Reactions of the cycloheptatrienyl complexes [MX(CO)$_2$(η-C$_7$H$_7$)] (M = Mo, X = Br; M = W, X = I) with CNBu^t: X-ray crystal structure of [WI(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)]

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Abstract

Reaction of [MX(CO)$_2$(η^7-C$_7$H$_7$)] (M = Mo, X = Br; M = W, X = I) with two equivalents of CNBu^t in toluene affords the trihapto-bonded cycloheptatrienyl complexes [MX(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)] (**1**, M = Mo, X = Br; **2**, M = W, X = I). The X-ray crystal structure of **2** reveals a pseudo-octahedral molecular geometry with an asymmetric ligand arrangement at tungsten in which one CNBu^t is located *trans* to the η^3-C$_7$H$_7$ ring. Treatment of **2** with tetracyanoethene results in 1,4-cycloaddition at the η^3-C$_7$H$_7$ ring to give [WI(CO)$_2$(CNBu^t)$_2${η^3-C$_9$H$_7$(CN)$_4$}], **3**. The principal reaction type of the molybdenum complex **1** is loss of carbonyl and bromide ligands to afford substituted products [MoBr(CNBu^t)$_2$(η^7-C$_7$H$_7$)] **4** or [Mo(CO)(CNBu^t)$_2$(η^7-C$_7$H$_7$)]Br. Reaction of [MoBr(CO)$_2$(η^7-C$_7$H$_7$)] with one equivalent of CNBu^t in toluene at 60°C affords [MoBr(CO)(CNBu^t)(η^7-C$_7$H$_7$)], **5**, which is a precursor to [Mo(CO)(CNBu^t)(NCMe)(η^7-C$_7$H$_7$)][BF$_4$], **6**, by reaction with Ag[BF$_4$] in acetonitrile. In contrast with the parent dicarbonyl systems [MoX(CO)$_2$(η^7-C$_7$H$_7$)], complexes of the Mo(CO)(CNBu^t)(η^7-C$_7$H$_7$) auxiliary, **5** and **6**, do not afford observable η^3-C$_7$H$_7$ products by ligand addition at the molybdenum centre. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Tungsten; Isocyanide; Cycloheptatrienyl; Hapticity; Allyl

1. Introduction

Complexes of the general formulation [MX(CO)$_2$-L$_2'$(η^3-allyl)] [M = Mo or W; X = halide or pseudo-halide; L′ = NCMe, L$_2'$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe), 2,2′-bipyridine (bipy), etc.] represent an important area of the organometallic chemistry of molybdenum and tungsten and investigations with an extensive range of η^3-allyl ligands (including allyl = C$_3$H$_5$ [1], pentadienyl [2], hexadienyl [3], cyclopentenoyl [4], cycloheptadienyl [5], cyclooctadienyl [6] or cycloheptatrienyl) have been reported. In a series of papers [7–11], we have examined the synthesis, structure, fluxional properties and reactivity of η^3-cycloheptatrienyl complexes of the type [MX(CO)$_2$L$_2'$(η^3-C$_7$H$_7$)] (M = Mo or W) and related cationic derivatives. The majority of this work

has employed the chelates bipy, dppe and dppm (Ph$_2$PCH$_2$PPh$_2$) as supporting L$_2'$ groups and these appear to define strong preferences for the geometric arrangement of ligands at the metal centre. In search of a more structurally flexible system, we examined the feasibility of employing monodentate L′ ligands as supporting groups. In fact the options for suitable mondentate L′ ligands are fairly restricted. Ligands such as NCMe are too labile (especially in η^3-cycloheptatrienyl complexes [11]) to provide a stable MX(CO)$_2$L$_2'$ auxiliary and, whilst [MoCl(CO)$_2${P(OMe)$_3$}$_2$(η^3-C$_3$H$_5$)] is known [12], in the cycloheptatrienyl system reaction of [MX(CO)$_2$(η^7-C$_7$H$_7$)] (M = Mo or W; X = halide) with PR$_3$ (R = Me or OMe) affords [MX(CO)(PR$_3$)(η^7-C$_7$H$_7$)] [13]. However a report [14] on the synthesis of [MoCl(CO)$_2$(CNBu^t)$_2$(η^3-C$_3$H$_5$)] prompted the successful use of CNBu^t as a supporting L′ ligand in the cyclohep-

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tatrienyl system and this paper describes the structure and properties of the resulting $[MX(CO)_2(CNBu^t)_2(\eta^3\text{-}C_7H_7)]$ complexes.

2. Results and discussion

Reaction of $[MX(CO)_2(\eta^7\text{-}C_7H_7)]$ (M = Mo, X = Br; M = W, X = I) with two equivalents of CNBu^t in toluene resulted in a colour change from green to red and the formation of the trihapto-bonded cycloheptatrienyl complexes $[MX(CO)_2(CNBu^t)_2(\eta^3\text{-}C_7H_7)]$ (**1**, M = Mo, X = Br; **2**, M = W, X = I; see Scheme 1 for specific reaction conditions). The preparation and purification of the molybdenum derivative **1** were carried out at low temperature to avoid reversion to $\eta^7\text{-}C_7H_7$ products through loss of labile Br or CO ligands (see later). Details of the characterisation of these and subsequently described complexes are presented in Table 1 (microanalytical and IR spectroscopic data) and Table 2 (^{1}H- and ^{13}C{^{1}H}-NMR spectroscopic data). The $\eta^7 \rightarrow \eta^3$ hapticity conversion at the cycloheptatrienyl ring is accompanied by characteristic spectroscopic changes in ν(CO) in the IR spectrum and δ(C$_7$H$_7$) in the ^{13}C{^{1}H}-NMR spectrum [11].

We have previously reported X-ray structural studies on the η^3-cycloheptatrienyl complexes $[MoX(CO)_2\text{-}L_2'(\eta^3\text{-}C_7H_6R)]$ (X = NCS, L$_2'$ = bipy, R = H; X = Cl, L$_2'$ = dppe, R = C$_6$H$_4$F-4 [11]) which, in common with a wide range of complexes of the type $[MX(CO)_2L_2'(\eta^3\text{-allyl})]$ (L$_2'$ = bidentate chelate ligand) demonstrate a marked structural dependence upon L$_2'$. However synthetic and structural investigations on complexes $[MX(CO)_2L_2'(\eta^3\text{-allyl})]$ (L' = monodentate ligand) are much more limited and, with the exception of L' = NCMe, we are aware only of crystallographic characterisations of $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$ [12] and $[MoBr(CO)_2(C_3H_4N_2)_2(\eta^3\text{-1-Ph-}C_3H_4)]$ (C$_3$H$_4$-N$_2$ = pyrazole) [15]. The structure type of complexes **1** and **2** was therefore of interest, further to define the ligand dependent molecular geometry of the $[MX(CO)_2L_2'(\eta^3\text{-allyl})]$ system. Complex **2** was selected for investigation because of the enhanced stability of the tungsten derivative with respect to reversion to $\eta^7\text{-}C_7H_7$ products and because it provides the first crystallographically characterised example of the cycloheptatrienyl ligand bonded trihapto to tungsten in a monometallic complex.

The molecular geometry of $[WI(CO)_2(CNBu^t)_2(\eta^3\text{-}C_7H_7)]$ **2** and the atomic numbering scheme employed are illustrated in Fig. 1 and details of important bond lengths and angles are presented in Table 3. The complex adopts a pseudo-octahedral geometry, with one CNBu^t ligand located *trans* to the η^3-C$_7$H$_7$ ring and the remaining ligands occupying an approximately equatorial plane, the carbonyl ligands being placed mutually

cis. An asymmetric ligand arrangement similar to that of $[MoBr(CO)_2(C_3H_4N_2)_2(\eta^3\text{-1-Ph-}C_3H_4)]$ is therefore adopted and it appears that despite the similar π-acceptor nature of CO and CNBu^t ligands, location of CO *trans* to the η^3-allyl type ligand is still the least favourable option. Some structural features of complex **2** are in common with the vast majority of systems $[MX(CO)_2L_2'(\eta^3\text{-allyl})]$ including the location of the two carbonyls directly beneath the terminal carbons of the η^3-allyl fragment and a shortening of the W–C (central allyl) distance by comparison with the W–C (terminal allyl) bonds. The η^3-cycloheptatrienyl ring is folded about the planes defined by [C(2)–C(1)–C(7)] and [C(2)–C(3)–C(4)–C(5)–C(6)–C(7)] with the angle between the planes (37°) similar to those reported for $[Mo(CO)_2(\eta^3\text{-}C_7H_7)Cp]$ (36°) [16], $[Mo(NCS)(CO)_2\text{-}(bipy)(\eta^3\text{-}C_7H_7)]$ (32°) and $[MoCl(CO)_2(dppe)(\eta^3\text{-}C_7H_6C_6H_4F\text{-}4)]$ (33°) [11].

^{13}C-NMR data for **1** and **2** suggest that the asymmetric ligand arrangement deduced for **2** in the solid state is retained in solution. The room temperature (r.t.) ^{13}C{^{1}H}-NMR spectra of **1** and **2** each show a singlet for the η^3-C$_7$H$_7$ ring consistent with a 1,2-shift process [8,17] which renders equivalent all positions in the cycloheptatrienyl ring. However each complex exhibits two discrete carbonyl resonances and, although slightly broad at r.t., two resonances for each of the C*N*CMe$_3$ and CN*C*Me$_3$ carbons. This inequivalence of both carbonyl and both isocyanide ligands is clearly consistent with the solid state structure of **2**. Further spectroscopic evidence for an asymmetric structure is provided by the variable temperature ^{13}C{^{1}H}-NMR spectrum of **2**. At − 30°C in CD$_2$Cl$_2$, the resonances assigned to the carbonyl and isocyanide ligands of **2** are sharpened by comparison with the r.t. spectrum but the resonance attributed to the cycloheptatrienyl ring is notably broadened, consistent with a reduced rate of the 1,2-shift process. At − 80°C, the signal at 102 ppm assigned to the C$_7$H$_7$ ring is absent but the region of the spectrum from 120 to 140 ppm exhibits six resonances (δ, CD$_2$Cl$_2$: 138.3, 137.5, 130.7, 128.2, 125.2, 124.7) attributable to two C*N*Bu^t carbons and the four diene carbons (C$_3$ and C$_4$—see Scheme 1 for NMR numbering system) of the cycloheptatrienyl ring. The inequivalence of all four diene carbons is again consistent with an asymmetric ligand arrangement at the metal centre.

Our previous investigations on complexes of the general type $[MX(CO)_2L_2'(\eta^3\text{-}C_7H_7)]$ have established two principal reactivity types. Where M = Mo, the dominant reaction type is reversion to an $\eta^7\text{-}C_7H_7$ product via loss of CO or X ligands. However, where M = W and the W–X bond is relatively strong (X = I), the complexes are resistant to fission of W–CO and W–X bonds so permitting reactions at the η^3-C$_7$H$_7$ ring to be explored. The derivatives prepared in the current work were designed to promote these two contrasting reactiv-
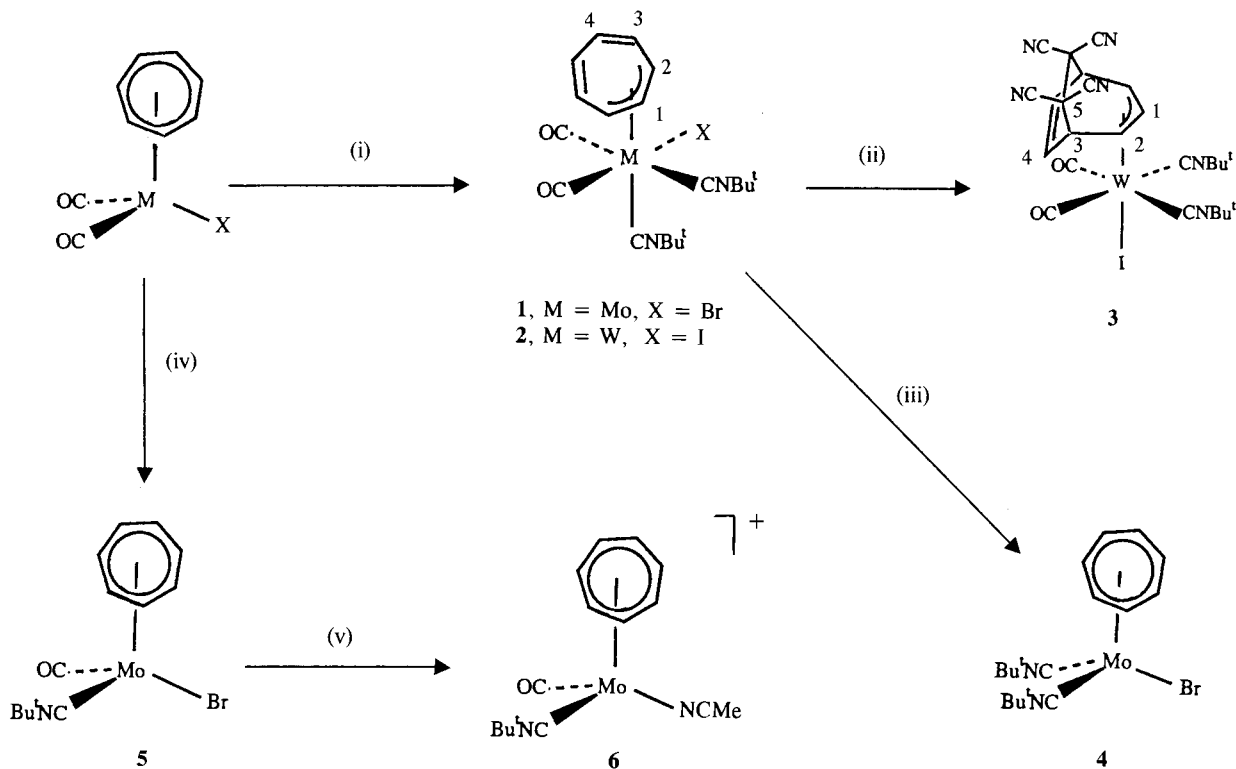
Scheme 1. Reagents and conditions: (i) M = Mo, X = Br; 2CNBu^t in toluene, 0°C, 30 min. M = W, X = I; 2CNBu^t in toluene, r.t., 4.5 h. (ii) M = W, X = I; tcne in CH$_2$Cl$_2$, 2 h. (iii) M = Mo, X = Br; reflux in toluene, 30 min. (iv) M = Mo, X = Br; CNBu^t (one equivalent) in toluene (60°C). (v) Ag[BF$_4$] in CH$_3$CN, 30 min.

ity types; thus the molybdenum derivative **1** with a weakly bonded bromide ligand should readily afford ligand substituted η^7-C$_7$H$_7$ products whereas the tungsten complex **2**, should be stable in the η^3-C$_7$H$_7$ form.

One reaction type, apparently exclusive to tungsten derivatives, is addition of tetracyanoethene (tcne) to the η^3-C$_7$H$_7$ ring. Thus we have demonstrated previously that reaction of [WI(CO)$_2$L$_2'$(η^3-C$_7$H$_7$)] (L$_2'$ = dppe or dppm) with tcne affords the isolable adducts [WI(CO)$_2$L$_2'$\{η^3-C$_9$H$_7$(CN)$_4$\}] with retention of an asymmetric ligand arrangement at the coordinated WI(CO)$_2$L$_2'$ metal group [8]. Similarly, reaction of [WI(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)], **2** with tcne affords

[WI(CO)$_2$(CNBu^t)$_2$\{η^3-C$_9$H$_7$(CN)$_4$\}], **3** as a deep purple solid. The ^{1}H and ^{13}C\{^{1}H\}-NMR data for **3** are fully consistent with the 1,4-addition of tcne to the cycloheptatrienyl ring, with the separate carbon environments of the C$_9$H$_7$(CN)$_4$ ligand clearly discernable. However, by comparison with the ^{13}C\{^{1}H\}-NMR spectra of the phosphine analogues [WI(CO)$_2$L$_2'$(η^3-C$_7$H$_7$)] (L$_2'$ = dppe or dppm), the data for **3** are unexpectedly simple. Thus, whereas for [WI(CO)$_2$(dppm)\{η^3-C$_9$H$_7$(CN)$_4$\}], the asymmetry of the WI(CO)$_2$(dppm) ligand arrangement is clear from the inequivalence of carbonyl ligands and otherwise identical carbons in the C$_9$H$_7$(CN)$_4$ ligand, in **3** both at r.t. and at -80°C, only seven discrete

Table 1
Microanalytical and IR spectroscopic data

Complex	Analysis(%)[a]			IR (cm^{-1})[b]	
	C	H	N	ν(CO)	ν(CN)
[MoBr(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)] **1**	46.4 (46.6)	5.0 (5.1)	5.4 (5.7)	1957, 1879	2177
[WI(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)][c] **2**	36.5 (36.5)	3.8 (4.0)	4.2 (4.5)	1953, 1877	2173
[WI(CO)$_2$(CNBu^t)$_2$\{η^3-C$_9$H$_7$(CN)$_4$\}] **3**	40.1 (39.9)	3.4 (3.3)	11.1 (11.2)	1989, 1933	2186, 2175
[MoBr(CNBu^t)$_2$(η^7-C$_7$H$_7$)] **4**	47.0 (47.1)	6.0 (5.8)	6.2 (6.5)		2127
[MoBr(CO)(CNBu^t)(η^7-C$_7$H$_7$)] **5**	40.9 (41.3)	4.3 (4.2)	3.4 (3.7)	1962	2144
[Mo(CO)(CNBu^t)(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] **6**	41.9 (42.3)	4.4 (4.5)	6.2 (6.6)	1983	2156

[a] Calculated values in parentheses. [b] Solution spectra in CH$_2$Cl$_2$. [c] FAB mass spectrum, m/z values based on ^{184}W, 624 (M^+), 568 ([$M-2$CO]$^+$), 497 ([$M-$I]$^+$), 469 ([$M-$CO$-$I]$^+$), 441 ([$M-2$CO$-$I]$^+$).

Table 2
^{1}H and ^{13}C{^{1}H}-NMR data[a]

Complex	^{1}H-NMR data		^{13}C{^{1}H}-NMR data					
	C_7H_7	CNCMe_3	CO	CNCMe_3	C_7H_7	CNCMe$_3$	CNCMe_3
1	5.57	1.54	224.3, 217.2	153.1, 149.5	106.3	57.5, 57.2	30.5
2	5.36	1.53	211.8, 207.1	142.3, 141.3	102.0	57.7, 57.4	30.5, 30.2
3[b]	6.43,m, 2H, H^4; 3.95,m, 1H, H^1;	1.49	204.6	133.9	136.4, C^4; 113.5, 112.8, CN; 52.8, C^1; 49.3, 48.5, C^{2,3}; 46.8, C^5	58.6	30.5
	3.80,m, 4H, H^{2,3}						
4[c]	5.17	1.17	—	173.1	90.2	57.7	31.6
5	5.22	1.48	227.4	157.5	91.8	57.6	30.7
6	5.44	1.55 (CNCMe_3), 2.42 (NCMe)					

[a] 300 MHz ^{1}H-NMR spectra, 75 MHz ^{13}C{^{1}H}-NMR spectra; all signals singlets unless stated otherwise, m = multiplet. Chemical shifts downfield from SiMe$_4$, spectra recorded in CDCl$_3$ unless stated otherwise, numbering as in Scheme 1. [b] ^{13}C{^{1}H}-NMR data in CD$_2$Cl$_2$, assignments made with the aid of a [^{1}H–^{13}C] HETCOR experiment. [c] In C$_6$D$_6$.
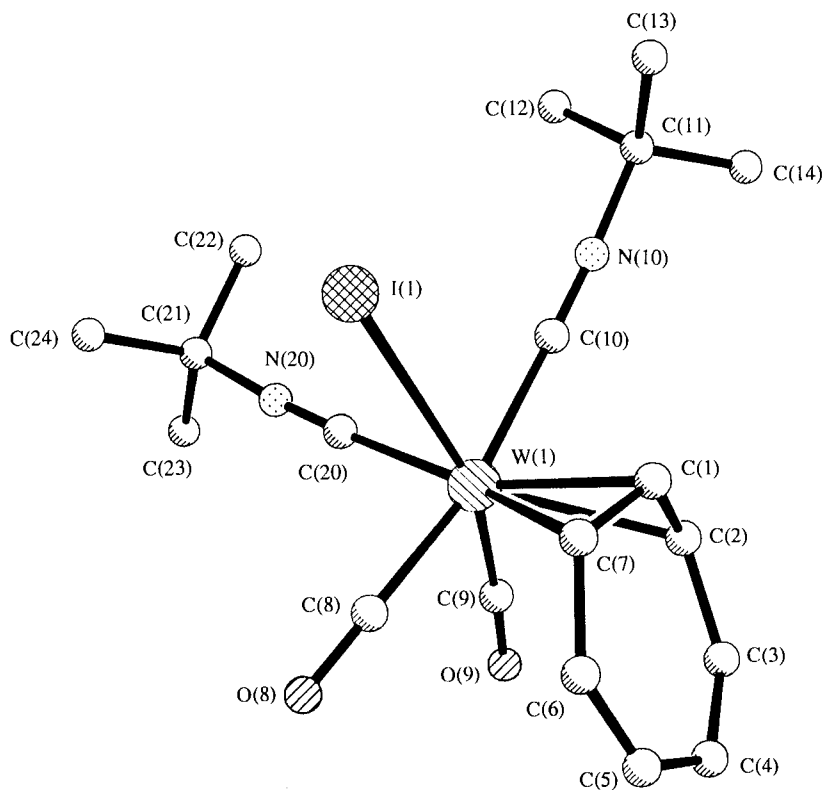
Fig. 1. The molecular structure of complex **2** showing the crystallographic numbering scheme (H atoms omitted for clarity).

resonances are attributable to the $C_9H_7(CN)_4$ ligand and moreover (in contrast with **2**) the pairs of carbonyl and CNBu^t ligands appear to be equivalent. Further evidence that the course of the reaction between tcne and **2** differs slightly from that with $[WI(CO)_2L_2'(\eta^3\text{-}C_7H_7)]$ (L_2 = dppe or dppm) is provided by IR data; the formation of **3** from **2** is accompanied by an increase in $\nu(CO)_{average}$ by 46 cm^{-1} but the corresponding shift on formation of $[WI(CO)_2(dppm)\{\eta^3\text{-}C_9H_7(CN)_4\}]$ is only 24 cm^{-1}. One possible rationalisation for these observations is that the formation of the tcne adduct **3** from **2** is accompanied by isomerisation at the metal centre to a symmetrical ligand arrangement in which the iodide ligand is located *trans* to the $C_9H_7(CN)_4$ group (see Scheme 1). Such a structure is consistent with the NMR data and a trigonal twist process (which has been shown to operate in many complexes of the type $[MX(CO)_2L_2'(\eta^3\text{-allyl})]$ [8,18]) provides a facile mechanism for isomerism. We suggest therefore that the $WI(CO)_2(CNBu^t)_2$ fragment can exhibit a flexible molecular geometry with the preferred structure dependent upon the identity of the η^3-bonded ligand. However, notwithstanding many attempts, we have been unable to obtain crystals of **3** suitable for X-ray characterisation, further to establish this hypothesis.

As predicted, the principal reaction type of the molybdenum complex $[MoBr(CO)_2(CNBu^t)_2(\eta^3\text{-}C_7H_7)]$ **1**, was reversion to products with an η^7-bonded cyclo-heptatrienyl ring by elimination of bromide and carbonyl ligands. The products of ligand elimination from complex **1** are markedly solvent dependent. Thus a short reflux of **1** in rigorously dried toluene resulted in loss of both carbonyl ligands and formation of $[MoBr(CNBu^t)_2(\eta^7\text{-}C_7H_7)]$, **4**. By contrast, in polar solvents such as acetone, elimination of bromide together with one carbonyl ligand to give $[Mo(CO)(CNBu^t)_2(\eta^7\text{-}C_7H_7)]Br$ is preferred and we have previously described the direct synthesis of $[Mo(CO)(CNBu^t)_2(\eta^7\text{-}C_7H_7)][PF_6]$ from $[MoBr(CO)_2(\eta^7\text{-}C_7H_7)]$, CNBu^t and $[NH_4][PF_6]$ in refluxing acetone [10]. The formation of both **4** and $[Mo(CO)(CNBu^t)_2(\eta^7\text{-}C_7H_7)][PF_6]$ can be described as associative ligand substitution processes which proceed via **1** in an $\eta^7 \rightarrow \eta^3 \rightarrow \eta^7$ pathway.

The syntheses of **1** and **2** from $[MX(CO)_2(\eta^7\text{-}C_7H_7)]$ and two equivalents of CNBu^t contrasts with analogous reactions with PR$_3$ [PR$_3$ = P(OMe)$_3$ or PMe$_3$] which proceed to give the carbonyl substituted products $[MX(CO)(PR_3)(\eta^7\text{-}C_7H_7)]$ or $[M(CO)(PR_3)_2(\eta^7\text{-}C_7H_7)]^+$ directly with no evidence for η^3-C_7H_7 adducts as intermediates. Indeed in the case (M = Mo, X = Br, PR$_3$ = PMe$_3$), a cationic intermediate $[Mo(CO)_2(PMe_3)(\eta^7\text{-}C_7H_7)]Br$, formed by substitution of Br by PMe$_3$, has been identified; subsequent warming to 80°C in toluene results in substitution of CO by the bromide counter anion to give $[MoBr(CO)(PMe_3)(\eta^7\text{-}C_7H_7)]$ [13]. In view of these findings

Table 3
Important bond lengths (Å) and angles (°) for complex **2**

Bond lengths (Å)

W(1)–I(1)	2.885(2)	C(6)–C(7)	1.437(20)
W(1)–C(1)	2.244(13)	C(8)–O(8)	1.172(19)
W(1)–C(2)	2.387(11)	C(9)–O(9)	1.202(20)
W(1)–C(7)	2.422(14)	C(10)–N(10)	1.157(19)
W(1)–C(8)	1.970(15)	N(10)–C(11)	1.441(19)
W(1)–C(9)	1.908(16)	C(11)–C(12)	1.481(23)
W(1)–C(10)	2.140(15)	C(11)–C(13)	1.554(28)
W(1)–C(20)	2.111(13)	C(11)–C(14)	1.502(27)
C(1)–C(2)	1.434(22)	C(20)–N(20)	1.142(17)
C(1)–C(7)	1.352(21)	N(20)–C(21)	1.478(17)
C(2)–C(3)	1.421(20)	C(21)–C(22)	1.483(27)
C(3)–C(4)	1.326(22)	C(21)–C(23)	1.537(31)
C(4)–C(5)	1.464(26)	C(21)–C(24)	1.490(25)
C(5)–C(6)	1.293(21)		

Bond angles (°)

I(1)–W(1)–C(1)	93.5(4)	C(7)–W(1)–C(20)	157.2(5)
I(1)–W(1)–C(2)	127.5(4)	C(8)–W(1)–C(20)	92.9(5)
C(1)–W(1)–C(2)	35.9(5)	C(9)–W(1)–C(20)	82.4(5)
I(1)–W(1)–C(7)	82.5(3)	C(10)–W(1)–C(20)	78.9(5)
C(1)–W(1)–C(7)	33.4(5)	W(1)–C(1)–C(2)	77.5(8)
C(2)–W(1)–C(7)	61.0(5)	W(1)–C(1)–C(7)	80.5(8)
I(1)–W(1)–C(8)	90.4(4)	C(2)–C(1)–C(7)	122.4(14)
C(1)–W(1)–C(8)	105.5(5)	W(1)–C(2)–C(1)	66.6(7)
C(2)–W(1)–C(8)	111.7(5)	W(1)–C(2)–C(3)	122.1(10)
C(7)–W(1)–C(8)	74.1(6)	C(1)–C(2)–C(3)	123.6(13)
I(1)–W(1)–C(9)	160.0(4)	C(2)–C(3)–C(4)	131.2(15)
C(1)–W(1)–C(9)	106.5(5)	C(3)–C(4)–C(5)	125.7(15)
C(2)–W(1)–C(9)	72.3(5)	C(4)–C(5)–C(6)	128.4(14)
C(7)–W(1)–C(9)	113.8(5)	C(5)–C(6)–C(7)	130.0(14)
C(8)–W(1)–C(9)	83.5(6)	W(1)–C(7)–C(1)	66.1(8)
I(1)–W(1)–C(10)	82.1(4)	W(1)–C(7)–C(6)	117.0(11)
C(1)–W(1)–C(10)	81.9(5)	C(1)–C(7)–C(6)	126.9(13)
C(2)–W(1)–C(10)	78.4(5)	W(1)–C(8)–O(8)	176.5(14)
C(7)–W(1)–C(10)	111.5(5)	W(1)–C(9)–O(9)	176.5(13)
C(8)–W(1)–C(10)	169.9(5)	W(1)–C(10)–N(10)	175.7(13)
C(9)–W(1)–C(10)	101.2(6)	W(1)–C(20)–N(20)	177.6(13)
I(1)–W(1)–C(20)	78.8(4)	C(10)–N(10)–C(11)	172.0(15)
C(1)–W(1)–C(20)	160.2(5)	C(20)–N(20)–C(21)	175.0(15)
C(2)–W(1)–C(20)	141.7(5)		

the possibility of the synthesis of an analogous CNBu^t complex was investigated. Reaction of [MoBr(CO)$_2$(η^7-C$_7$H$_7$)] with one equivalent of CNBu^t resulted in a red solution probably due to partial conversion to **1**. However subsequent warming to 60°C gave a green solution from which the desired product, pale green, mono-substituted [MoBr(CO)(CNBu^t)(η^7-C$_7$H$_7$)], **5**, was isolated.

We have previously reported that, with the exception of [Mo(CO)(CNBu^t)$_2$(η^7-C$_7$H$_7$)][PF$_6$], only dicarbonyl complexes of the type [MoX(CO)$_2$(η^7-C$_7$H$_7$)]$^{n+}$ ($n = 0$, X = one-electron ligand; $n = 1$, X = two-electron ligand) undergo $\eta^7 \rightarrow \eta^3$ hapticity conversion at the cycloheptatrienyl ring [11]. However, as a result of the similar donor/acceptor properties of the CO and CNBu^t ligands, it might be expected that the auxiliaries Mo(CO)L(η^7-C$_7$H$_7$) (L = CO or CNBu^t) would

confer closely related reactivity and therefore the possibility of $\eta^7 \rightarrow \eta^3$ hapticity conversion in **5** was investigated. Complex **5**, in solution in toluene, did not react with further CNBu^t at r.t. and although heating to 80°C resulted in substitution of CO by CNBu^t to give [MoBr(CNBu^t)$_2$(η^7-C$_7$H$_7$)], **4**, there was no evidence for the intermediacy of an η^3-C$_7$H$_7$ bonded adduct. Treatment of an acetonitrile solution of **5** with Ag[BF$_4$] resulted in bromide abstraction and formation of [Mo(CO)(CNBu^t)(NCMe)(η^7-C$_7$H$_7$)][BF$_4$], **6**. However, in contrast with the analogous reaction of [MoI(CO)$_2$(η^7-C$_7$H$_7$)], which in acetonitrile affords [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_7$)]$^+$ as a mixture with [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)]$^+$ [9], complex **6** appears to be unreactive towards addition of further acetonitrile. These results further establish the requirement for the dicarbonyl M(CO)$_2$(η-C$_7$H$_7$) (M = Mo or W) auxiliary in the design of complexes reactive towards $\eta^7 \rightarrow \eta^3$-C$_7H_7$ hapticity conversion.

3. Experimental

3.1. General procedures

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 compounds [MoBr(CO)$_2$(η^7-C$_7$H$_7$)] and [WI(CO)$_2$(η^7-C$_7$H$_7$)] were prepared by published procedures [19] and the chemicals CNBu^t, tetracyanoethene and Ag[BF$_4$] were supplied by Aldrich. 300 MHz ^{1}H- and 75 MHz ^{13}C{^{1}H}-NMR spectra were recorded on Bruker AC 300 E or Varian Associates XL 300 spectrometers. IR spectra were obtained on a Perkin Elmer FT 1710 spectrometer and FAB mass spectra using a Kratos Concept 1S instrument. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

3.2. Preparation of [MoBr(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)] 1

A green solution of [MoBr(CO)$_2$(η^7-C$_7$H$_7$)] (0.495 g, 1.53 mmol) in toluene (50 cm^3) was cooled to 0°C and then treated with CNBu^t (0.264 g, 3.18 mmol). After stirring for 30 min, the resulting red reaction mixture was evaporated to dryness and the residue recrystallised from diethylether/n-hexane to give **1** as a red–brown solid; yield 0.353 g (47%). The red–brown tungsten derivative [WI(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)] **2** was prepared in 73% yield starting from [WI(CO)$_2$(η^7-C$_7$H$_7$)] (0.866 g, 1.89 mmol) and CNBu^t (0.331 g, 3.99 mmol) in toluene by a similar method except that the reaction was allowed to proceed at r.t. for 4.5 h.

Table 4
Crystal and data collection parameters for complex **2**

Crystal data	
Formula	$C_{19}H_{18}WN_2O_2I$
Mass	617.1
Crystal system	Triclinic
Crystal colour, habit	Red, block
Space group	$P\bar{1}$
a (Å)	6.823 (2)
b (Å)	10.235 (4)
c (Å)	17.014 (6)
α (°)	74.89 (3)
β (°)	83.56 (3)
γ (°)	84.98 (3)
Volume (Å^3)	1137.8 (7)
Temperature (°C)	22
No. of molecules in unit cell, Z	2
$D_{calc.}$ (g cm^{-3})	1.801
$F(000)$	578
μ (mm^{-1})	6.540 (Mo–K$_\alpha$)
Crystal dimensions (mm)	$0.14 \times 0.08 \times 0.05$
Data collection/reduction	
Diffractometer	Nicolet R3m/V
Radiation λ (Å)	Mo–K$_\alpha$ (0.71073)
2θ range (°)	2.5–50.0
Scan type	$2\theta-\theta$
Index ranges	$0 \le h \le 8$, $-12 \le k \le 12$, $-20 \le l \le 20$
Absorption correction	Semi-empirical
Total data	4397
Unique data	4025
'Observed' data [$F > 4\sigma(F)$], N_o	2868
Solution and refinement	
Least squares variables, N_v	226
R^a	0.055
R_w^a	0.055
Goodness-of-fit, S^a	1.17
Difference map features (e Å^{-3})	$+0.83$, -0.76

^{a} $R = \Sigma|\Delta|/\Sigma|F_o|$; $R_w = (\Sigma w \Delta^2/\Sigma w F_o^2)^{1/2}$; $S = [\Sigma w \Delta^2/(N_o - N_v)]^{1/2}$; $\Delta = F_o - F_c$.

3.3. Preparation of [WI(CO)$_2$(CNBu^t)$_2$\{η^3-C$_9$H$_7$(CN)$_4$\}] 3

Reaction of a solution of [WI(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)] (0.594 g, 0.95 mmol) in CH$_2$Cl$_2$ (50 cm^3) with tetracyanoethene (0.123 g, 0.96 mmol) resulted in the rapid formation of a purple reaction mixture. After 2 h the solution was filtered, reduced in volume and *n*-hexane added to precipitate the crude product. Recrystallisation from CH$_2$Cl$_2$/*n*-hexane gave **3** as a deep purple solid; yield 0.433 g (61%).

3.4. Preparation of [MoBr(CNBu^t)$_2$(η^7-C$_7$H$_7$)] 4 from [MoBr(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)]

A red solution of [MoBr(CO)$_2$(CNBu^t)$_2$(η^3-C$_7$H$_7$)] **1** (0.270 g, 0.55 mmol) in toluene (60 cm^3) was refluxed

for 30 min to give a green solution which was filtered, reduced in volume and treated with *n*-hexane to precipitate **4** as a green solid; yield 0.125 g (53%).

3.5. Preparation of [MoBr(CO)(CNBu^t)(η^7-C$_7$H$_7$)] 5

A stirred solution of [MoBr(CO)$_2$(η^7-C$_7$H$_7$)] (0.335 g, 1.04 mmol) in toluene (60 cm^3) was treated with CNBu^t (0.087 g, 1.05 mmol) resulting in a colour change from green to red. The reaction mixture was then warmed to 60°C and, over a period of 1 h, the colour of the solution reverted to green. The reaction mixture was then evaporated to dryness and the residue recrystallised from CH$_2$Cl$_2$/*n*-hexane to give **5** as a light green solid; yield 0.069 g (18%).

3.6. Preparation of [Mo(CO)(CNBu^t)(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] 6

A stirred solution of [MoBr(CO)(CNBu^t)(η^7-C$_7$H$_7$)] **5** (0.547 g, 1.45 mmol) in acetonitrile (50 cm^3) was treated with Ag[BF$_4$] (0.283 g, 1.45 mmol) resulting in the rapid formation of a precipitate of AgBr. After 30 min, the reaction mixture was filtered to give a green solution which was then evaporated to dryness. Recrystallisation of the residue from CH$_2$Cl$_2$/*n*-hexane gave **6** as a green solid; yield 0.384 g (56%).

3.7. Crystal structure analysis of 2

The majority of details of the structure analysis carried out on **2** are presented in Table 4. Dark red crystals of **2** were obtained by slow diffusion of a hexane layer into a toluene solution of the compound. The structure was solved by Patterson methods and refined by full-matrix least-squares. Non-H atoms were refined anisotropically but the hydrogen atoms were included as a riding model with a fixed isotropic U. The crystallographic weighting scheme employed was $w^- 1 = \sigma^2(F_0) + 0.0005F_0^2$. Neutral atom scattering factors were taken from reference [20] and all calculations were performed using the Nicolet SHELXTL [21] crystallographic software package.

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References

[1] R. Davis, L.A.P. Kane-Maguire, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 3, 1st ed., Pergamon, New York, 1982, pp. 1156–1158.

[2] G.-H. Lee, S.-M. Peng, F.-C. Liu, D. Mu, R.-S. Liu, Organometallics 8 (1989) 402.

[3] M.A. Paz-Sandoval, P. Juárez Saavedra, G. Durán Pomposo, P. Joseph-Nathan, P. Powell, J. Organomet. Chem. 387 (1990) 265.

[4] K. Mauthner, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 15 (1996) 181.

[5] Z.I. Hussain, A.-L.A.B. de Souza, M.W. Whiteley, J. Organomet. Chem. 544 (1997) 121.

[6] R.L. Beddoes, D.M. Spencer, M.W. Whiteley, J. Chem. Soc. Dalton Trans. (1995) 2915.

[7] R. Breeze, S. Endud, M.W. Whiteley, J. Organomet. Chem. 302 (1986) 371.

[8] R.A. Brown, S. Endud, J. Friend, J.M. Hill, M.W. Whiteley, J. Organomet. Chem. 339 (1988) 283.

[9] R. Breeze, M.S. Plant, A. Ricalton, D.J. Sutton, M.W. Whiteley, J. Organomet. Chem. 356 (1988) 343.

[10] J.R. Hinchliffe, A. Ricalton, M.W. Whiteley, Polyhedron 10 (1991) 267.

[11] R.L. Beddoes, Z.I. Hussain, A. Roberts, C.R. Barraclough, M.W. Whiteley, J. Chem. Soc. Dalton Trans. (1996) 3629.

[12] B.J. Brisdon, D.A. Edwards, K.E. Paddick, M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1980) 1317.

[13] R.W. Grime, M.W. Whiteley, J. Chem. Soc. Dalton Trans. (1994) 1671.

[14] R.B. King, M.S. Saran, Inorg. Chem. 13 (1974) 2453.

[15] F.A. Cotton, R.L. Luck, Acta Crystallogr. Sect. C 46 (1990) 138.

[16] F.A. Cotton, B.G. DeBoer, M.D. Laprade, Proc. 23rd Int. Congr. Pure Appl. Chem., Boston, MA, 6 (1971) 1.

[17] J.W. Faller, Inorg. Chem. 8 (1969) 767.

[18] J.W. Faller, D.A. Haitko, R.D. Adams, D.F. Chodosh, J. Am. Chem. Soc. 101 (1979) 865.

[19] R.B. King, A. Fronzaglia, Inorg. Chem. 5 (1966) 1837.

[20] D.T. Cromer, J.T. Waber, International Tables for X-Ray Crystallography, vol. 4, Kynoch Press, Birmingham, UK, 1974.

[21] G.M. Sheldrick, SHELXTL, Göttingen, 1985.