

Synthesis and reactivity of the cycloheptatrienyl-bridged bimetallic complexes $[M(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)M'(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]$ ($M = \text{Cr, Mo or W; } M' = \text{Fe or Ru; } R = \text{H or Me}$)

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Abstract

The cycloheptatrienyl-bridged bimetallics $[M(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)M'(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]$ ($R = \text{H, } M' = \text{Ru: } \mathbf{1}, M = \text{Cr; } \mathbf{2}, M = \text{Mo; } \mathbf{3}, M = \text{W; } R = \text{Me, } M = \text{Mo: } \mathbf{4}, M' = \text{Ru; } \mathbf{5}, M' = \text{Fe}$) have been synthesised by reaction of $[M(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ with $[M'(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]^-$ in THF. ^1H and ^{13}C NMR studies on complexes $\mathbf{2}$ to $\mathbf{5}$ indicate the operation of a dynamic process involving a 1,2 shift of the η^1 -bound M' metal group around the cycloheptatrienyl ring. Complex $\mathbf{5}$ undergoes ready fission of the $\text{Fe-C}_7\text{H}_7$ bond to yield the homobimetallic products $[\text{Fe}_2(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2]$ and $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$, and infrared data indicate the intermediacy of unstable $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_2\text{Cp}]$ $\mathbf{6}$ in the formation of analogous homobimetallics from the reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]\text{PF}_6$ with $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$. Thermolysis of $\mathbf{2}$, $\mathbf{3}$ and $\mathbf{4}$ gives, in addition to homobimetallic products, the heterobimetallic, metal-metal bonded complexes $[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{R}_5)M(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ ($M = \text{Mo, } R = \text{H or Me; } M = \text{W, } R = \text{H}$). A heterobimetallic complex $[\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5]$ $\mathbf{8}$ is also generated by thermolysis of $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5]$ $\mathbf{7}$ together with $\text{Re}_2(\text{CO})_{10}$ and $[\text{Re}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_7)]$. Stirring $\mathbf{4}$ or $\mathbf{7}$ in NCMc at room temperature results in detachment of the η^6 -bound $\text{Mo}(\text{CO})_3$ group and the respective formation of $[\text{Ru}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ $\mathbf{9}$ and $[\text{Re}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_5]$.

Keywords: Bridging ligand; Cycloheptatrienyl; Iron; Molybdenum; Rhenium; Ruthenium

1. Introduction

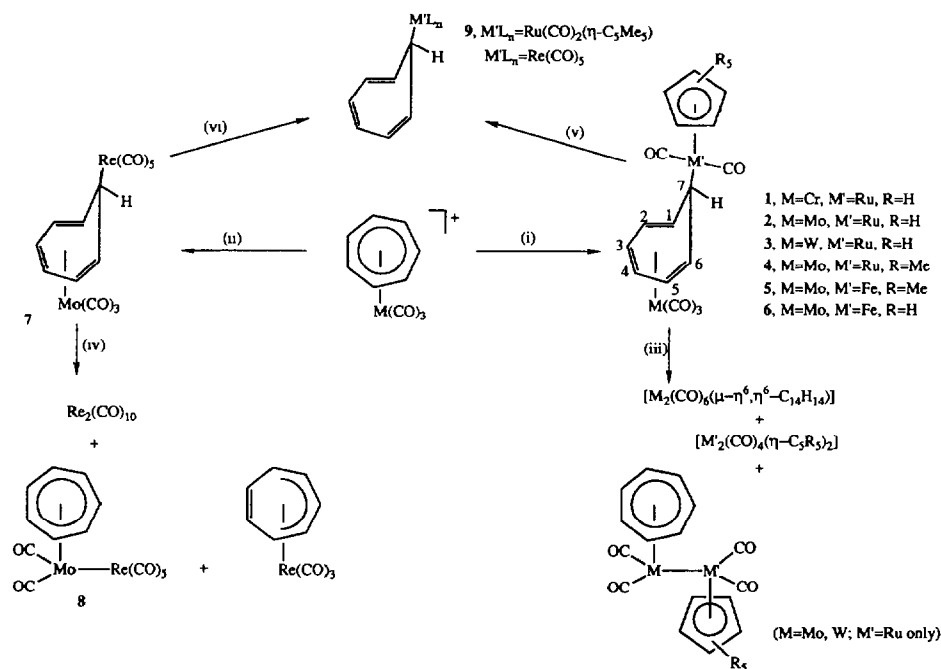
The ability of the cycloheptatrienyl ligand to function as a versatile bridging group between two metal centres is evident from the four well established bonding types: $\mu\text{-}\eta^1\text{:}\eta^2$ [1], $\mu\text{-}\eta^1\text{:}\eta^6$ [2], $\mu\text{-}\eta^2\text{:}\eta^3$ [3,4] and $\mu\text{-}\eta^3\text{:}\eta^4$ [5–8]. However, with the notable exception of the work of Takats and coworkers [6,7] on $\mu\text{-}\eta^3\text{:}\eta^4$ systems, the reactivity of cycloheptatrienyl-bridged bimetallics is largely unexplored. We have previously described the unexpected formation of the $\eta^1\text{:}\eta^6$ -bridged complex $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ $\mathbf{4}$ from the reaction of $[\text{MoBr}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ with $\text{K}[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ and established its structure by X-ray crystallography [9]. In this paper we report a more general route to a range of derivatives $[\text{M}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)M'(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]$ ($M = \text{Cr, Mo or W; } M' = \text{Fe or Ru; } R = \text{H or Me}$) and, by extending our investigations to $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5]$ [2], we

have established two reaction types of the known $\eta^1\text{:}\eta^6\text{-C}_7\text{H}_7$ -bridged bimetallics which involve decomplexation, either of the η^1 - or the η^6 -bonded metal centre, from the cycloheptatrienyl ring.

2. Results and discussion

Reaction of cooled THF solutions of the cycloheptatrienyl cations $[\text{M}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]\text{PF}_6$ ($M = \text{Cr, Mo or W}$) with the anions $M''[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]$ ($R = \text{H, } M'' = \text{Na; } R = \text{Me, } M'' = \text{K}$) led to the formation of cycloheptatrienyl-bridged $[\text{M}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]$ ($R = \text{H; } \mathbf{1}, M = \text{Cr; } \mathbf{2}, M = \text{Mo; } \mathbf{3}, M = \text{W; } \mathbf{4}, R = \text{Me, } M = \text{Mo;}$ Scheme 1) which were isolated, in moderate yield, as red or orange-red solids. One example of an Fe derivative $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ $\mathbf{5}$ was also obtained as a red solid, thermally sensitive in solution, by reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]\text{PF}_6$ with $\text{K}[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$. With the exception of $[\text{Mn}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_5]$, which has

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Scheme 1. Reagents and conditions: (i) M = Cr, Mo or W, $[M'(CO)_2(\eta^1-C_5R_5)]^-$ in THF ($-78^\circ C$), 1 h. (ii) M = Mo, $Na[Re(CO)_5]$, conditions as in Ref. [2]. (iii) M' = Fe, stir in THF or toluene, room temperature; M' = Ru, heat in methylcyclohexane ($100^\circ C$). (iv) Reflux in methylcyclohexane, 0.5 h. (v) M = Mo, M' = Ru, R = Me, stir in NCMe, room temperature, 15 min. (vi) Stir in NCMe, room temperature, 15 min.

been observed by low temperature matrix isolation studies [10], complex 5 is the only example of a first row transition metal bonded η^1 to the cycloheptatrienyl ligand. The formation of complexes 1 to 5 was accompanied by the generation of the homobimetallic by-products $[M'_2(CO)_4(\eta^1-C_5R_5)_2]$ and bicycloheptatriene-bridged $[M'_2(CO)_6(\mu-\eta^6:\eta^6-C_{14}H_{14})]$ [11]; in some cases infrared data indicated the additional formation of $[M(CO)_3(\eta^6-C_{14}H_{14})]$, as has been reported in the synthesis of $[Mo(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Re(CO)_5]$ [2]. De-

tails of the characterisation of 1 to 5, and of subsequently described complexes, are presented in Tables 1 (microanalytical, IR and mass spectroscopic data) and 2 (1H and ^{13}C NMR data); data for complex 4, previously reported in Ref. [9] are included here for comparison.

The infrared spectra of each of complexes 1 to 5 exhibit five strong, discrete carbonyl bands which, to a first approximation, can be identified with the two separate metal centres. Three monometallic $\eta^1-C_7H_7$ complexes have been reported previously: $[M'(\eta^1-$

Table 1
Microanalytical, infrared and mass spectroscopic data

Complex	Anal. Found (Calc.) (%)		Infrared $\nu(CO)$ (cm^{-1}) ^a	Mass spectral data ^b
	C	H		
1	45.7 (45.4)	3.0 (2.7)	2021(m), 1981(s), 1965(m), 1921(m), 1898(m)	332, $[M-4CO]^+$
2	40.9 (41.4)	2.4 (2.4)	2021(m), 1986(s), 1966(m), 1924(m), 1898(m) ^c	468, $[M-CO]^+$; 440, $[M-2CO]^+$; 412, $[M-3CO]^+$
3	34.9 (35.1)	2.0 (2.1)	2020(m), 1983(s), 1966(m), 1919(m), 1891(m)	582, M^+ ; 524, $[M-2CO]^+$; 497, $[M-3CO]^+$; 469, $[M-4CO]^+$ ^d
4	46.4 (46.9)	3.8 (3.9)	2004(w), 1980(s), 1951(m), 1917(m), 1891(m)	535, $[M-CO]^+$; 479, $[M-3CO]^+$; 424, $[M-5CO]^+$
5	50.9 (51.0)	4.1 (4.3)	1993(m), 1978(s), 1941(m), 1918(m), 1893(m)	519, M^+ ; 464, $[M-2CO]^+$ ^d
8	29.4 (29.5)	1.3 (1.2)	2087(m), 2011(w), 1985(s), 1979(sh), 1967(m), 1952(w), 1920(w)	570, M^+ ; 542, $[M-CO]^+$; 514, $[M-2CO]^+$; 486, $[M-3CO]^+$; 458, $[M-4CO]^+$ ^d
9	59.0 (59.5)	5.8 (5.7)	1999(s), 1947(s)	384, M^+ ; 356, $[M-CO]^+$; 328, $[M-2CO]^+$

^a Solution spectra in hexane unless stated otherwise, s = strong, m = medium, w = weak intensity, sh = shoulder. ^b By EI mass spectroscopy unless stated otherwise. ^c Infrared data for 2 also recorded in CH_2Cl_2 : $\nu(CO)$ (CH_2Cl_2) 2016(m), 1973(s), 1956(sh), 1903(m), 1867(m) cm^{-1} .

^d By FAB mass spectroscopy.

$C_7H_7)(CO)_5$ ($M' = Mn$ [10] or Re [10,12]) and $[Ru(\eta^1-C_7H_7)(CO)_2Cp]$ [13], and a new example, $[Ru(\eta^1-C_7H_7)(CO)_2(\eta^5-C_5Me_5)]$ **9**, is described in this work (see below). For purposes of comparison, pertinent infrared data are: $[Re(\eta^1-C_7H_7)(CO)_5]$, $[\nu(CO)$ (cyclohexane) 2120, 2015, 1983 cm^{-1}] [12], $[Ru(\eta^1-C_7H_7)(CO)_2Cp]$, $[\nu(CO)$ (cyclohexane) 2015, 1961, 1959(sh) cm^{-1}] [13] and, for the cycloheptatriene complex $[Mo(CO)_3(\eta^6-C_7H_8)]$, $[\nu(CO)$ (hexane) 1997, 1933 and 1908 cm^{-1}]. Thus for **2**, $\nu(CO)$ 1986, 1924 and 1898 cm^{-1} , are comparable with the carbonyl stretching bands of $[Mo(CO)_3(\eta^6-C_7H_8)]$, whilst $\nu(CO)$ 2021, 1966 cm^{-1} (which are essentially invariant with M in complexes **1** to **3**) correspond with those of $[Ru(\eta^1-C_7H_7)(CO)_2Cp]$. Similar correlations can be made for **4** and for $[Mo(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Re(CO)_5]$ **7** [$\nu(CO)$ (hexane) 2123, 2074, 2047, 2017, 1986, 1926, 1898 cm^{-1}]. By comparison with the discrete monometallic analogues, each of the bimetallic complexes **1** to **4** and **7** exhibits a small but consistent increase in $\nu(CO)$ of the η^1 -bound metal and a corresponding shift to lower wavenumber for $\nu(CO)$ of the η^6 -bound metal, consonant with a limited transfer of electron density through the cycloheptatrienyl bridge from the Ru or Re centre to the $M(CO)_3$ centre.

The ambient temperature 1H NMR spectra of **1**, **2** and **3** are well resolved and very similar except for a small M (Cr , Mo or W) dependence of chemical shifts; the low field shift of H^7 in each case is consistent with H^7 located *endo* [14] with respect to the $M(CO)_3$ unit and the $M(CO)_3$ and $M'(CO)_2(\eta^5-C_5R_5)$ groups disposed mutually *trans* as established by the X-ray crystal structure of **4** [9]. However, in the ^{13}C NMR spectra the

carbonyls attached to M were not resolved at room temperature, an observation which we attribute to a dynamic process involving rotation of the $M(CO)_3$ group with respect to the η^6 -bound ring, as established previously for the cycloheptatriene complexes $[Cr(CO)_2L(\eta^6-C_7H_8)]$ ($L = PMe_3$, etc.) [15]. On cooling a solution of **2** in CD_2Cl_2 to $-40^\circ C$, the limiting low temperature ^{13}C NMR spectrum exhibited three well resolved carbonyl carbon signals; those at 231.6 and 219.7 (1:2 intensity ratio) are assigned to the Mo -bound carbonyls. The C_5Me_5 derivatives **4** and **5** presented more complex, temperature dependent NMR behaviour. In addition to the dynamic process involving the M -bound carbonyl ligands, complexes **4** and **5** exhibited a second fluxional process which resulted in significant broadening of the cycloheptatrienyl ring protons in the room temperature 1H NMR spectra. Cooling to $-40^\circ C$ resulted in well resolved spectra but the high temperature behaviour was M' (Fe or Ru) dependent. Thus, in toluene- d_8 the Ru derivative **4** displayed progressive broadening of the cycloheptatrienyl proton resonances until at $90^\circ C$ only two, very broad resonances, centred at δ 5.65, 3.85, were observed. Some broadening of the 1H NMR resonances of $[M(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Ru(CO)_2Cp]$, (**2**, $M = Mo$; **3**, $M = W$) was also apparent in toluene- d_8 at $90^\circ C$, but the individual resonances remained discrete. By contrast, 1H NMR studies established that solutions of the Fe derivative **5** in toluene- d_8 underwent rapid decomposition (see below) at ambient temperature. It is probable that the variable temperature 1H NMR behaviour of complexes **2** to **5** can be attributed to migration of the $M'(CO)_2(\eta^5-C_5Me_5)$ around the cycloheptatrienyl ring, analogous to the pro-

Table 2
Proton and ^{13}C NMR spectral data for the complexes $[M(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)M'(CO)_2(\eta^5-C_5R_5)]^a$

Complex	1H NMR data					^{13}C NMR data					
	$H^{3,4}$	$H^{2,5}$	$H^{1,6}$	H^7 ($J, H^{1,6}-H^7$)	C_5R_5	CO (M)	CO (M')	C^1-C^6	C^7	C_5R_5	R
1 ^b	5.82	3.81	3.40	4.10, t(6)	4.20, s	234.9 (broad)	201.5	100.5, 100.2, 86.5	14.7	89.2	
2 ^{b,c,d,e}	5.64 (6.19)	3.91 (4.40)	3.66 (4.31)	4.15, t(8) (4.51), t(8)	4.22, s (5.18), s	231.6, 219.7	201.7	101.3 ($C^{2,5}$), 99.4 ($C^{3,4}$), 89.6 ($C^{1,6}$)	17.5	89.1	
3 ^{b,f,g}	5.61	3.87	3.67	4.48, t(8)	4.23, s		201.7	99.5, 94.8, 80.4	17.4	88.9	
4 ^{b,h,e}	5.77 (6.11)	3.98 (4.20)	3.98 (4.23)	3.30 (broad) (3.11), t(8)	1.40 (1.73), s	232.7, 220.7	203.9	100.3, 99.3, 90.4	26.3	99.3	10.8
5 ⁱ	5.57	3.80	3.69	2.95, t(8)	1.12, s	233.7, 220.2	218.0	100.3, 99.4, 88.7	30.2	94.7	9.6
9	5.82	5.12	5.25	2.91, t(8)	1.83, s		204.6	140.2, 135.0, 121.4	25.5	99.3	10.3

^a 300 MHz 1H NMR spectra, 75 MHz ^{13}C NMR spectra; all 1H NMR signals multiplets unless stated otherwise. s = singlet, t = triplet; chemical shifts downfield from $SiMe_4$, coupling constants in Hz, in CD_2Cl_2 solution unless stated otherwise; numbering as in Scheme 1; data for complex **7**. 1H NMR δ ($CDCl_3$) 5.35 (C_7H_7). ^{13}C NMR (CD_2Cl_2) 220.7 ($Mo-CO$), 198.2 ($Re-CO$), 90.5 (C_7H_7). ^b 1H NMR data recorded in C_6D_6 . ^c 1H NMR data in parentheses recorded in CD_2Cl_2 . ^d Assignments in ^{13}C NMR spectrum made with the aid of a HETCOR experiment. ^e ^{13}C NMR data recorded at $-40^\circ C$. ^f W -bound carbonyls not observed in ^{13}C spectrum. ^g ^{13}C NMR data recorded in acetone- d_6 . ^h 1H NMR data in parentheses recorded in CD_2Cl_2 at $-40^\circ C$. ⁱ In toluene- d_8 (1H NMR, $-20^\circ C$; ^{13}C NMR, $-60^\circ C$).

cesses established for $[\text{Ru}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_2\text{Cp}]$ and $[\text{Re}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_5]$. In support of this, a spin saturation transfer ^{13}C NMR experiment on **2** at 35°C in CD_2Cl_2 revealed that saturation of the C^7 resonance resulted in a reduction in intensity of the $\text{C}^{1,6}$ resonance of approximately 40% by comparison with the off resonance spectrum, but only small changes were observed for the $\text{C}^{2,5}$ and $\text{C}^{3,4}$ resonances. These data are indicative of the operation of a 1, 2 shift process in complexes **2** to **5** and are in accord with the major migratory process determined for $[\text{Re}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_5]$ [12] and $[\text{Ru}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_2\text{Cp}]$ [13].

The thermal stability of the complexes $[\text{M}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{M}'(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]$ is markedly dependent on M' and R with enhanced stability conferred by $\text{M}' = \text{Ru}$, $\text{R} = \text{Me}$. First row transition metals bonded η^1 to the cycloheptatrienyl ligand are considered to possess very low $\text{M}-\text{C}$ bond dissociation energies [12] and poor stability is manifest in the reports of unsuccessful syntheses of $[\text{Mn}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_5]$ [16] and $[\text{Fe}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_2\text{Cp}]$ [13]. Our success in the isolation of the iron derivative $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ **5** is therefore atypical and is probably attributable to the stabilising effect of the C_5Me_5 ligand, the importance of which is further established by the distinct thermal sensitivity of the unsubstituted cyclopentadienyl analogue $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_2\text{Cp}]$ **6**. The synthesis of **6** was attempted by reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ with $[\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]]$ in THF at -40°C , but all efforts to isolate **6** from the orange reaction mixture, even with a low temperature work up, were unsuccessful, the major isolable products being $[\text{Fe}_2(\text{CO})_4\text{Cp}_2]$ and $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ (Scheme 1). However, evidence for the intermediacy of **6** was obtained by infrared monitoring of samples withdrawn from the reaction mixture and redissolved in hexane (required to achieve good resolution of carbonyl bands). Freshly prepared samples exhibited a complex, nine-band infrared spectrum in the carbonyl stretching region [$\nu(\text{CO})$ (hexane) 2006(m), 1997(m), 1984(s), 1960(s), 1935(sh), 1925(m), 1908(w), 1898(m), 1793(m) cm^{-1}]. Further monitoring revealed a rapid decrease in the intensity of $\nu(\text{CO})$ 1984, 1925, 1898 cm^{-1} and simplification to a six-band spectrum with [$\nu(\text{CO})$ 2006, 1960, 1793 cm^{-1}] characteristic of $[\text{Fe}_2(\text{CO})_4\text{Cp}_2]$ and [$\nu(\text{CO})$ 1997, 1935, 1910 cm^{-1}] attributable to a bicycloheptatriene product, most probably $[\text{Mo}(\text{CO})_3(\eta^6\text{-C}_{14}\text{H}_{14})]$, for which published $\nu(\text{CO})$ data in light petroleum are in excellent agreement [11]. Synthetic studies establish that a major product of this reaction is the essentially hexane insoluble dimolybdenum complex $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ but, in the hexane solvent used to monitor the reaction, $[\text{Mo}(\text{CO})_3(\eta^6\text{-C}_{14}\text{H}_{14})]$ is selectively observed. In polar solvents the infrared active carbonyl stretching bands of $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ and $[\text{Mo}(\text{CO})_3(\eta^6\text{-C}_{14}\text{H}_{14})]$ cannot be satisfactorily resolved. The transient carbonyl stretching bands [$\nu(\text{CO})$ 1984, 1925, 1898 cm^{-1}] are consistent with expected values for the η^6 -bonded $\text{Mo}(\text{CO})_3$ group of **6**; the remaining two bands due to the η^1 -bonded $\text{Fe}(\text{CO})_2\text{Cp}$ of **6** are predicted to be at approximately 2000 and 1960 cm^{-1} and would therefore be obscured by the carbonyl bands of the other reaction products. That **6** is a credible intermediate in the formation of $[\text{Fe}_2(\text{CO})_4\text{Cp}_2]$ and $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ was confirmed by monitoring the thermolysis of **5**, both by ^1H NMR and infrared spectroscopy. A solution of **5** in toluene- d_8 was monitored by NMR as the temperature was increased from 0 to 60°C , which resulted in the progressive and complete conversion of the ^1H NMR resonances from those of **5** to those of $[\text{Fe}_2(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2]$ [δ (toluene- d_8) 1.76] and $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ [δ (toluene- d_8) 5.22, 2H; 4.30, 2H; 2.98, 2H; 1.25, 1H]. Infrared spectroscopic investigations, both on the products of the NMR study and on a separate study of the thermolysis of **5**, also established the formation of $[\text{Fe}_2(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2]$ and $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$. Thus the cycloheptatrienyl bridged complexes **5** and **6** can be considered as intermediates in the generation of homobimetallic products from the cation–anion reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ with $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]^-$ in a process which parallels the intermediacy of $[\text{Fe}(\text{CO})_3(\mu\text{-}\eta^4\text{:}\eta^1\text{-C}_5\text{H}_7)\text{Mo}(\text{CO})_3\text{Cp}]$ in the formation of homo-dimers from the reaction of $[\text{Fe}(\text{CO})_3(\eta^5\text{-pentadienyl})]^+$ with $[\text{Mo}(\text{CO})_3\text{Cp}]^-$ [17]. Finally, it is possible that the formation of $[\text{Mn}_2(\text{CO})_{10}]$ and $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ from reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ with $[\text{Mn}(\text{CO})_5]^-$ [18] proceeds via cycloheptatrienyl-bridged $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Mn}(\text{CO})_5]$, analogous to the stable Re analogue **7**, but our attempts to detect such an intermediate by infrared monitoring of the reaction mixture were unsuccessful.

The ruthenium complexes **1** to **4** are substantially resistant to thermally induced fission of the Ru–cycloheptatrienyl bond, as evidenced by the feasibility of high temperature NMR studies. However, we expected that under appropriate conditions the thermolysis of complexes **1** to **4** would proceed to parallel that of the Fe derivatives, giving the homo-bimetallics $[\text{Ru}_2(\text{CO})_4(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}$ or Me) and $[\text{M}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ ($\text{M} = \text{Cr}$, Mo or W) as the major products. In the event, this straightforward outcome was observed only for $[\text{Cr}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_2\text{Cp}]$ **1**: complexes **2** to **4**, which contain only second or third row transition metals, each gave an additional heterobimetallic product. When solutions of the Mo, Ru complexes **2** and **4** in methylcyclohexane were heated just below reflux [1.5 h (**2**), 16 h (**4**)] a colour change from red/purple–red to green was observed. Work up of the reaction mixtures yielded the expected $[\text{Ru}_2(\text{CO})_4(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}$ or Me) and $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$.

The ruthenium complexes **1** to **4** are substantially resistant to thermally induced fission of the Ru–cycloheptatrienyl bond, as evidenced by the feasibility of high temperature NMR studies. However, we expected that under appropriate conditions the thermolysis of complexes **1** to **4** would proceed to parallel that of the Fe derivatives, giving the homo-bimetallics $[\text{Ru}_2(\text{CO})_4(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}$ or Me) and $[\text{M}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ ($\text{M} = \text{Cr}$, Mo or W) as the major products. In the event, this straightforward outcome was observed only for $[\text{Cr}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_2\text{Cp}]$ **1**: complexes **2** to **4**, which contain only second or third row transition metals, each gave an additional heterobimetallic product. When solutions of the Mo, Ru complexes **2** and **4** in methylcyclohexane were heated just below reflux [1.5 h (**2**), 16 h (**4**)] a colour change from red/purple–red to green was observed. Work up of the reaction mixtures yielded the expected $[\text{Ru}_2(\text{CO})_4(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}$ or Me) and $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$.

$C_{14}H_{14}$], and additionally the heterobinuclear metal–metal bonded complexes $[Ru(CO)_2(\eta-C_5R_5)Mo(CO)_2(\eta-C_7H_7)]$ ($R = H$ or Me ; Scheme 1), which we have reported previously as the products of reaction of $[MoBr(CO)_2(\eta-C_7H_7)]$ with $[Ru(CO)_2(\eta-C_5R_5)]^-$ [9]. Similar thermolysis of the W Ru derivative **3** gave $[Ru(CO)_2CpW(CO)_2(\eta-C_7H_7)]$ as evidenced by infrared data. The thermolysis of **2** and **4** proceeded with extensive decomposition and the complexes $[Ru(CO)_2(\eta-C_5R_5)Mo(CO)_2(\eta-C_7H_7)]$ were isolated in low yield, but nevertheless they represented a major reaction product as evidenced by infrared spectroscopy of the crude reaction mixtures.

The unexpected formation of heterobimetallics from thermolysis of the Ru derivatives **2**, **3** and **4** led us to explore the generality of this process in $\mu-\eta^1:\eta^6-C_7H_7$ -bridged bimetallics with an investigation of the thermolysis of previously reported $[Mo(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Re(CO)_5]$ **7**. Thermal decomposition of **7**, in a process paralleling that established for the Ru analogues **2**, **3** and **4**, would be predicted to result in formation of the heterobimetallic $[Mo(CO)_2(\eta-C_7H_7)Re(CO)_5]$ ($Mo-Re$) **8**. For purposes of identification the new complex **8**, an analogue of previously reported [19] $[Mo(CO)_2(\eta-C_7H_7)Mn(CO)_5]$, was synthesised by reaction of $[MoBr(CO)_2(\eta-C_7H_7)]$ with $Na[Re(CO)_5]$ and isolated as a green solid. Reflux of cycloheptatrienyl-bridged **7** in methylcyclohexane for 30 min resulted in a brown reaction mixture from which three products were isolated as described in the Experimental section. These were identified, by a range of techniques, as $Re_2(CO)_{10}$, $[Re(CO)_3(\eta^5-C_7H_7)]$ [1,10] and, in accord with the predicted reaction, $[Mo(CO)_2(\eta-C_7H_7)Re(CO)_5]$ **8**. In conclusion our results suggest that the generation of metal–metal bonded heterobimetallics from thermolysis of $\mu-\eta^1:\eta^6$ cycloheptatrienyl-bridged bimetallics is a fairly general process with the exception of derivatives in which one or both of the cycloheptatrienyl-bridged groups incorporate a first row transition metal.

The second reaction type of $\mu-\eta^1:\eta^6-C_7H_7$ -bridged bimetallics that we have observed is decomplexation of an η^6 -bonded $Mo(CO)_3$ group, so providing an alternative synthesis of η^1 -cycloheptatrienyl monometallics including the new complex $[Ru(\eta^1-C_7H_7)(CO)_2(\eta-C_5Me_5)]$ **9**. It is well established that nitriles displace the $Mo(CO)_3$ group from the cycloheptatriene complex $[Mo(CO)_3(\eta^6-C_7H_8)]$ [20], and we have now estab-

lished that this reactivity extends to $\eta^1:\eta^6-C_7H_7$ -bridged bimetallics. Thus, stirring a purple–red solution of $[Mo(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Ru(CO)_2(\eta-C_5Me_5)]$ **4** in NCMe resulted in a colour change to orange–yellow and the formation of $[Mo(CO)_3(NCMe)_3]$ and $[Ru(\eta^1-C_7H_7)(CO)_2(\eta-C_5Me_5)]$ **9**. Complex **9** was isolated in moderate yield as an orange solid following purification by column chromatography. Similarly, stirring a solution of $[Mo(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Re(CO)_5]$ **7** in NCMe led to the isolation of known $[Re(\eta^1-C_7H_7)(CO)_5]$. However, we were unable to effect complete conversion of $[Mo(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Ru(CO)_2Cp]$ **2** to $[Ru(\eta^1-C_7H_7)(CO)_2Cp]$ by reaction with NCMe at room temperature, and gentle heating of the solution led only to the rapid generation of $[Ru_2(CO)_4Cp_2]$.

3. 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. $[Mo(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Re(CO)_5]$ **7** was prepared by the literature procedure [2] and $Re_2(CO)_{10}$ was supplied by Aldrich Chemical Co.; alumina (Brockmann activity II) for column chromatography was purchased from Merck. 300 MHz 1H and 75 MHz ^{13}C NMR spectra were recorded on Bruker AC 300 E or Varian Associates XL 300 spectrometers. Infrared spectra were obtained on a Perkin Elmer FT 1710 spectrometer and mass spectra using VG Trio 2000 or Kratos Concept IS instruments. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

3.1. Preparation of $[Cr(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Ru(CO)_2-Cp]$ **1**

A solution of $Na[Ru(CO)_2Cp]$ in THF (15 cm³) [prepared from $[Ru_2(CO)_4Cp_2]$ (0.150 g, 0.34 mmol) in THF, stirred over sodium amalgam (0.16 g, 6.96 mmol) Na in Hg (1 cm³) for 4 h], after separation from the amalgam, was cooled to $-78^\circ C$ and solid $[Cr(CO)_3(\eta-C_7H_7)]PF_6$ (0.251 g, 0.68 mmol) added. The resulting red solution was stirred and allowed to slowly warm to room temperature over a period of 1 h, then solvent was

Table 3
Experimental details for the preparation of $[M(CO)_3(\mu-\eta^6:\eta^1-C_7H_7)Ru(CO)_2(\eta-C_5R_5)]$

Complex	M	R	$[Ru_2(CO)_4(\eta-C_5R_5)_2]$ g (mmol)	$[M(CO)_3(\eta-C_7H_7)]PF_6$ g (mmol)	Yield g (%)	Colour
1	Cr	H	0.150 (0.34)	0.251 (0.68)	0.118 (39)	red
2	Mo	H	0.889 (2.00)	1.666 (4.00)	0.823 (42)	orange–red
3	W	H	0.184 (0.41)	0.414 (0.82)	0.148 (31)	red
4	Mo	Me	0.500 (0.86)	0.709 (1.70)	0.125 (13)	purple–red

removed in vacuo. The red residue was extracted with toluene and the filtered extract reduced to dryness. Subsequent recrystallisation of the residue from diethylether–n-hexane gave **1** as a red solid; yield 0.118 g (39%). The complexes **2**, **3** and **4** were obtained by very similar procedures, essential details of the preparations are given in Table 3.

3.2. Preparation of $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ **5**

$[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]\text{[PF}_6\text{]}$ (0.830 g, 2.00 mmol) was added to a cooled (-78°C) THF solution (50 cm^3) of $\text{K}[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$, [prepared from $[\text{Fe}_2(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2]$ (0.491 g, 0.99 mmol) stirred over Na/K alloy for 5 days]. The reaction mixture was maintained at -78°C for 40 min then warmed to -20°C and the solvent removed in vacuo to give a red, solid residue. Extraction of the residue with diethylether at -40°C followed by filtration through a chilled sinter, then addition of n-hexane and cooling to -78°C resulted in the precipitation of **5** as a red solid, yield 0.209 g (20%).

3.3. Reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]\text{[PF}_6\text{]}$ with $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$

$[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]\text{[PF}_6\text{]}$ (2.36 g, 5.67 mmol) was added to a cooled (-78°C) THF solution (35 cm^3) of $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$, [prepared from $[\text{Fe}_2(\text{CO})_4\text{Cp}_2]$ (1.004 g, 2.84 mmol) stirred over Na/Hg amalgam for 18 h]. The reaction was allowed to proceed for 1.5 h whilst slowly warming to room temperature, then solvent removed in vacuo. The residue was extracted with toluene and the extract filtered, resulting in the separation of a soluble, purple product from an insoluble orange residue. The toluene insoluble material was recrystallised from CH_2Cl_2 –n-hexane to give $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{14})]$ as an orange solid; yield 0.924 g (60%). The toluene soluble, purple fraction was transferred, in toluene (20 cm^3), to an alumina–n-hexane chromatography column and elution with CH_2Cl_2 gave a purple band which afforded $[\text{Fe}_2(\text{CO})_4\text{Cp}_2]$ as a purple solid after recrystallisation from CH_2Cl_2 –n-hexane; yield 0.505 g (50%).

3.4. Formation of $[\text{Ru}(\text{CO})_2\text{CpMo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ by thermolysis of $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_2\text{Cp}]$ **2**

Complex **2** (0.289 g, 0.59 mmol) was heated in methylcyclohexane (65 cm^3) at 100°C for 1.5 h after which the solvent was removed leaving a green residue. The residue, dissolved in toluene, was transferred to an n-hexane–alumina chromatography column and elution with neat toluene gave two bands. The first collected, a green band, yielded $[\text{Ru}(\text{CO})_2\text{CpMo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ as

a green solid following further purification by recrystallisation from diethylether–n-hexane; yield 0.016 g (6%). Anal. Found: C, 41.8; H, 2.8. $\text{C}_{16}\text{H}_{12}\text{O}_4\text{MoRu}$ Calc.: C, 41.3; H, 2.6%. The second, orange band eluted from the column yielded $[\text{Ru}_2(\text{CO})_4\text{Cp}_2]$. Thermolysis of $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ **4** (0.491 g, 0.87 mmol) was carried out by a similar procedure except that the reaction time was 16 h. The reaction residue was extracted with diethylether and filtered, and after two recrystallisations from diethylether–n-hexane, $[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ was isolated as a green solid; yield 0.038 g (8%).

3.5. Preparation of $[\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5]$ (*Mo-Re*) **8**

$[\text{MoBr}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ (0.500 g, 1.55 mmol) was added to a cooled (-78°C) THF (15 cm^3) solution of $\text{Na}[\text{Re}(\text{CO})_5]$, [prepared from $\text{Re}_2(\text{CO})_{10}$ (0.500 g, 0.77 mmol) stirred over sodium amalgam (0.32 g, 13.91 mmol) Na in Hg (2 cm^3) for 2 h]. The stirred reaction mixture was slowly warmed to room temperature over a period of 1 h, then solvent removed in vacuo. The resulting green residue was extracted with toluene and the filtered extract reduced to dryness. Subsequent recrystallisation of the residue from diethylether–n-hexane and cooling to -78°C gave **8** as a green solid; yield 0.597 g (68%).

3.6. Formation of $[\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5]$ **8** by thermolysis of $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5]$ **7**

A solution of **7** (0.306 g, 0.51 mmol) in methylcyclohexane (50 cm^3) was refluxed for 30 min, then filtered hot and solvent removed in vacuo to give a green residue. The residue was extracted with diethylether and the extract solution filtered then treated with n-hexane to precipitate a green solid which was separated and dried. The remaining mother liquors were evaporated to dryness and a vacuum sublimation carried out on the residue, heated to 70°C . A yellow sublimate separated from a green residue. The yellow sublimate was dissolved in n-hexane and two products separated by fractional crystallisation at -78°C . The first precipitate was identified as $[\text{Re}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_7)]$, yield 0.023 g (12%). IR $\nu(\text{CO})$ (hexane) 2035, 1963, 1940 cm^{-1} . Mass spectrum (FAB), 362, M^+ ; 334, $[\text{M-CO}]^+$; 306, $[\text{M-2CO}]^+$; 278, $[\text{M-3CO}]^+$. $^1\text{H NMR}$ δ (CDCl_3) 6.71 (1H), 5.46 (2H), 4.88 (2H), 3.67 (2H). Anal. Found: C, 33.2; H, 2.0. $\text{C}_{10}\text{H}_7\text{O}_3\text{Re}$ Calc.: C, 33.2; H, 1.95%. The second, more soluble material was identified as $\text{Re}_2(\text{CO})_{10}$ by IR spectroscopy. The two separate green solids obtained in the purification procedure were combined, dissolved in toluene and transferred to an n-hexane–alumina chromatography column. Elution with n-hexane–toluene gave a green band from which

$[\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5]$ **8** was isolated as a green solid and identified by IR, mass spectral and ^1H NMR data; yield 0.034 g (12%). Anal. Found: C, 29.3; H, 1.3%. $\text{C}_{14}\text{H}_7\text{O}_7\text{MoRe}$ Calc.: C, 29.5; H, 1.2%.

3.7. Preparation of $[\text{Ru}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ **9**

Purple–red $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ **4** (0.369 g, 0.66 mmol) was dissolved in CH_3CN and the reaction mixture stirred for 15 min, after which infrared spectroscopy indicated completion of the reaction and the formation of **9** together with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ [$\nu(\text{CO})$ (NCMe) 1920, 1796 cm^{-1}]. The reaction mixture was evaporated to dryness and the orange–yellow residue dissolved in toluene and transferred to an n-hexane–alumina chromatography column. Elution with toluene gave an orange band from which solvent was removed. The residue was dissolved in n-hexane, and the solution filtered and cooled to -78°C to precipitate **9** as an orange solid; yield 0.090 g (36%). A similar procedure, starting from $[\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5]$ (0.432 g, 0.72 mmol) dissolved in NCMe and product purification by recrystallisation from n-hexane, gave the known complex $[\text{Re}(\eta^1\text{-C}_7\text{H}_7)(\text{CO})_5]$ as an orange solid, yield 0.202 g (67%). Anal. Found: C, 34.7; H, 2.0. $\text{C}_{12}\text{H}_7\text{O}_5\text{Re}$ Calc.: C, 34.5; H, 1.7%.

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