

Preliminary communication

The formation and synthetic applications of new acetonitrile derivatives of cycloheptatrienyl-molybdenum and -tungsten complexes; synthesis of binuclear



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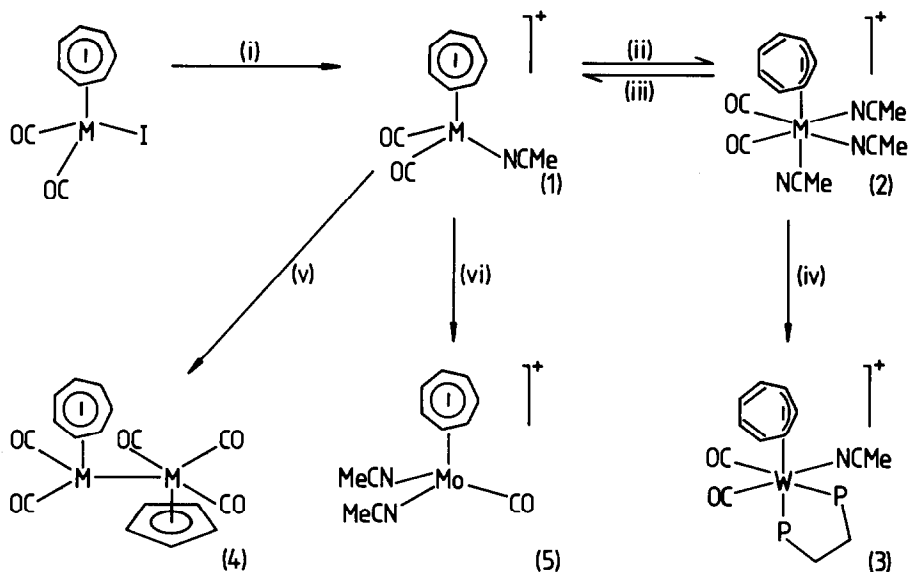
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Abstract

Reaction of $[\text{W}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ with $\text{Ag}[\text{BF}_4]$ in acetonitrile yields the tri-haptocycloheptatrienyl complex $[\text{W}(\text{CO})_2(\text{NCCH}_3)_3(\eta^3\text{-C}_7\text{H}_7)][\text{BF}_4]$ which affords $[\text{W}(\text{CO})_2(\text{NCCH}_3)(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$ (**1a**) on stirring in CH_2Cl_2 . A similar reaction sequence is observed starting from $[\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ but a mixture of $[\text{Mo}(\text{CO})_2(\text{NCCH}_3)_3(\eta^3\text{-C}_7\text{H}_7)][\text{BF}_4]$ (**2b**) and $[\text{Mo}(\text{CO})_2(\text{NCCH}_3)(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$ (**1b**) is formed in CH_3CN . Treatment of $[\text{M}(\text{CO})_2(\text{NCCH}_3)(\eta\text{-C}_7\text{H}_7)]^+$ (M = Mo, W) with $\text{Li}[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{R}_5)]$ (M = Mo, R = H or Me; M = W, R = H) affords asymmetric homobinuclear complexes $[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ (**4**). Ultraviolet irradiation of $[\text{Mo}(\text{CO})_2(\text{NCCH}_3)(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$ in CH_3CN forms $[\text{Mo}(\text{CO})(\text{NCCH}_3)_2(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$ (**5**) whilst irradiation of $[\text{Cr}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ in CH_3CN followed by addition of $\text{P}(\text{OMe})_3$ gives $[\text{Cr}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$.

The formation and extensive synthetic applications of acetonitrile complexes such as $[\text{Mo}(\text{CO})_2(\text{NCCH}_3)_2(\eta^5\text{-indenyl})]^+$ and $[\text{M}(\text{CO})_{3-n}(\text{NCCH}_3)_n(\eta\text{-C}_5\text{R}_5)]^+$ ($n = 1$ or 2 ; M = Fe, R = Me; M = Ru, R = H) is well documented [1–3]. However, prior to this work, acetonitrile derivatives of related cycloheptatrienyl complexes have been limited to $[\text{Mo}(\text{NCCH}_3)_3(\eta\text{-C}_7\text{H}_7)]^+$ and molybdenumphosphine compounds exemplified by $[\text{Mo}(\text{NCCH}_3)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ (dppe = $\text{Ph}_2\text{PCH}_2\text{-CH}_2\text{PPh}_2$) and $[\text{Mo}(\text{NCCH}_3)_2(\text{PPh}_3)(\eta\text{-C}_7\text{H}_7)]^+$ [4] which, although exhibiting a range of synthetic applications [4,5], are expected to have very different properties to those of the analogous carbonyl derivatives. We now report the synthesis of the parent dicarbonylacetonitrile compounds (**1**) (Scheme 1) of both molybdenum and



Scheme 1. M = Mo or W, $\overline{\text{P}} = \text{P} = \text{dppe}$. (i) $\text{Ag}[\text{BF}_4]$ in CH_3CN (ii) CH_3CN (iii) CH_2Cl_2 (iv) M = W, dppe in CH_3CN (v) $\text{Li}[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{R}_5)]$ in thf (vi) M = Mo, UV, CH_3CN .

tungsten, a 'ring slip' process resulting in cationic trihapto-cycloheptatrienyl complexes (2) and, our initial studies on the synthetic applications of 1 including formation of asymmetric homobinuclear species 4.

Treatment of an acetonitrile solution of $[\text{W}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ with $\text{Ag}[\text{BF}_4]$ affords a deep yellow solution which, after work up, yields **2a** (M = W) [6*], the first example of a cationic trihapto-cycloheptatrienyl complex and a close analogue of the known allyl complex $[\text{W}(\text{CO})_2(\text{NCCH}_3)_3(\eta^3\text{-C}_3\text{H}_5)]^+$ [7]. The molecular geometry assigned to **2a** with a facial arrangement of acetonitrile ligands and *cis* carbonyl groups is based upon the relative intensities of the two infrared-active carbonyl stretching frequencies [8] and, in the ^{13}C NMR spectrum, the observation of a single signal in the carbonyl carbon region. The ^1H NMR spectrum of (**2a**) in CD_3CN reveals ready exchange of all three acetonitrile ligands and accordingly treatment with dppe in CH_3CN results in displacement of two CH_3CN ligands from (**2a**) and formation of the orange-red bisphosphine complex (**3**). Complex **3**, which can also be synthesised by reaction of $[\text{W}(\text{CO})_2(\text{dppe})(\eta^3\text{-C}_7\text{H}_7)]$ with $\text{Ag}[\text{BF}_4]$ in acetonitrile, exhibits two inequivalent phosphorus environments in the ^{31}P NMR and, as discussed for $[\text{W}(\text{CO})_2(\text{dppe})(\eta^3\text{-C}_7\text{H}_7)]$ [9], the spectroscopic data are consistent with two of four possible geometric arrangements of ligands in a pseudo-octahedral structure. By contrast, in solvents such as CH_2Cl_2 or thf devoid of added donor ligands, displacement of two CH_3CN ligands from **2a** is accompanied by reversion of the cycloheptatrienyl ring to the heptahapto bonding mode and formation of green **1a** (M = W).

An essentially similar sequence of reactions is observed for the analogous

* Reference number with asterisk indicates a note in the list of references.

molybdenum system but with one important difference. Thus reaction of $[\text{MoI}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ with $\text{Ag}[\text{BF}_4]$ in CH_3CN affords a green solution exhibiting four infrared carbonyl stretching frequencies (2034 , 1989 cm^{-1} and 1960 , 1887 cm^{-1}) which are assigned to an equilibrium mixture of **1b** and **2b** ($\text{M} = \text{Mo}$). The presence of the $\eta^7\text{-C}_7\text{H}_7$ complex **1b** was confirmed by removal of CH_3CN from the equilibrium mixture and dissolution of the residue in CH_2Cl_2 providing a synthesis of pure, isolable **1b**. The identification of the second component of the mixture as **2b** may be inferred from the isolation of the tungsten analogue **2a**, which, in CH_3CN , exhibits closely comparable infrared carbonyl stretching frequencies at 1956 and 1880 cm^{-1} .

An important synthetic method in cycloheptatrienyl-molybdenum and -tungsten chemistry involves replacement of anionic ligands at the metal centre. For example the halides $[\text{MX}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been widely employed in syntheses of complexes such as $[\text{MR}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ ($\text{R} = \text{Me}, \text{Ph}, \text{C}\equiv\text{CPh}$) [10,11] and metal-metal bonded $[\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)\text{Mn}(\text{CO})_5]$ [12]. However, the limitations of this route are demonstrated by the failure of $[\text{MoI}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ to react with the relatively poor nucleophile $\text{Li}[\text{Mo}(\text{CO})_3(\eta\text{-Cp})]$ even after overnight reflux in thf. By contrast, addition of thf solutions of $\text{Li}[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{R}_5)]$ ($\text{M} = \text{Mo}, \text{R} = \text{H}$ or Me ; $\text{M} = \text{W}, \text{R} = \text{H}$) to acetonitrile complexes (**1**) rapidly affords the neutral, binuclear complexes, **4a** ($\text{M} = \text{W}, \text{R} = \text{H}$), **4b** ($\text{M} = \text{Mo}, \text{R} = \text{H}$) and **4c** ($\text{M} = \text{Mo}, \text{R} = \text{Me}$). The structure attributed to complexes **4** is based upon spectroscopic data but a definitive assignment awaits X-ray crystallographic studies. However the presence of a metal-metal bond in complexes **4** is consistent with the ready formation of $[\{\text{M}(\text{CO})_3(\eta\text{-Cp})\}_2]$ from **4b** initiated by UV photolysis, and a global carbonyl scrambling process [13] observed for the molybdenum derivatives **4b** and **4c**. Thus the room temperature ^{13}C NMR spectrum of tungsten complex **4a** in CD_2Cl_2 exhibits three carbonyl signals (226.0 , 216.7 , 207.8 ppm) of approximate relative intensity $1:2:2$. By contrast, the room temperature ^{13}C NMR spectrum of **4c** reveals a single, sharp carbonyl signal at 230.6 ppm which resolves into three separate signals only after cooling to -80°C .

We have further developed the chemistry of cycloheptatrienylacetonitrile complexes by the synthesis of the bis(acetonitrile)molybdenum complex (**5**). Ultraviolet irradiation of **1b** in CH_3CN for 6 h gives a green solution yielding **5** after work up; alternatively in situ treatment with dppe affords known $[\text{Mo}(\text{CO})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ [14] as its $[\text{BF}_4]$ salt. Analogous syntheses of the chromium derivatives of **1** and **5** are precluded by the inaccessibility of $[\text{CrX}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ ($\text{X} = \text{halide}$). However, UV irradiation of an orange, acetonitrile solution of $[\text{Cr}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ gives a deep purple-red solution which, although too unstable for direct characterisation, undergoes further reactions which advocate its formulation as $[\text{Cr}(\text{CO})(\text{NCCH}_3)_2(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$. For example, UV irradiation of $[\text{Cr}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ for 2 h in CH_3CN followed by in situ treatment with 2 equivalents of $\text{P}(\text{OMe})_3$ affords yellow-green $[\text{Cr}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ [$\nu\text{CO}(\text{CH}_2\text{Cl}_2)$ 1958 cm^{-1} ; ^1H NMR (CD_3CN , 300 MHz) δ 3.54, 18H, $\text{P}(\text{OMe})_3$, $J(\text{P-H})$ 5 Hz , δ 5.80, 7H, C_7H_7 , $J(\text{P-H})$ 3 Hz] thus providing a convenient route to the first reported example of a phosphite-substituted cycloheptatrienylchromium complex.

We are currently extending this work by investigating the further reactions of all new acetonitrile complexes reported and by comparing the chemistry of binuclear complexes **4** with that of $[\{\text{M}(\text{CO})_3(\eta\text{-Cp})\}_2]$ ($\text{M} = \text{Mo}, \text{W}$).

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 - 1a; yield 69% from (2a); νCO (CH_2Cl_2) 2022, 1969 cm^{-1} ; $^1\text{H NMR}$ (CD_2Cl_2) δ 5.68, 7H, C_7H_7 , δ 2.50, 3H, NCMe.
 - 1b; yield 61% from $[\text{MoI}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$; $\nu\text{CO}(\text{CH}_2\text{Cl}_2)$ 2036, 1993 cm^{-1} .
 - 2a; yield 75% from $[\text{Wl}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$; νCO (CH_3CN) 1956, 1880 cm^{-1} ; $^{13}\text{C NMR}$ (CD_3CN) 214.3 ppm, CO, 100.9 ppm, C_7H_7 .
 - (3); yield 43% from (2a); $\nu\text{CO}(\text{CH}_2\text{Cl}_2)$ 1949, 1878 cm^{-1} ; $^{31}\text{P NMR}$ (CD_3CN , 32.4 MHz) 42.5 ppm, $J(\text{P-P})$ 7, $J(\text{P-}^{183}\text{W})$ 229 Hz, 35.9 ppm, $J(\text{P-P})$ 7, $J(\text{P-}^{183}\text{W})$ 213 Hz.
 - (4a); yield 31%, νCO (hexane) 1973(w), 1941(vs), 1914(m), 1873(w), 1854(m) cm^{-1} ; $^{13}\text{C NMR}$ (CD_2Cl_2 , room temperature) 226.0, 216.7, 207.8 ppm, CO, 91.7 89.4 ppm, C_7H_7 and Cp.
 - (4b); yield 27%; νCO (hexane) 1980(w), 1942(vs), 1932(m), 1874(w), 1856(m) cm^{-1} ; Mo, Found 38.7%, Required 39.3%.
 - (4c); yield 32%, νCO (hexane) 1973, 1922, 1845 cm^{-1} ; $^{13}\text{C NMR}$ (CD_2Cl_2 , -80°C) 240.4, 233.7, 220.7 ppm CO, 103.0 93.0 ppm, C_7H_7 and C_5Me_5 ; 10.6 ppm C_5Me_5 ; Mo, Found 34.7, Required 34.4%.
 - (5); yield 25%; νCO (CH_2Cl_2) 1984 cm^{-1} ; $^1\text{H NMR}$ (CD_2Cl_2) δ 5.36, 7H, C_7H_7 , δ 2.39, 6H, NCMe. Satisfactory analytical data (C, H and N) were obtained for all new complexes.
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