Journal of Organometallic Chemistry, 421 (1991) 285–298
Elsevier Sequoia S.A., Lausanne
JOM 22196

Heterometallic analogues of $[\{M(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (M = Fe, Ru, Os). The synthesis of the tetracarbonylcyclopentadienylcycloheptatrienyl complexes $[M(CO)_2(\eta\text{-}C_5H_5)M'(CO)_2(\eta\text{-}C_7H_7)]$ (M = Fe, Ru; M′ = Mo, W). Crystal structures of $[Ru(CO)_2(\eta\text{-}C_5H_5)Mo(CO)_2(\eta\text{-}C_7H_7)]$ (Ru–Mo) and $[Mo(CO)_3(\mu\text{-}\eta^6, \eta^1\text{-}C_7H_7)Ru(CO)_2(\eta\text{-}C_5Me_5)]$

Roy L. Beddoes, E. Stephen Davies, Madeleine Helliwell and Mark W. Whiteley *
Department of Chemistry, University of Manchester, Manchester M13 9PL (UK)

(Received July 9th, 1991)

Abstract

The heterobimetallic, metal–metal-bonded complexes $[M(CO)_2(\eta\text{-}C_5H_5)M'(CO)_2(\eta\text{-}C_7H_7)]$ (**1**, M = Ru, M′ = Mo; **2**, M = Fe, M′ = Mo; **3**, M = Ru, M′ = W) have been synthesised by reaction of $Na[M(CO)_2(\eta\text{-}C_5H_5)]$ with $[M'Br(CO)_2(\eta\text{-}C_7H_7)]$. The X-ray crystal structure of **1** reveals an unsupported Ru–Mo bond length of 2.952(1) Å and a *cis* arrangement of C_5H_5 and C_7H_7 rings, but solution infrared studies suggest a solvent-dependent conformation. Treatment of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ with $K[Ru(CO)_2(\eta\text{-}C_5Me_5)]$ gives $[Ru(CO)_2(\eta\text{-}C_5Me_5)Mo(CO)_2(\eta\text{-}C_7H_7)]$ (**4**) in very low yield together with the major product, cycloheptatrienyl-bridged $[Mo(CO)_3(\mu\text{-}\eta^6, \eta^1\text{-}C_7H_7)Ru(CO)_2(\eta\text{-}C_5Me_5)]$ (**5**), which has been characterised crystallographically.

Introduction

The versatility of the cycloheptatrienyl ligand in bonding to transition metals is nicely illustrated by a consideration of the structures of bimetallic complexes. In addition to examples where C_7H_7 is bonded exclusively to one metal centre [1,2] it may also act as a bridging ligand with an extensive variety of coordination modes [3–6]. In this paper we describe the synthesis of the metal–metal-bonded heterobimetallic complexes $[M(CO)_2(\eta\text{-}C_5H_5)M'(CO)_2(\eta\text{-}C_7H_7)]$ (M = Fe or Ru; M′ = Mo or W) and the unexpected formation of a cycloheptatrienyl-bridged bimetallic $[Mo(CO)_3(\mu\text{-}\eta^6,\eta^1\text{-}C_7H_7)Ru(CO)_2(\eta\text{-}C_5Me_5)]$. Tetracarbonyl complexes $[M(CO)_2(\eta\text{-}C_5H_5)M'(CO)_2(\eta\text{-}C_7H_7)]$ are of especial interest as heterometallic analogues of the unbridged form of $[\{M(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (M = Fe, Ru or Os).

Results and discussion

The complexes $[M(CO)_2(\eta\text{-}C_5H_5)M'(CO)_2(\eta\text{-}C_7H_7)]$ (**1**, M = Ru, M' = Mo; **2**, M = Fe, M' = Mo; **3**, M = Ru, M' = W) were synthesised via reaction of $[M'Br(CO)_2(\eta\text{-}C_7H_7)]$ with $Na[M(CO)_2(\eta\text{-}C_5H_5)]$ in THF. Work up via column chromatography and recrystallisation to effect separation from $[\{M(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (M = Fe or Ru) afforded moderate to low yields of the products as green (**1** and **3**) or brown (**2**) solids. Complex **1** is relatively stable and only partial decomposition to $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ was observed after refluxing a sample in hexane for 24 h. By contrast **2** is both thermally and photochemically quite sensitive; ultraviolet irradiation of a toluene solution of **2** resulted in rapid conversion to $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ and $[Mo_2(CO)_6(\eta^6, \eta^6\text{-}C_{14}H_{14})]$ [7].

Both the complexes **1** and **2** have been referred to previously in the literature [8,9] but we are unaware of any published characterisation data. Full details of the characterisation of complexes **1**, **2** and **3** by microanalysis, infrared and mass spectroscopy (Table 1) and ^1H and ^{13}C NMR spectroscopy (Table 2) are given in the appropriate table and, in the case of **1**, the heterobimetallic metal–metal-bonded formulation has been confirmed by an X-ray crystallography study.

The molecular configuration of $[Ru(CO)_2(\eta\text{-}C_5H_5)Mo(CO)_2(\eta\text{-}C_7H_7)]$ (**1**) (and the crystallographic numbering scheme adopted) is illustrated in Fig. 1 and details of important bond lengths and angles are presented in Table 3. The molecule consists of $Ru(CO)_2(\eta\text{-}C_5H_5)$ and $Mo(CO)_2(\eta\text{-}C_7H_7)$ fragments linked by an unsupported Ru–Mo bond of length 2.952(1) Å. Reports of crystallographically determined Ru–Mo bond lengths in bimetallic complexes are exceedingly scarce

Table 1

Microanalytical, infrared and mass spectral data

Complex	Analysis [a] (%)		ν(CO) (cm^{-1})		Mass spectral data [f]
	C	H	(solution) [b]	(KBr) [b]	
1	40.9 (41.3)	2.5 (2.6)	(2004w, 1947s, 1924s) [c] (1991m, 1940s, 1913s) [d] (1988s, 1932m, 1912m) [e]	1986, 1979sh, 1918, 1897, 1887	464 M^+ [g], 408 $[M-2CO]^+$, 382 $[M-3CO]^+$, 354 $[M-4CO]^+$
2	45.9 (45.7)	3.0 (2.9)	(1997w, 1934s, 1917s) [c] (1984m, 1927s, 1906s) [d] (1982s, 1927m, 1906m) [e]	1981br, 1905, 1893, 1870	422 M^+, 394 $[M-CO]^+$, 366 $[M-2CO]^+$ [h]
3	34.6 (34.7)	2.2 (2.2)	(2004w, 1944s, 1925s) [c] (1991s, 1937s, 1914s) [d] (1988s, 1932m, 1912m) [e]	1986, 1978, 1917, 1889 1882	554 M^+, 498 $[M-2CO]^+$, 470 $[M-3CO]^+$, 442 $[M-4CO]^+$
4	46.8 (47.1)	4.4 (4.1)	(1991m, 1929s, 1911s) [c] (1980s, 1918sh, 1901s) [d] (1977s, 1916sh, 1904m) [e]	1970w, 1919s 1894s, 1876s	534 M^+ [j]
5	46.4 (46.9)	3.8 (3.9)	2004w, 1980s, 1951m, 1917m, 1891m [c]		482 $[M-3CO]^+$, 426 $[M-5CO]^+$ [k]

[a] Calculated values are given in parentheses. [b] s, strong; m, medium; w, weak intensity; sh, shoulder; br, broad. [c] In hexane. [d] In CH_2Cl_2. [e] In acetone. [f] By FAB unless stated otherwise; m/z values based on ^{98}Mo, ^{102}Ru and ^{184}W isotopes, M = molecular ion. [g] M^+ calculated 468. [h] By positive ion chemical ionisation. [j] M^+ calculated 538. [k] By electron impact mass spectroscopy.

Table 2

^1H and ^{13}C NMR spectral data [a]

Complex	^1H [b]	^{13}C [c]
1	4.82 (s, 5H, C_5H_5), 4.80 (s, 7H, C_7H_7)	215.4 (CO), 90.6 (C_7H_7), 87.6 (C_5H_5)
2	4.77 (s, 7H, C_7H_7), 4.43 (s, 5H, C_5H_5)	222.8 (CO), 91.1 (C_7H_7), 85.0 (C_5H_5)
3	4.88 (s, 5H, C_5H_5), 4.74 (s, 7H, C_7H_7)	211.3, br, 204.6, br, (CO), 85.6 (C_5H_5), 84.9 (C_7H_7) [d]
4	4.90 (s, 7H, C_7H_7), 1.82 (s, 15H, C_5Me_5)	218.6 (CO), 99.5 (C_5Me_5), 89.6 (C_7H_7), 10.7 ($C_5\mathit{Me}_5$) [e]
5 [f]	6.11 (m, 2H, H(4), H(5)), 4.23 (m, 2H, H(2), H(7)), 4.20 (m, 2H, H(3), H(6)) 3.11 (t, 1H, H(1), *J*[H(1)–H(2)/(7)], 7.5), 1.73 (s, 15H, C_5Me_5)	232.7, 220.7, 203.9 (CO), 100.3, 99.3, 90.4 (C_5Me_5 and C(2)--C(7), 26.3 (C(1)), 10.8 ($C_5\mathit{Me}_5$)

[a] Chemical shifts downfield from $SiMe_4$, s = singlet, triplet, m = multiplet, br = broad, δ in ppm, *J* values in Hz. [b] In benzene-d_6, 20 °C, unless stated otherwise. [c] In CD_2Cl_2, −80 °C, unless stated otherwise. [d] Spectrum also recorded at +20 °C: 207.9 (CO), 85.9 (C_5H_5), 84.9 (C_7H_7). [e] Recorded at +20 °C. [f] In CD_2Cl_2 at −40 °C; numbering as in Fig. 3.

and, of the two examples known to us [10,11], neither are directly comparable with the unsupported bond in **1**. A view along the Ru–Mo bond reveals an unexpected arrangement of the two rings and four carbonyl ligands. Essentially a *cis* structure is adopted, not dissimilar to that determined for *cis*-$[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ [12] with the clear exception that in **1** all four carbonyl ligands are basically terminal. Thus the carbonyl ligands C(24)–O(24) and C(22)–O(22) are almost eclipsed

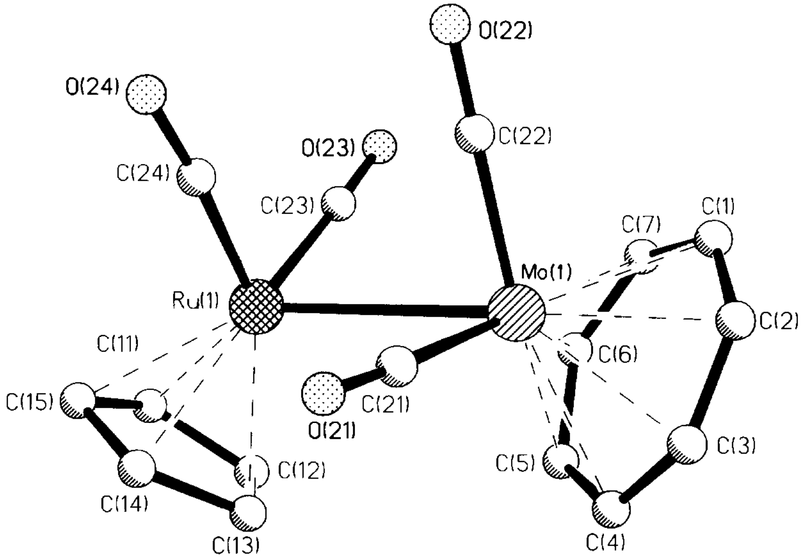

Fig. 1. The molecular structure of **1** showing atomic labelling scheme; hydrogen atoms are omitted.

Table 3

Selected bond lengths (Å) and angles (°) for **1**

Mo(1)–C(1)	2.295(7)	Mo(1)–C(2)	2.268(8)
Mo(1)–C(3)	2.263(12)	Mo(1)–C(4)	2.327(10)
Mo(1)–C(5)	2.322(13)	Mo(1)–C(6)	2.278(10)
Mo(1)–C(7)	2.301(10)	Mo(1)–C(21)	1.998(7)
Mo(1)–C(22)	1.984(8)	Mo(1)–Ru(1)	2.952(1)
C(1)–C(2)	1.383(17)	C(1)–C(7)	1.377(17)
C(2)–C(3)	1.359(20)	C(3)–C(4)	1.416(22)
C(4)–C(5)	1.409(22)	C(5)–C(6)	1.400(17)
C(6)–C(7)	1.364(15)	C(21)–O(21)	1.150(9)
C(22)–O(22)	1.146(9)	Ru(1)–C(11)	2.240(7)
Ru(1)–C(12)	2.264(7)	Ru(1)–C(13)	2.269(7)
Ru(1)–C(14)	2.244(7)	Ru(1)–C(15)	2.235(7)
Ru(1)–C(23)	1.854(7)	Ru(1)–C(24)	1.859(7)
C(11)–C(12)	1.432(10)	C(11)–C(15)	1.383(13)
C(12)–C(13)	1.404(11)	C(13)–C(14)	1.396(10)
C(14)–C(15)	1.415(10)	C(23)–O(23)	1.155(9)
C(24)–O(24)	1.146(9)		
C(1)–Mo(1)–C(21)	142.2(4)	C(2)–Mo(1)–C(21)	111.1(3)
C(3)–Mo(1)–C(21)	92.5(4)	C(4)–Mo(1)–C(21)	95.9(4)
C(5)–Mo(1)–C(21)	116.4(3)	C(6)–Mo(1)–C(21)	147.9(3)
C(7)–Mo(1)–C(21)	177.0(3)	C(1)–Mo(1)–C(22)	87.1(3)
C(2)–Mo(1)–C(22)	98.5(4)	C(3)–Mo(1)–C(22)	126.3(4)
C(4)–Mo(1)–C(22)	162.1(4)	C(5)–Mo(1)–C(22)	158.5(4)
C(6)–Mo(1)–C(22)	123.5(4)	C(7)–Mo(1)–C(22)	97.2(3)
C(21)–Mo(1)–C(22)	81.7(3)	C(1)–Mo(1)–Ru(1)	143.2(3)
C(2)–Mo(1)–Ru(1)	177.4(3)	C(3)–Mo(1)–Ru(1)	144.8(3)
C(4)–Mo(1)–Ru(1)	113.0(3)	C(5)–Mo(1)–Ru(1)	91.7(2)
C(6)–Mo(1)–Ru(1)	91.0(2)	C(7)–Mo(1)–Ru(1)	111.6(3)
C(21)–Mo(1)–Ru(1)	71.1(2)	C(22)–Mo(1)–Ru(1)	83.1(2)
C(2)–C(1)–C(7)	129.5(10)	C(1)–C(2)–C(3)	128.7(11)
C(2)–C(3)–C(4)	128.0(13)	C(3)–C(4)–C(5)	128.5(11)
C(4)–C(5)–C(6)	127.0(11)	C(5)–C(6)–C(7)	128.8(10)
C(1)–C(7)–C(6)	128.9(10)	Mo(1)–C(21)–O(21)	175.1(6)
Mo(1)–C(22)–O(22)	179.2(6)	Mo(1)–Ru(1)–C(11)	139.5(2)
Mo(1)–Ru(1)–C(12)	102.8(2)	Mo(1)–Ru(1)–C(13)	89.2(2)
Mo(1)–Ru(1)–C(14)	111.3(2)	Mo(1)–Ru(1)–C(15)	147.6(2)
Mo(1)–Ru(1)–C(23)	77.4(2)	C(11)–Ru(1)–C(23)	103.8(3)
C(12)–Ru(1)–C(23)	105.0(3)	C(13)–Ru(1)–C(23)	134.8(3)
C(14)–Ru(1)–C(23)	163.9(3)	C(15)–Ru(1)–C(23)	132.0(3)
Mo(1)–Ru(1)–C(24)	94.1(2)	C(11)–Ru(1)–C(24)	125.9(3)
C(12)–Ru(1)–C(24)	157.9(3)	C(13)–Ru(1)–C(24)	131.9(3)
C(14)–Ru(1)–C(24)	100.4(3)	C(15)–Ru(1)–C(24)	97.3(3)
C(23)–Ru(1)–C(24)	92.4(3)	C(12)–C(11)–C(15)	108.4(7)
C(11)–C(12)–C(13)	107.1(7)	C(12)–C(13)–C(14)	108.2(6)
C(13)–C(14)–C(15)	108.5(7)	C(11)–C(15)–C(14)	107.9(7)
Ru(1)–C(23)–O(23)	175.0(5)	Ru(1)–C(24)–O(24)	174.7(5)

(C(22)–Mo(1)–Ru(1)–C(24) torsion angle ca. 20.5°) whilst carbonyls C(21)–O(21) and C(23)–O(23) (which point across the Ru–Mo bond) are disposed essentially *trans* to each other (torsion angle C(21)–Mo(1)–Ru(1)–C(24) ca. 154.5°). The C_7H_7 and C_5H_5 rings lie *cis* across the Ru–Mo bond with closest inter-ring contacts between H(5) and H(12) (2.52(1) Å) and H(5) and H(13) (2.80(1) Å). Whilst C(21)–O(21) and C(23)–O(23) must strictly be considered as terminal carbonyl ligands, the respective bridge asymmetries [13] of 0.49 and 0.69 demonstrate that these carbonyls are directed across the Ru–Mo bond and, in the case of C(21)–O(21), the non-bonded separation Ru(1)---C(21) is as short as 2.981(7) Å.

From an initial consideration the *cis* solid state molecular geometry of **1** seems unusual, especially by comparison with the established *trans* conformation of related complexes such as $[Mo(CO)_3(\eta\text{-}C_5H_5)Mo(CO)_2(\eta\text{-}C_7H_7)]$(*Mo–Mo*) [14] and $[Fe(CO)_2(\eta\text{-}C_5H_5)Ru(CO)_2(\eta\text{-}C_5H_5)]$(*Fe–Ru*) [15]. However, in the solid state, complexes of general formulation $[\{M(CO)_2(\eta^5\text{-}C_5R_5)\}_2]$ (M = Fe or Ru; C_5R_5 = cyclopentadienyl or substituted cyclopentadienyl) adopt a carbonyl bridged structure and therefore, in the absence of a crystallographic study on $[\{Os(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (spectroscopically formulated as a non-carbonyl bridged structure [16]), the molecular geometry of **1** would appear to have no close comparison. We cannot rationalise the solid state *cis* conformation of **1** on the basis of abnormally close intermolecular contacts, nor does it seem likely that the crystal chosen for study represents the chance selection of a minor form (see infrared studies). However we note that in **1** the slight twisting away from the almost perfect *cis* conformation of *cis*-$[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ simultaneously reduces the non-bonded interactions which span the Ru–Mo bond between carbonyl C(21)–O(21) and the C_5H_5 ring (shortest non-bonded contact O(21)---H(14), 2.98(1) Å) and between carbonyl C(23)–O(23) and the C_7H_7 ring (shortest non-bonded contact C(23)---H(6), 2.89(1) Å).

The spectroscopic properties of complexes **1**, **2** and **3** are of interest because the solution characteristics of bimetallic tetracarbonyl complexes with an unsupported metal–metal bond can be investigated, unhindered by the complications of coexistent bridged forms.

The ^1H and ^{13}C NMR spectra of **1**, **2** and **3** in each case confirm the presence of discrete cyclopentadienyl and cycloheptatrienyl rings. Moreover in the ambient temperature ^{13}C NMR spectra only a single resonance is observed for the carbonyl carbons, an observation that we attribute to an intermetallic carbonyl scrambling process. Intermetallic carbonyl scrambling is well documented for $[\{M(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (M = Fe or Ru) and is thought to proceed via interchange of terminal and bridging carbonyl ligands [17]. Whilst there is no infrared evidence for bridging carbonyls in complexes **1**, **2** and **3** the X-ray structure of **1** has established that, in the solid state at least, two carbonyl ligands are directed across the Ru–Mo bond and this arrangement may facilitate exchange. To further probe any carbonyl exchange process the ^{13}C NMR spectra of **1**, **2** and **3** were recorded at −80 °C in CD_2Cl_2. In common with $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ [15,17] the low temperature ^{13}C NMR spectra of **1** and **2** exhibited only a single, albeit broadened, carbonyl resonance. However, in accord with our observations for $[M(CO)_3(\eta\text{-}C_5H_5)M(CO)_2(\eta\text{-}C_7H_7)]$ (M = Mo or W) [1], replacement of Mo by W impedes carbonyl exchange and, at −80 °C, the ^{13}C NMR spectrum of $[Ru(CO)_2(\eta\text{-}C_5H_5)W(CO)_2(\eta\text{-}C_7H_7)]$ (**3**) exhibited two broad carbonyl resonances with chemical shifts comparable with typical values for carbonyls bound terminally to the fragments $Ru(\eta\text{-}C_5H_5)$ [15] and $W(\eta\text{-}C_7H_7)$ [1].

The solution infrared spectra of complexes **1** to **3** are fully consistent with an all terminal carbonyl structure. However, whilst a *cis* conformation was observed for **1**

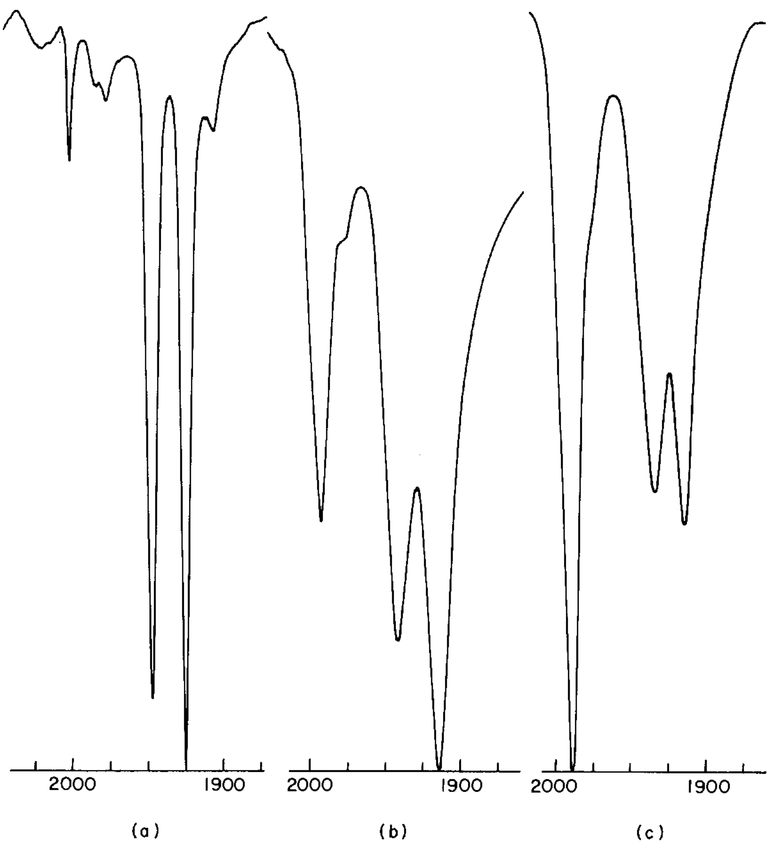

Fig. 2. Solution infrared spectra of 1 in the carbonyl stretching region (a) in hexane; (b) in CH_2Cl_2; (c) in acetone.

in the solid state, the solution infrared spectra of each of **1**, **2** and **3** exhibit a marked, but closely related, solvent dependence indicative of a change in preferred conformation with change in solvent polarity. Figure 2 illustrates the infrared spectra of **1** in the carbonyl stretching region recorded in hexane, dichloromethane and acetone; the most striking feature is the increase in the relative intensity of the high wavenumber band with increased solvent polarity. These results bear a strong resemblance to the solvent polarity dependence of carbonyl stretching frequency intensities deduced for unbridged $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ [18] but, for **1**, **2** and **3** the changes are not obscured by bands originating from coexistent carbonyl-bridged forms.

An analysis of the activity and relative intensity of carbonyl stretching frequencies in the infrared spectrum of non carbonyl bridged $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ has been reported. [18] Assuming C_{2v} and C_{2h} symmetry respectively for *cis* and *trans* conformations, the results suggest that an increase in the relative intensity of the high wavenumber carbonyl stretching frequency, observed with increase in solvent polarity, is consistent with an increased preference for the *cis* conformation. Clearly in the case of complexes **1** to **3** *cis* and *trans* conformers cannot have precise C_{2v} or C_{2h} symmetry but the appearance of the hexane spectra with only two strong carbonyl stretching frequencies encourages the assumption that an analysis based on pseudo C_{2v} or C_{2h} symmetry may be reasonable. So, by analogy with the analysis reported for $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ the spectra shown in Fig. 2 could be considered compatible with a conformational change of **1** from mainly *trans* in hexane to mainly *cis* in acetone.

The association of a *cis* conformation with a high intensity, high wavenumber carbonyl stretching frequency is also in accord with the solid state infrared spectra of **1**, **2** and **3**. All the spectra are similar (including a result for **1** recorded on the crystallographic sample) and, whilst there is some splitting of bands, the high wavenumber band has a strong relative intensity consistent with the crystallographically determined *cis* conformation. We also attempted to investigate the coexistence of different conformers by examination of the solvent dependence of the ^1H NMR spectrum of **1**. In $CDCl_3$ and CD_2Cl_2 small additional signals with chemical shifts typical of C_5H_5 and C_7H_7 rings were observed but unequivocal evidence for a conformer mixture was not obtained.

It is well established that for the homobimetallic complexes $[\{M(CO)_2(\eta\text{-}C_5R_5)\}_2]$ (M = Fe or Ru; R = H or alkyl), alkyl substitution in the cyclopentadienyl ring leads to an increased preference for the *trans* bridged form [19]. In view of the relatively large steric requirements of the cycloheptatrienyl ring [20] and the close inter-ring contacts observed in the solid state for **1**, it can be reasoned that ring-substituted derivatives $[M(CO)_2(\eta\text{-}C_5Me_5)\ Mo(CO)_2(\eta\text{-}C_7H_7)]$ (M = Fe or Ru) might adopt a *trans* conformation. We therefore attempted the synthesis of the complexes $[M(CO)_2(\eta\text{-}C_5Me_5)Mo(CO)_2(\eta\text{-}C_7H_7)]$ in the expectation that they could provide further insight into the interpretation of infrared data.

Treatment of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ with $K[Fe(CO)_2(\eta\text{-}C_5Me_5)]$ in thf gave, after work up a green solid which was tentatively formulated as $[Fe(CO)_2(\eta\text{-}C_5Me_5)Mo(CO)_2(\eta\text{-}C_7H_7)]$. However, the complex was very unstable with respect to decomposition to $[\{Fe(CO)_2(\eta\text{-}C_5Me_5)\}_2]$ and a pure sample was not obtained thus precluding a reliable interpretation of infrared data. By contrast reaction of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ with $K[Ru(CO)_2(\eta\text{-}C_5Me_5)]$ gave a purple-red solution from which, after extensive work up, two products were isolated. The minor product, green $[Ru(CO)_2(\eta\text{-}C_5Me_5)Mo(CO)_2(\eta\text{-}C_7H_7)]$ (**4**) was identified on the basis of the data given in Tables 1 and 2. In solution, the infrared spectrum of **4** in the carbonyl stretching region exhibits a solvent dependence very similar to that observed for complexes **1**, **2** and **3**. However, the solid state infrared spectrum of **4** differs substantially from those of **1**, **2** and **3** in that, for **4**, only a weak high wavenumber carbonyl band was observed and this may be indicative of the predicted *trans* conformation of **4** in the solid state.

The formation of the major reaction product, purple-red, cycloheptatrienyl-bridged $[Mo(CO)_3(\mu\text{-}\eta^6,\ \eta^1\text{-}C_7H_7)Ru(CO)_2(\eta\text{-}C_5Me_5)]$ (**5**) was totally unexpected and its identity was only fully established from the results of an X-ray crystallographic study. The molecular structure of **5** and the atomic numbering scheme adopted are illustrated in Fig. 3; selected interatomic distances and angles are presented in Table 4. The $Mo(CO)_3$ and $Ru(CO)_2(\eta\text{-}C_5Me_5)$ fragments are located *trans* across a bridging cycloheptatrienyl ring to which they are bonded η^6 and η^1 respectively; alternatively **5** can be described as a ring-substituted derivative of $[Mo(CO)_3(\eta^6\text{-cycloheptatriene})]$ with $Ru(CO)_2(\eta\text{-}C_5Me_5)$ attached *exo* at C(1). Both **5** and closely related $[Mo(CO)_3(\mu\text{-}\eta^6,\ \eta^1\text{-}C_7H_7)Re(CO)_5]$ exhibit

Table 4

Selected bond lengths (Å) and angles (°) for **5**

Ru(1)–C(1)	2.182(6)	O(16)–C(16)	1.135(6)
Ru(1)–C(11)	2.252(6)	O(17)–C(17)	1.146(7)
Ru(1)–C(12)	2.256(6)	C(1)–C(2)	1.495(7)
Ru(1)–C(13)	2.259(5)	C(1)–C(7)	1.478(8)
Ru(1)–C(14)	2.290(5)	C(2)–C(3)	1.369(8)
Ru(1)–C(15)	2.254(5)	C(3)–C(4)	1.423(9)
Ru(1)–C(16)	1.873(6)	C(4)–C(5)	1.38(1)
Ru(1)–C(17)	1.859(7)	C(5)–C(6)	1.42(1)
Mo(1)–C(2)	2.511(6)	C(6)–C(7)	1.382(8)
Mo(1)–C(3)	2.356(7)	C(11)–C(12)	1.426(8)
Mo(1)–C(4)	2.332(7)	C(11)–C(15)	1.424(9)
Mo(1)–C(5)	2.329(6)	C(11)–C(18)	1.50(1)
Mo(1)–C(6)	2.347(6)	C(12)–C(13)	1.431(9)
Mo(1)–C(7)	2.470(5)	C(12)–C(19)	1.49(1)
Mo(1)–C(8)	1.962(6)	C(13)–C(14)	1.420(9)
Mo(1)–C(9)	1.961(8)	C(13)–C(20)	1.51(1)
Mo(1)–C(10)	1.958(6)	C(14)–C(15)	1.421(8)
O(8)–C(8)	1.156(6)	C(14)–C(21)	1.49(1)
O(9)–C(9)	1.159(8)	C(15)–C(22)	1.50(1)
O(10)–C(10)	1.175(7)		

C(1)–Ru(1)–C(11)	141.8(2)	C(4)–Mo(1)–C(10)	95.5(2)
C(1)–Ru(1)–C(12)	146.1(2)	C(5)–Mo(1)–C(8)	149.3(2)
C(1)–Ru(1)–C(13)	109.2(2)	C(5)–Mo(1)–C(9)	95.6(3)
C(1)–Ru(1)–C(14)	89.5(2)	C(5)–Mo(1)–C(10)	119.8(2)
C(1)–Ru(1)–C(15)	105.0(2)	C(6)–Mo(1)–C(8)	114.8(2)
C(1)–Ru(1)–C(16)	90.9(2)	C(6)–Mo(1)–C(9)	90.6(3)
C(1)–Ru(1)–C(17)	90.9(2)	C(6)–Mo(1)–C(10)	154.2(2)
C(11)–Ru(1)–C(16)	95.0(2)	C(7)–Mo(1)–C(8)	86.0(2)
C(11)–Ru(1)–C(17)	126.5(3)	C(7)–Mo(1)–C(9)	107.8(2)
C(12)–Ru(1)–C(16)	121.5(2)	C(7)–Mo(1)–C(10)	166.7(2)
C(12)–Ru(1)–C(17)	97.4(2)	C(8)–Mo(1)–C(9)	90.1(3)
C(13)–Ru(1)–C(16)	156.3(2)	C(8)–Mo(1)–C(10)	90.7(2)
C(13)–Ru(1)–C(17)	100.5(2)	C(9)–Mo(1)–C(10)	85.1(3)
C(14)–Ru(1)–C(16)	135.9(3)	Ru(1)–C(1)–C(2)	117.0(4)
C(14)–Ru(1)–C(17)	132.7(2)	Ru(1)–C(1)–C(7)	111.9(4)
C(15)–Ru(1)–C(16)	101.9(2)	C(2)–C(1)–C(7)	112.8(4)
C(15)–Ru(1)–C(17)	158.9(2)	Mo(1)–C(2)–C(1)	91.3(4)
C(16)–Ru(1)–C(17)	91.4(3)	Mo(1)–C(2)–C(3)	67.5(4)
C(2)–Mo(1)–C(8)	87.4(2)	C(1)–C(2)–C(3)	129.1(5)
C(2)–Mo(1)–C(9)	167.3(2)	Mo(1)–C(3)–C(2)	80.0(4)
C(2)–Mo(1)–C(10)	107.4(2)	Mo(1)–C(3)–C(4)	71.4(4)
C(3)–Mo(1)–C(8)	115.5(2)	C(2)–C(3)–C(4)	129.4(6)
C(3)–Mo(1)–C(9)	154.0(2)	Mo(1)–C(4)–C(3)	73.2(4)
C(3)–Mo(1)–C(10)	90.3(2)	Mo(1)–C(4)–C(5)	72.7(4)
C(4)–Mo(1)–C(8)	150.0(3)	C(3)–C(4)–C(5)	127.2(6)
C(4)–Mo(1)–C(9)	119.6(2)	Mo(1)–C(5)–C(4)	73.0(4)
Mo(1)–C(5)–C(6)	73.0(4)		
C(4)–C(5)–C(6)	127.6(6)		
Mo(1)–C(6)–C(5)	71.6(4)		
Mo(1)–C(6)–C(7)	78.3(3)		
C(5)–C(6)–C(7)	129.0(6)		
Mo(1)–C(7)–C(1)	93.3(3)		
Mo(1)–C(7)–C(6)	68.5(3)		

Table 4 (continued)

C(1)-C(7)-C(6)	128.5(6)
Mo(1)-C(8)-O(8)	177.7(5)
Mo(1)-C(9)-O(9)	178.3(6)
Mo(1)-C(10)-O(10)	177.5(6)
C(12)-C(11)-C(15)	108.5(6)
C(11)-C(12)-C(13)	107.5(6)
C(12)-C(13)-C(14)	107.8(5)
C(13)-C(14)-C(15)	108.6(6)
C(11)-C(15)-C(14)	107.5(6)
Ru(1)-C(16)-O(16)	174.3(5)
Ru(1)-C(17)-O(17)	176.6(6)

mononuclear analogues, $[Ru(\eta^1\text{-}C_7H_7)(CO)_2(\eta\text{-}C_5H_5)]$ [21] and $[Re(\eta^1\text{-}C_7H_7)(CO)_5]$ [22]; in all cases the relative stability of these complexes is probably explained by strong Ru–C or Re–C σ bonds.

Details of the spectroscopic characterisation of 5 are presented in Tables 1 and 2; the most notable feature is the variable temperature behaviour of the NMR spectra. At ambient temperature in CD_2Cl_2 both ^1H and ^{13}C NMR spectra of 5 exhibit significant broadening of the cycloheptatrienyl ring signals but limiting low temperature spectra were obtained on cooling to $-40\,°C$. In toluene-d_8 a ^1H NMR investigation on 5 over the temperature range 20 to 90 °C revealed progressive broadening of the cycloheptatrienyl ring signals and the coalescence temperature was approached at 90 °C. We attribute the variable temperature behaviour to migration of $Ru(CO)_2(\eta\text{-}C_5Me_5)$ around the cycloheptatrienyl ring by a process similar to that reported for $[Re(\eta^1\text{-}C_7H_7)(CO)_5]$ [23], $[Ru(\eta^1\text{-}C_7H_7)(CO)_2(\eta\text{-}C_5H_5)]$ [21] and $[Mo(CO)_3(\mu\text{-}\eta^6, \eta^1\text{-}C_7H_7)Re(CO)_5]$ [4]. In the ^1H NMR of 5 the

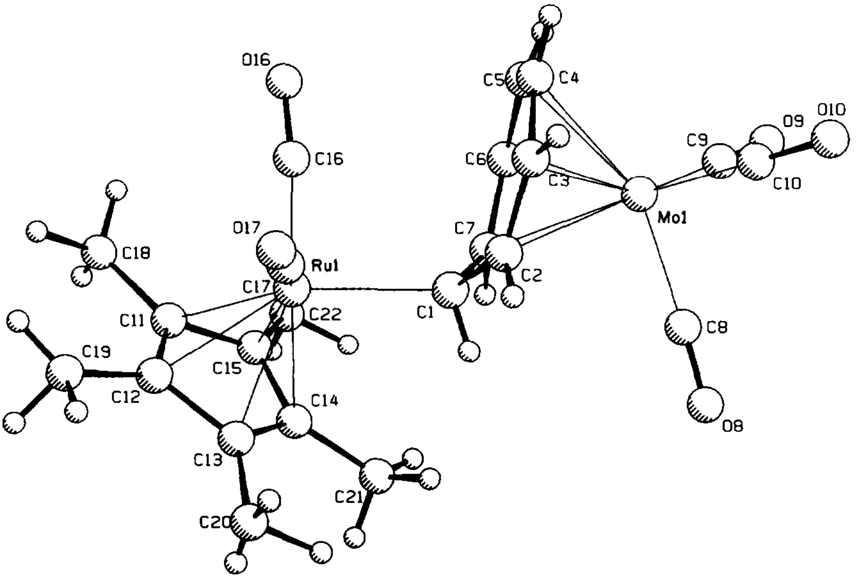

Fig. 3. The molecular structure of 5 showing atomic labelling scheme.

low field shift of H(1) (crystallographic numbering scheme) is consistent with its location *endo* with respect to the $Mo(CO)_3$ group [24].

The mechanism of formation of **5** from $K[Ru(CO)_2(\eta\text{-}C_5Me_5)]$ and $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ is not clear; reaction of **4** with carbon monoxide at room temperature did not yield **5**. However, the reported synthesis of $[Mo(CO)_3(\mu\text{-}\eta^6, \eta^1\text{-}C_7H_7)Re(CO)_5]$ from $[Mo(CO)_3(\eta\text{-}C_7H_7)]^+$ and $Na[Re(CO)_5]$ [4] suggested a more rational route to **5**. Thus treatment of $[Mo(CO)_3(\eta\text{-}C_7H_7)][PF_6]$ with $K[Ru(CO)_2(\eta\text{-}C_5Me_5)]$ in THF at −78 °C afforded moderate yields of **5** after work up. This latter reaction represents the formation of a ligand-bridged complex via an organometallic anion–cation annihilation process [25] and studies on the formation and thermal decomposition of cycloheptatrienyl-bridged complexes analogous to **5** are in progress.

Experimental

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complexes $[\{Ru(CO)_2(\eta\text{-}C_5R_5)\}_2]$ (R = H, [26]; R = Me [27]) and $[MBr(CO)_2(\eta\text{-}C_7H_7)]$ (M = Mo, W [28]) were prepared by published procedures. Aldrich Chemical Co. supplied C_5Me_5H; Alumina (Brockmann activity II) and silica (230–400 mesh) for column chromatography were purchased from B.D.H. Chemicals and Merck respectively. Hydrogen-1 NMR spectra were recorded on a Bruker AC 300 E instrument and ^{13}C NMR spectra at 75 MHz on a Varian Associates XL 300 spectrometer. Infrared spectra were obtained on a Perkin–Elmer FT 1710 spectrometer and mass spectra using Kratos Concept IS or Kratos MS 25 instruments. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparation of $[Ru(CO)_2(\eta\text{-}C_5H_5)Mo(CO)_2(\eta\text{-}C_7H_7)]$ *(1)*

A solution of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (0.62 g, 1.4 mmol) in thf (25 cm^3) was stirred for 5 h over sodium amalgam (prepared from 0.35 g (15 mmol) Na in Hg (3.6 cm^3)) to give a brown solution of $Na[Ru(CO)_2(\eta\text{-}C_5H_5)]$ [29] which was separated from the amalgam and transferred to a cooled (−78 °C) flask containing $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ (0.90 g, 2.8 mmol). The stirred mixture was allowed to warm slowly to room temperature and, after 1.5 h, solvent was removed to give a deep green residue which was dissolved in toluene and the resulting solution was filtered then transferred to a n-hexane alumina chromatography column. Elution, initially with hexane but subsequently with neat toluene gave a green band which was collected, solvent removed and the residue recrystallised from diethyl ether n-hexane. Cooling the solution to −78 °C resulted in precipitation of **1** as a dark green solid; yield 0.62 g (48%).

The preparation of green $[Ru(CO)_2(\eta\text{-}C_5H_5)W(CO)_2(\eta\text{-}C_7H_7)]$ (**3**) in 27% yield from $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (0.55 g, 1.24 mmol) and $[WBr(CO)_2(\eta\text{-}C_7H_7)]$ (1.00 g, 2.43 mmol) followed an identical procedure to that described for **1** except that the reaction mixture was stirred for 3 h and chromatography was carried out on silica. Three recrystallisations of the columned material from diethylether n-hexane were required to obtain an analytical sample.

Preparation of [Fe(CO)$_2$(η-C$_5$H$_5$)Mo(CO)$_2$(η-C$_7$H$_7$)] (2)

A stirred, cooled (−78 °C) solution of [MoBr(CO)$_2$(η-C$_7$H$_7$)] (1.92 g, 5.94 mmol) in thf (25 cm^3) was treated with a solution of Na[Fe(CO)$_2$(η-C$_5$H$_5$)] (prepared from [{Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] (1.27 g, 3.59 mmol)) in THF (35 cm^3) stirred over Na (0.91 g, 39.56 mmol) amalgamated with Hg (9 cm^3)). The mixture was warmed to room temperature and after 2 h solvent was removed *in vacuo*. The residue was extracted with toluene and the resulting solution filtered then transferred to a n-hexane alumina chromatography column. Elution with hexane and subsequently hexane toluene (1 : 1) gave two bands; the first, brown band contained [Fe(CO)$_2$(η-C$_5$H$_5$)Mo(CO)$_2$(η-C$_7$H$_7$)] (**2**), the second, red band was identified as [{Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] by infrared spectroscopy. The solution containing **2** was evaporated to dryness and the residue recrystallised from diethylether n-hexane to give **2** as a brown solid; yield 0.27 g (11%).

Reaction of [MoBr(CO)$_2$(η-C$_7$H$_7$)] with K[Ru(CO)$_2$(η-C$_5$Me$_5$)]

A stirred, cooled (−78 °C) solution of [MoBr(CO)$_2$(η-C$_7$H$_7$)] (1.81 g, 5.60 mmol) in thf (35 cm^3) was treated with a solution of K[Ru(CO)$_2$(η-C$_5$Me$_5$)] [30] (prepared from [{Ru(CO)$_2$(η-C$_5$Me$_5$)}$_2$] (1.50 g, 2.57 mmol) in THF (80 cm^3) stirred over Na/K alloy for 3 d). The mixture was allowed to warm slowly to room temperature and, after 1.5 h, solvent was removed to give a red-brown residue which was extracted with toluene and the resulting solution filtered then evaporated to dryness. Recrystallisation from diethyl ether n-hexane and cooling to −78 °C resulted in precipitation of [Mo(CO)$_3$(μ-η^6,η^1-C$_7$H$_7$)Ru(CO)$_2$(η-C$_5$Me$_5$)] (**5**) as a red-purple solid; yield 0.80 g (28%).

The remaining mother liquors were evaporated to dryness and the resulting green residue was dissolved in toluene and the solution transferred to a n-hexane silica chromatography column. Elution with n-hexane gave a green band which was collected, solvent removed and the residue recrystallised from n-hexane to give [Ru(CO)$_2$(η-C$_5$Me$_5$)Mo(CO)$_2$(η-C$_7$H$_7$)] (**4**) as a green solid; yield 0.01 g (0.3%).

Reaction of [Mo(CO)$_3$(η-C$_7$H$_7$)][PF$_6$] with K[Ru(CO)$_2$(η-C$_5$Me$_5$)]

A solution of K[Ru(CO)$_2$(η-C$_5$Me$_5$)] in THF (35 cm^3) (prepared from [{Ru(CO)$_2$(η-C$_5$Me$_5$)}$_2$] (0.50 g, 0.86 mmol) stirred over Na/K alloy) was added to [Mo(CO)$_3$(η-C$_7$H$_7$)][PF$_6$] (0.71 g, 1.71 mmol). The reaction mixture was rapidly cooled to −78 °C then allowed to warm to ambient temperature during 1.5 h. Subsequent removal of solvent gave a purple red residue, which was extracted with toluene and the resulting solution filtered and evaporated to dryness. Recrystallisation from diethyl ether n-hexane resulted in precipitation of **5** which was washed with cold hexane then dried; yield 0.125 g (13%).

Crystal structure analyses of 1 and 5

The majority of details of the structure analyses carried out on **1** and **5** are given in Table 5; non-hydrogen atom positional parameters for **1** and **5** are listed in Tables 6 and 7 respectively. Dark green crystals of **1** were obtained from heptane at −20 °C and red, pyramidal crystals of **5** were grown from hexane at −20 °C. X-ray diffraction measurements were made on single crystals using a Nicolet R3m/V diffractometer and Mo-K_α radiation for **1** and a Rigaku AFC5R diffractometer with Cu-K_α radiation for **5**. Cell dimensions for **1** were determined from

Table 5
Structure analyses of **1** and **5**

	1	**5**
Crystal data		
Formula	$C_{16}H_{12}O_4MoRu$	$C_{22}H_{22}O_5MoRu$
M	465.3	563.42
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	13.524(5)	10.1492(4)
b (Å)	7.013(3)	12.5718(6)
c (Å)	16.687(6)	8.9816(4)
α (°)	90	101.622(4)
β (°)	106.85(3)	91.122(3)
γ (°)	90	95.995(4)
U (Å^3)	1514.6(9)	1115.39(8)
T (K)	295	293
Z	4	2
D_c (g cm^{-3})	2.040	1.677
F(000)	904	560
μ (cm^{-1})	18.01 (Mo-K_α)	105.59 (Cu-K_α)
Data collection reduction		
Crystal dimension (mm)	0.37×0.28×0.16	0.10×0.13×0.19
Wavelength (Å)	0.71073 (Mo-K_α)	1.54178 (Cu-K_α)
θ range (°)	3–55	2.5–60
Scan mode	$\omega/2\theta$	$\omega/2\theta$
Scan width	$(0.60+0.35\tan\theta)$	$(1.31+0.30\tan\theta)$
Total data	3943	2860
Unique data	3497	2692
'Observed' data (NO)	2100	2436
Observation criterion ($F > n\sigma(F)$)	4	6
Refinement		
Least squares variables (NV)	199	328
R[a]	0.039	0.032
R_w	0.041	0.042
S	1.16	1.82
Difference map features (e Å^{-3})	+0.81, −0.59	+0.39, −0.63

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$; $R_w = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$; $S = [\Sigma w\Delta^2/(NO - NV)]^{1/2}$; $\Delta = F_o - F_c$.

the setting angles, θ of 30 reflections in the range $10.17 < \theta < 19.90$ ° and for **5** from 25 reflections in the range $39.26 < \theta < 39.90$ °. The absorption correction for **1** was made with ψ-scans using 4 reflections whilst for **5** an empirical absorption correction using the program DIFABS [31] was applied. No extinction corrections were made but the data for **5** were corrected for Lorentz and polarisation effects. The structures were solved by heavy atom (direct or Patterson) methods; both structures were refined by full-matrix least squares. All non-hydrogen atoms were assigned anisotropic vibrational parameters; hydrogen atoms in **1** were given isotropic parameters but in **5** hydrogen atoms were assigned a vibrational parameter dictated by the attached carbon. For **1** individual reflections were assigned weights $w = [\sigma^2(F_o) + 0.0004F_o^2]^{-1}$ whilst for **5** $w = 4F_o^2/\sigma^2(F_o^2)$ with a p-factor

Table 6

Atomic coordinates for **1**

Atom	*x*	*y*	*z*
Mo(1)	0.3263(1)	0.1291(1)	0.0398(1)
C(1)	0.3876(9)	−0.0054(15)	0.1702(4)
C(2)	0.4565(7)	0.1330(20)	0.1614(5)
C(3)	0.4371(11)	0.3164(21)	0.1353(6)
C(4)	0.3413(14)	0.4139(15)	0.1140(6)
C(5)	0.2420(10)	0.3394(17)	0.1052(5)
C(6)	0.2171(7)	0.1519(18)	0.1207(5)
C(7)	0.2817(9)	0.0031(14)	0.1518(5)
C(21)	0.3728(5)	0.2347(10)	−0.0545(4)
O(21)	0.4049(4)	0.2857(8)	−0.1076(3)
C(22)	0.3605(5)	−0.1153(11)	−0.0060(4)
O(22)	0.3795(4)	−0.2575(8)	−0.0318(3)
Ru(1)	0.1502(1)	0.1270(1)	−0.1140(1)
C(11)	0.0005(5)	0.2799(11)	−0.1691(5)
C(12)	0.0564(5)	0.3819(10)	−0.0956(5)
C(13)	0.1472(5)	0.4504(10)	−0.1101(4)
C(14)	0.1478(6)	0.3921(11)	−0.1899(4)
C(15)	0.0566(6)	0.2867(11)	−0.2263(5)
C(23)	0.1161(5)	−0.0663(9)	−0.0510(4)
O(23)	0.0875(5)	−0.1846(7)	−0.0150(3)
C(24)	0.2124(5)	−0.0425(10)	−0.1701(4)
O(24)	0.2471(4)	−0.1396(8)	−0.2103(3)

Table 7

Atomic coordinates for **5**

Atom	*x*	*y*	*z*
Ru(1)	0.15776(4)	0.23056(3)	0.05522(5)
Mo(1)	0.52336(4)	0.21448(3)	0.42586(5)
O(8)	0.6448(5)	0.4513(3)	0.4175(6)
O(9)	0.5643(6)	0.2621(5)	0.7791(6)
O(10)	0.8052(5)	0.1347(4)	0.4321(6)
O(16)	0.0602(5)	0.0384(4)	0.1907(6)
O(17)	0.2914(5)	0.0906(4)	−0.1953(6)
C(1)	0.3387(5)	0.2667(4)	0.1998(7)
C(2)	0.4489(5)	0.1985(5)	0.1532(7)
C(3)	0.4705(6)	0.0998(5)	0.1860(8)
C(4)	0.4148(7)	0.0469(5)	0.2998(9)
C(5)	0.3353(7)	0.0894(6)	0.4142(9)
C(6)	0.2922(6)	0.1951(6)	0.4450(8)
C(7)	0.3103(5)	0.2768(5)	0.3625(7)
C(8)	0.6021(6)	0.3632(5)	0.4222(7)
C(9)	0.5473(6)	0.2452(5)	0.6481(9)
C(10)	0.6997(6)	0.1645(5)	0.4263(7)
C(11)	−0.0471(6)	0.2816(5)	0.0368(8)
C(12)	0.0196(6)	0.2937(5)	−0.0980(8)
C(13)	0.1314(6)	0.3741(5)	−0.0543(8)
C(14)	0.1304(6)	0.4126(5)	0.1055(8)
C(15)	0.0230(6)	0.3533(5)	0.1631(8)
C(16)	0.1035(6)	0.1103(5)	0.1417(7)
C(17)	0.2435(6)	0.1436(5)	−0.0967(8)
C(18)	−0.1758(7)	0.2115(8)	0.041(1)
C(19)	−0.0257(9)	0.2382(8)	−0.255(1)
C(20)	0.223(1)	0.4204(8)	−0.162(1)
C(21)	0.221(1)	0.5053(6)	0.195(1)
C(22)	−0.020(1)	0.3724(7)	0.324(1)

of 0.03 to weightdown strong reflections. Complex neutral atom scattering factors were taken from ref. 32; calculations for **1** were carried out with programs of the SHELXTL package [33] and for **5** using the TEXSAN crystallographic software package supplied by Molecular Structure Corporation [34].

Lists of H-atom coordinates, thermal parameters, and structure factors are available from the authors.

Acknowledgement

We are grateful to the SERC for the award of a Research Studentship to E.S.D.

References

1 A. Ricalton and M.W. Whiteley, J. Organomet. Chem., 361 (1989) 101.
2 E.F. Ashworth, J.C. Green, M.L.H. Green, J. Knight, R.B.A. Pardy and N.J. Wainwright, J. Chem. Soc., Dalton Trans., (1977) 1693.
3 M.J. Bennett, J.L. Pratt, K.A. Simpson, L.K.K. Li ShingMan and J. Takats, J. Am. Chem. Soc., 98 (1976) 4810.
4 H.-J. Müller, U. Nagel, M. Steinmann, K. Polborn and W. Beck, Chem. Ber., 122 (1989) 1387.
5 J.A.K. Howard and P. Woodward, J. Chem. Soc., Dalton Trans., (1977) 366.
6 A. Vasudavamurthy and J. Takats, Organometallics, 6 (1987) 2005.
7 H. Adams, N.A. Bailey, D.G. Willett and M.J. Winter, J. Organomet. Chem., 333 (1987) 61.
8 M.L. Ziegler, H.E. Sasse and B. Nuber, Z. Naturforsch. B, 30 (1975) 26.
9 S.A.R. Knox, J. Organomet. Chem., 400 (1990) 255.
10 J.S. Drage, M. Tilset, P.C. Vollhardt and T.W. Weidman, Organometallics, 3 (1984) 812.
11 B. Chaudret, F. Dahan and S. Sabo, Organometallics, 4 (1985) 1490.
12 R.F. Bryan, P.T. Greene, M.J. Newlands and D.S. Field, J. Chem. Soc. (A), (1970) 3068.
13 R.J. Klinger, W.M. Butler and M.D. Curtis, J. Am. Chem. Soc., 100 (1978) 5034.
14 R.L. Beddoes, A. Ricalton and M.W. Whiteley, Acta Crystallogr., Sect. C, 44 (1988) 2025.
15 B.P. Gracey, S.A.R. Knox, K.A. Macpherson, A.G. Orpen and S.R. Stobart, J. Chem. Soc., Dalton Trans., (1985) 1935.
16 R.D. Fischer, A. Vogler and K. Noack, J. Organomet. Chem., 7 (1967) 135.
17 D.C. Harris, E. Rosenberg and J.D. Roberts, J. Chem. Soc., Dalton Trans., (1974) 2398.
18 P. McArdle and A.R. Manning, J. Chem. Soc. (A), (1970) 2128.
19 N.A. Bailey, S.L. Radford, J.A. Sanderson, K. Tabatabaian, C. White and J.M. Worthington, J. Organomet. Chem., 154 (1978) 343.
20 C.E. Davies, I.M. Gardiner, J.C. Green, M.L.H. Green, N.J. Hazel, P.D. Grebenik, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Dalton Trans., (1985) 669.
21 D.M. Heinekey and W.A.G. Graham, J. Am. Chem. Soc., 104 (1982) 915.
22 D.M. Heinekey and W.A.G. Graham, J. Organomet. Chem., 232 (1982) 335.
23 D.M. Heinekey and W.A.G. Graham, J. Am. Chem. Soc., 101 (1979) 6115.
24 P.L. Pauson, G.H. Smith and J.H. Valentine, J. Chem. Soc. (C), (1967) 1061.
25 R.E. Lehmann and J.K. Kochi, Organometallics, 10 (1991) 190.
26 N.M. Doherty and S.A.R. Knox, Inorg. Synth., 25 (1989) 180.
27 G.O. Nelson and C.E. Sumner, Organometallics, 5 (1986) 1983.
28 G. Hoch, R. Panter and M.L. Ziegler, Z. Naturforsch. B, 31 (1976) 294.
29 T. Blackmore, M.I. Bruce and F.G.A. Stone, J. Chem. Soc. (A), (1968) 2158.
30 A. Stasunik, D.R. Wilson and W. Malisch, J. Organomet. Chem., 270 (1984) C18.
31 N. Walker and D. Stuart, Acta. Crystallogr., Sect. A, 39 (1983) 158.
32 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press Birmingham, 1974.
33 G.M. Sheldrick, SHELXTL, Gottingen, 1985.
34 TEXSAN-TEXRAY Structure analysis package, Molecular Structure Corporation, 1985.