) (yield = 0.918 g, 85%), which were suitable for X-ray crystallography. Anal: (C₁₉H₃₇O₄P₂IW) requires C, 32.5%; H, 5.3%. Found: C, 32.8%, H, 5.3%. IR (CH₂Cl₂) $\nu(\text{C}\equiv\text{O}) = 1910(\text{s})$ and $1808(\text{s}) \text{ cm}^{-1}$; (KBr) $\nu(\text{C}\equiv\text{O}) = 1913(\text{s})$ and $1811(\text{s}) \text{ cm}^{-1}$. ¹H NMR (25°C, CDCl₃) $\delta = 5.5(\text{s}, 1\text{H}, \text{CH})$, $2.2(\text{m}, 12\text{H}, \text{CH}_2\text{-P})$, $2.0(\text{s}, 6\text{H}, \text{OC-CH}_3)$, $1.2(\text{m}, 18\text{H}, \text{CH}_3)$.

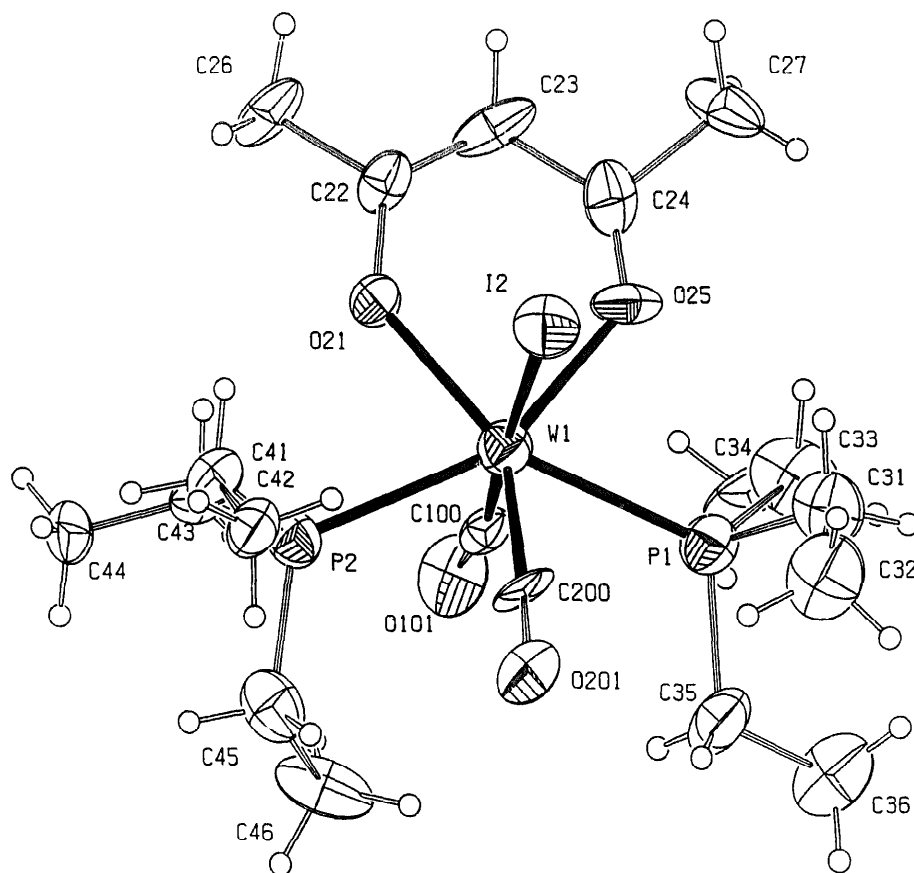


Fig. 2. X-ray structure of (**2**). Thermal ellipsoids shown at 30% probability. Hydrogen atoms included with small arbitrary radii.

A similar method using $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ (0.27 g, 0.52 mmol) afforded red-orange crystals of $[\text{MoI}(\text{acac})(\text{CO})_2(\text{PEt}_3)_2]$ (**1**) (yield = 0.27 g, 73%) which were suitable for X-ray crystallography. Anal: ($\text{C}_{19}\text{H}_{37}\text{O}_4\text{P}_2\text{IMo}$) requires C, 37.2%; H, 6.1%. Found: C, 37.1%; H, 6.7%; IR(CH_2Cl_2) $\nu(\text{C}\equiv\text{O}) = 1921(\text{s})$ and $1809(\text{s}) \text{ cm}^{-1}$. $^1\text{H NMR}$ (25°C, CDCl_3) $\delta = 5.5$ (s, 1H, CH), 2.3 (m, 12H, CH_2P), 2.0 (s, 6H, OCCCH_3), 1.1 (m, 18H, CH_3).

3.2. X-ray crystallography

Crystal data are given in Table 1, together with refinement details. Data for both crystals were collected with MoK α radiation using the MARresearch Image Plate System. The crystals were positioned at 75 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [22]. Both structures were solved using direct methods with the Shelx86 program [23]. In both structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions. An empirical absorption correction was applied to **2** [24]. The quality of the data for **2** was poor as indicated by misshapen spot slopes and many superfluous spots. While the a and c dimensions are equivalent, an $R(\text{int})$ value of 0.61 was obtained in an orthorhombic unit cell and twinned refinement was not successful. Both structures were then refined using Shelxl [25]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

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