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Preliminary communication

The interconversion of η^5 and η^3 hapticities in cycloheptadienyl complexes of molybdenum and tungsten

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Abstract

$[Mo(CO)_4(\eta^5\text{-}C_7H_9)]^+$ (1) reacts with acetonitrile to give $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)]^+$ (3), which is precursor of a wide range of η^5-cycloheptadienyl complexes $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ [6, L = PPh$_3$; 7, L$_2$ = Ph$_2$PCH$_2$PPh$_2$; 8, L$_2$ = 1,3-cyclohexadiene; 9, L$_2$ = 2,2′-dipyridyl]; 9 reacts reversibly with NCMe to give $[Mo(CO)_2(NCMe)(dipy)(\eta^3\text{-}C_7H_9)]^+$ (10).

The variable hapticity of dienyl ligands and the interconversion of η^5,η^3 and η^1 bonding modes have commanded much recent attention in the literature both for ‘open’ acyclic pentadienyl groups [1] and for ‘closed’ cyclic cyclopentadienyl and indenyl ligands [2]. However the analogous chemistry of ‘open’ pentadienyls incorporated in closed rings such as cyclohexadienyl [3] or cycloheptadienyl [4] is almost unexplored. We have previously reported on the interconversion of η^7 and η^3 hapticities in cycloheptatrienyl complexes of Mo and W [5–7] but our attempts to isolate intermediate η^5-C$_7$H$_7$ species have been unsuccessful; it is probable that C$_7$H$_7$ bonded pentahapto to Mo or W is a very transient species [8] although $\eta^3 \rightarrow \eta^5 \rightarrow \eta^3$-C$_7H_7$ transformations have been established in Ru chemistry [9]. To extend our investigations to $\eta^5 \rightarrow \eta^3$ ring slip processes in seven-membered rings coordinated to Mo and W we have developed an existing route to cycloheptadienyl complexes [10,11] and now report the first confirmed examples of $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ hapticity interconversions of the cycloheptadienyl ligand together with the accompanying ligand substitution reactions at the metal centre. Our studies also promote some interesting comparisons of structure and reactivity both with analogous indenyl and ‘open’ acyclic pentadienyl complexes and with corresponding cycloheptatrienyl derivatives of Mo and W.

Treatment of CH$_2$Cl$_2$ solutions of the cycloheptatriene complexes $[Mo(CO)_2L(\eta^6\text{-}C_7H_8)]$ (L = CO or PPh$_3$) with H[BF$_4$] in the presence of a vigorous stream of carbon monoxide affords the new cycloheptadienyl complexes $[Mo(CO)_3L(\eta^5\text{-}C_7H_9)]^+$ [1, L = CO; 2, L = PPh$_3$ (Scheme 1)]. When $[Mo(CO)_4(\eta^5\text{-}C_7H_9)]^+$ (1) was stirred at ambient temperature in acetonitrile, CO was evolved to give high yields of the trihapto-bonded cycloheptadienyl complex [Mo(CO)$_2$(NCMe)$_3$(η^3-

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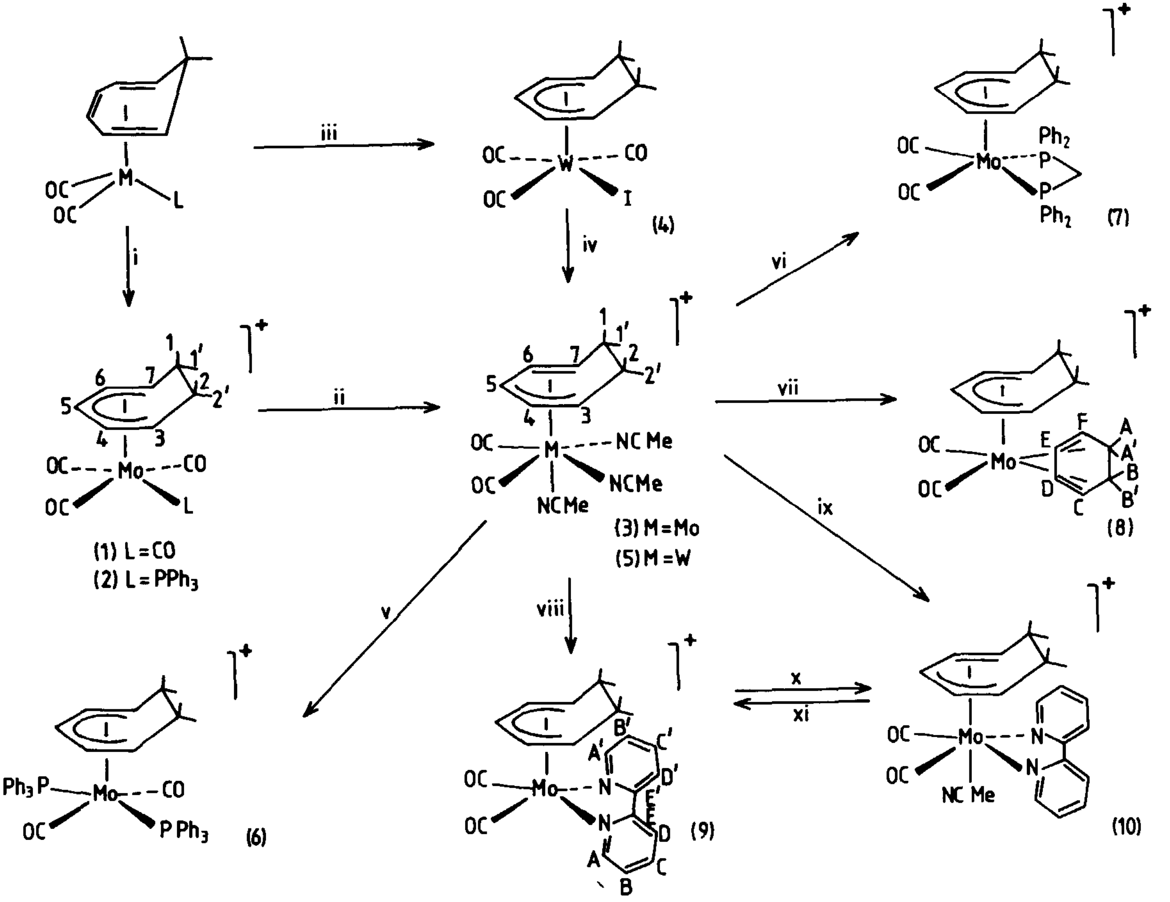
$C_7H_9)]^+$ (3) which is closely analogous to the cycloheptatrienyl complexes $[M(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ (M = Mo or W) [6]. The structure assigned to **3** was determined from ^1H and ^{13}C NMR spectra which, in contrast with spectra for the cycloheptatrienyl complex $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$, revealed a non-fluxional seven-membered ring for **3** at room temperature. The ^{13}C NMR spectrum of **3** in CD_3CN exhibits resonances at 131.6 and 130.4 ppm characteristic of uncoordinated alkene carbons and three resonances at 82.2, 80.5 and 77.0 ppm typical of Mo bonded to an η^3-allyl group [12]; this pattern is clearly distinct from ^{13}C NMR spectra of the pentahapto-bonded cycloheptadienyl ligand in complexes such as **2**, **4** and **6** (or even the asymmetric derivatives **7**, **8** and **9**) for which the pentadienyl carbons resonate essentially in the range 110 to 90 ppm. The ^1H NMR spectrum of **3** (which was assigned with the aid of [^1H–^{13}C] HETCOR, [^1H–^1H] COSY and ^1H–^1H double irradiation experiments) is also consistent with the assigned structure and the pattern of chemical shifts differs from that of $\eta^5\text{-}C_7H_9$ derivatives.

We have not been successful in isolating the tungsten analogue of **1** but treatment of $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ with $H[BF_4]$ in diethylether followed by reaction with NaI in acetone afforded moderate yields of $[WI(CO)_3(\eta^5\text{-}C_7H_9)]$ (**4**); subsequent reaction of **4** with $Ag[BF_4]$ in CH_3CN gave the tungsten analogue of **3**, $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)]^+$ (**5**) in a process which parallels the formation of $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ from $[WI(CO)_2(\eta^7\text{-}C_7H_7)]$ [6].

The interconversion of η^5 and η^3 hapticities of the cycloheptadienyl ligand has been proposed previously [4] but the formation of **3** from **1** and of **5** from **4** provides firmly established examples of such transformations. A preliminary investigation of the chemistry of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)]^+$ (**3**) also revealed that the η^5 hapticity of the cycloheptadienyl ligand is readily restored via reaction of **3** with bidentate ligands L_2 or two equivalents of monodentate ligands L to give complexes of the type $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ (L = phosphine, phosphite, isocyanide; $L_2 = Ph_2P(CH_2)_nPPh_2$ ($n = 1$, dppm; $n = 2$ dppe), 2,2′-dipyridyl (dipy) or diene]. The reaction sequence **1** → **3** → $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ proceeds rapidly at room temperature and the formal substitution of CO in $[Mo(CO)_4(\eta^5\text{-}C_7H_9)]^+$ (**1**) via $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5\text{-}C_7H_9$ hapticity conversions mirrors the substitution mechanism attributed to the 'indenyl effect' [2,13,14]. For example (**3**) reacts with two equivalents of PPh_3 in CH_2Cl_2 to give moderate yields of $[Mo(CO)_2(PPh_3)_2(\eta^5\text{-}C_7H_9)]^+$ (**6**) which is assigned a *trans* arrangement of CO ligands on the basis of relative intensities of the infrared active carbonyl stretching frequencies. Similarly, treatment of **3** with chelating ligands L_2 gave *cis* dicarbonyl complexes $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ [**7**, L_2 = dppm; **8**, L_2 = 1,3-cyclohexadiene (1,3-chd); **9**, L_2 = dipy]. Room temperature NMR spectra of **6** (also **2** and **4**) are consistent with a low energy rotation process of the cycloheptadienyl ring and/or a mirror plane which bisects the C_7H_9 ligand. By contrast the dppm and 1,3-chd complexes **7** and **8** exhibited broad signals in their ambient temperature NMR spectra and low temperature studies revealed asymmetric molecules as evidenced by the separate signals for each individual carbon/hydrogen of the C_7H_9 ring; asymmetry was also apparent from NMR signals of the ancillary ligands and variable temperature ^{31}P NMR studies on **7** revealed an AB doublet of doublets pattern at $-20\,^\circ C$ which coalesced to a singlet at $+20\,^\circ C$. The asymmetry of the dipyridyl complex **9** was even further pronounced and could be clearly observed in room temperature ^1H and ^{13}C NMR spectra.



Scheme 1. Reagents and conditions: i, M = Mo, L = CO or PPh$_3$; H[BF$_4$]/CO in CH$_2$Cl$_2$ (−10 °C); ii, L = CO, stir in CH$_3$CN; iii, M = W, L = CO, (a) HBF$_4$ in ether, (b) NaI in acetone (−78 °C); iv, Ag[BF$_4$] in CH$_3$CN; v, M = Mo, PPh$_3$ in CH$_2$Cl$_2$; vi, M = Mo, dppm in CH$_3$CN; vii, M = Mo, 1,3-cyclohexadiene in CH$_2$Cl$_2$; viii, M = Mo, 2,2′-dipyridyl in THF; ix, M = Mo, 2,2′-dipyridyl in CH$_3$CN; x, stir in CH$_3$CN; xi, stir in CH$_2$Cl$_2$.

A more complete understanding of the origin of the asymmetry in the η^5-C_7H_9 complexes **7**, **8** and **9** must await crystallographic studies but we note that asymmetry in some related cycloheptadienyl complexes of W [15] has been attributed to a high barrier to rotation of the C_7H_9 ligand and also that the acyclic pentadienyl complex $[Mo(CO)_2(dppe)(\eta^5\text{-}C_5H_7)]^+$ has an asymmetric ground state molecular geometry [16]. An alternative possibility, that **7**, **8** and **9** are effectively 16-electron species with a trihapto-bonded C_7H_9 ligand and a weakly coordinated BF_4^- counter ion analogous to the structure of $[Mo(CO)_2(dipy)(\eta^3\text{-}C_5H_7)][BF_4]$ [17], seems unlikely from a consideration of NMR data and the close correspondence of ν(CO) data for **7** and **8** by comparison with their η^5-indenyl analogues $[Mo(CO)_2L_2(\eta^5\text{-indenyl})]^+$ (L_2 = dppe or 1,3-chd) [18].

The isolation of cycloheptadienyl complexes **6–9** provides an engaging opportunity for reactivity comparisons with both cyclopentadienyl/indenyl and acyclic pentadienyl molybdenum analogues. Our primary interest centres on the ease of η^5–η^3 hapticity transformations and reports that both $[Mo(CO)_2(dppe)(\eta^5\text{-}C_5H_7)]^+$ and $[Mo(CO)_2(dipy)(\eta^3\text{-}C_5H_7)]^+$ react with acetonitrile to give isolable η^3-pentadienyl species $[Mo(CO)_2(NCMe)L_2(\eta^3\text{-}C_5H_7)]^+$ (L_2 = dppe or dipy) [16,17] stimulated our preliminary investigations. Stirring $[Mo(CO)_2(dipy)(\eta^5\text{-}C_7H_9)]^+$ (**9**) in CH_3CN resulted in formation of the ring-slipped product $[Mo(CO)_2(NCMe)(dipy)(\eta^3\text{-}C_7H_9)]^+$ (**10**), which was also synthesised via reaction of **3** with 2,2′ dipyridyl in CH_3CN. The identity of **10** as an η^3-C_7H_9 complex was established by NMR studies with ^{13}C NMR signals at 132.2, 129.4, 81.1, 79.7 and 77.9 ppm (CD_3CN) especially characteristic; the formation of **10** from **9** is also accompanied by a significant shift to lower wavenumber of the infrared active ν(CO), an observation found to be diagnostic for $\eta^7 \rightarrow \eta^3$ ring slip in related cycloheptatrienyl complexes of Mo and W [5–7]. The formation of **10** from **9** is a reversible process, thus stirring **10** in CH_2Cl_2 leads to rapid and total reformation of **9**; it is also probable that the NCMe ligand in **10** is very weakly bonded since attempts to isolate **10** from acetonitrile solutions consistently resulted in a product contaminated with small quantities of **9**. By contrast acetonitrile did not promote $\eta^5 \rightarrow \eta^3$-$C_7H_9$ ring slip in $[Mo(CO)_2(dppm)(\eta^5\text{-}C_7H_9)]^+$ (**7**), an observation which may indicate that $\eta^5 \rightarrow \eta^3$ hapticity conversions proceed less readily in cycloheptadienyl complexes than in related acyclic pentadienyl species.

Finally it is probable that the steric requirements and flexibility of the cycloheptadienyl ligand are intermediate between acyclic pentadienyl and closed-ring cycloheptatrienyl ligands (the latter are not significantly distorted from planarity even when bonded trihapto to Mo [19]) and the work promises to lead to some interesting structural comparisons between analogous cycloheptadienyl, cycloheptatrienyl and acyclic pentadienyl species.

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Selected data for new complexes

Satisfactory microanalytical data (C, H, N) were obtained for each of complexes **1–9**. ^1H NMR spectra were assigned with the aid of ^1H–^1H double irradiation experiments and, for **3**, **8**, **9** and **10**, by [^1H–^1H] COSY. Numbering/lettering for NMR assignments is given in Scheme 1, chemical shifts in ppm, coupling constants (J) in Hz.

1 Yield 84%; ν(CO) (CH_2Cl_2) 2112, 2065, 2008 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) 7.58, 1H, H(5); 6.12, 2H, H(3) H(7); 5.99, 2H, H(4) H(6); 2.76, 2.53, 4H, H(1,1′) H(2,2′); M^+ 303 (FAB mass spectroscopy).

2 Yield 44%; ;ν(CO) (CH_2Cl_2) 2059, 2018 (weak), 1964 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.57, 7.31, 15H, Ph; 6.14, 1H, H(5); 5.26, 2H, H(4) H(6); 5.22, 2H, H(3) H(7); 2.37, 2.21, 4H, H(1,1′) H(2,2′); ^{13}C NMR (75 MHz, $CDCl_3$) 219.4 219.2 CO; 133.2, 133.0, 132.3, 130.1, 130.0, Ph; 108.2, 102.4, 99.1, C(3)–C(7); 34.7, C(1) C(2); M^+ 537 (FAB mass spectroscopy).

3 Yield 86%; ν(CO) (CH_3CN) 1958, 1887; ν(CN) (Nujol) 2347 (weak), 2319, 2290 cm^{-1}; ^{1}H NMR (CD_3CN) 6.14, 1H, H(6), J[H(6)–H(7)] 11.4, J[H(6)–H(5)] 6.4; 5.40, 1H, H(7); 5.01, 1H, H(5); 4.92, 1H, H(3); 4.19, 1H, H(4), J[H(4)–H(5)] 6.0, J[H(4)–H(3)] 6.8; 2.57, 2.10, 2.01, 1.43, 4H, H(1,1′) H(2,2′); (rapid exchange of coordinated CH_3CN for CD_3CN); ^{13}C NMR (CD_3CN) 224.8, 223.3, CO; 131.6, C(6) 130.4, C(7); 82.2, C(5); 80.5, C(3); 77.0, C(4); 30.8, 28.6, C(1) C(2).

4 Yield 31%; ν(CO) (CH_2Cl_2) 2035, 1959 (broad) cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.78, 1H, H(5); 5.31, 2H, H(4) H(6); 4.88, 2H, H(3) H(7); 2.62, 4H, H(1,1′) H(2,2′); ^{13}C NMR ($CDCl_3$) 215.5, 202.9, CO; 101.1, 91.7, 88.5, C(3)–C(7); 33.5, C(1) C(2).

5 Yield 10%; ν(CO) (CH_3CN) 1952, 1869 cm^{-1}; ^{1}H NMR (CD_3CN) 6.21, 1H, H(6); 5.26, 1H, H(7); 4.69, 1H, 4.66, 1H, H(3) H(5); 3.61, 1H, H(4); 2.65,2 .11, 1.40, 4H, H(1,1′) H(2,2′); ^{13}C NMR (CD_3CN) 214.6, 213.0, CO; 131.3, 128.2, C(6) C(7); 70.6, 69.4, 68.4, C(3) C(4) C(5); 30.0, 27.8, C(1) C(2).

6 Yield 41%; ν(CO) (CH_2Cl_2) 1980, 1908 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.54, 30H, Ph; 5.30, 1H, H(5); 5.17, 2H, H(4) H(6); 4.82, 2H, H(3) H(7); 1.75, 1.22, 4H, H(1,1′) H(2,2′); ^{13}C NMR ($CDCl_3$) 229.0, J(P–C) 25, CO; 133.4, 131.7, 129.3, Ph; 104.2, 100.4, 99.2, C(3)–C(7); 33.9, C(1) C(2).

7 Yield 53%; ν(CO) (CH_2Cl_2) 2014, 1924 cm^{-1}; ^{31}P NMR (32.4 MHz, CD_2Cl_2, −60 °C) −5.37, −7.11, J(P–P) 75; ^{13}C NMR (CD_2Cl_2, −20°) 225.1, 222.8 (broad), CO, 135.2–130.2, Ph; 106.5, 102.5, 100.4, 99.9, 82.3, C(3)–C(7); 43.6, J(P–C) 26, CH_2 (dppm); 33.5, 32.3, C(1) C(2).

8 Yield 64%; ν(CO) (CH_2Cl_2) 2046, 2008 cm^{-1}; ^{1}H NMR (CD_2Cl_2, −40 °C) 6.54, 1H, H(5); 6.44, 1H, H(4); 5.64, 1H, H(6); 5.30, 1H, H(7); 4.57, 1H, H(3); 2.74, 2.50, 2.20–2.00, 1.70, 4H, H(1,1′) H(2,2′); 6.02, 1H, 5.59, 1H, H(D) H(E); 4.34, 1H, 4.06, 1H, H(C) H(F); 2.27, 2.20–2.00, 4H, H(A,A′) H(B,B′); ^{13}C NMR (CD_2Cl_2, −40 °C) 218.5, 214.9, CO; 107.0, 104. 1, 101.2, 100.0, 95.8, 81.8, 78.9, 78.5, 73.3, C(3)–C(7), C(C)–C(F); 37.5, 27.9, 25.6, 23.7, C(1) C(2) C(A) C(B).

9 Yield 42%; ν(CO) (CH_2Cl_2) 1988, 1922 cm^{-1}; ^{1}H NMR (CD_2Cl_2) 9.38, 1H, 8.92, 1H, H(D,D′); 8.66, 1H, 8.58, 1H, H(A,A′); 8.37, 1H, 8.15, 1H, H(B,B′); 7.91, 1H, 7.56, 1H, H(C,C′); 6.16, 1H, H(5); 5.75, 1H, H(4); 4.70, 1H, H(6), 4.65, 1H, H(7); 4.03 1H, H(3); 2.06, 1.41, 4H, H(1,1′) H(2,2′); ^{13}C NMR (CD_2Cl_2) 243.2, 234.7, CO; 156.9, 153.6, C(A,A′); 155.2, 154.0, C(E,E′); 140.7, 139.4, C(C,C′); 128.5, 126.9, C(B,B′); 125.0, 124.6 C(D,D′); 113.3, 111.8, 98.1 91.9, 82.3, C(3)–C(7); 34.3, 27.1, C(1) C(2); (assignments for the dipyridyl ligand were made with the aid of data in ref. 20).

10 ν(CO) (CH_3CN) 1952, 1872 cm^{-1}; ^{1}H NMR (CD_3CN) 9.06, 1H, 8.87, 1H H(D,D′); 8.42, 2H, H(A,A′); 8.26, 2H, H(B,B′); 7.72, 2H, H(C,C′); 6.29, 1H, H(6); 5.43, 1H, H(7); 4.77, 1H, H(3); 4.64, 1H, H(5); 3.40, 1H, H(4); 2.60, 2.24, 2.11, 1.54, 4H, H(1,1′) H(2,2′); ^{13}C NMR (CD_3CN) 227.0, 225.9, CO; 155.1, 155.0, C(E,E′); 154.3, 153.4, C(A,A′); 141.6, 141.2, C(C,C′); 132.2, 129.4, C(6) C(7); 128.1, 128.0, C(B,B′); 124.6, 124.5 C(D,D′); 81.1, 79.7, 77.9, C(3) C(4) C(5); 31.1, 28.7, C(1) C(2).

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