Notes

Cyclodimerization of the Tropylium Ring by Reduction of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]^+$ To Give $[\{Mo(CO)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_7H_7\text{-}C_7H_7)][PPN]_2$

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Summary: Reductive activation of the tropylium ring in $[(\eta^7\text{-}C_7H_7)M(CO)_3]BF_4$ *(M = Cr, Mo, W) leads to cyclodimerization and formation of* $[\{M(CO)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_7H_7\text{-}C_7H_7)][PPN]_2$*, which was isolated and characterized for M = Mo and may also be formed by reduction of the neutral dimer* $[\{Mo(CO)_3\}_2(\eta^6{:}\eta^6\text{-}C_7H_7\text{-}C_7H_7)]$*. The chromium and tungsten analogues were identified spectroscopically.*

Electrochemical reduction of organometallic compounds and its synthetic applications constitute an important area of research.[1,2] More recently, the enhanced reactivity of 19e species to undergo rapid electron transfer catalyzed carbonyl substitution has been reported.[3] In the case of complexes of π-acids such as cyclopentadienyl or arenes, reduction may result in dimerization and C−C bond formation (e.g. $[CpFe^I(arene)]^+$). However, permethylation of the Cp ring, which decreases the spin density on the arene ligand, increases the rate of dimerization so that spin density is not the dominant factor in this case; instead, the 19e species $[CpFe^I(arene)]$ is considered to be in equilibrium with the 18e species $[CpFe^{II}(\eta^5\text{-arene})]$ with the electron localized on an arene C sp^3 orbital.[4,5] Although there have been extensive studies of the electrochemical reduction of the $[(arene)Cr(CO)_3]$ series,[6−13] relatively few have been made of the closely related tropylium tricarbonyl group VI metal complexes $[(\eta^7\text{-}C_7H_7)M(CO)_3]BF_4$ (I, M = Cr; II, M = Mo; III, M = W). Reduction of I−III with a variety of reagents, including zinc dust, sodamide, and phenyllithium, gives the neutral dimers $[\{M(CO)_3\}_2\eta^6{:}\ \eta^6\text{-}C_7H_7\text{-}C_7H_7)]$ (IV, M = Cr; V, M = Mo; VI, M = W) possibly formed by radical coupling.[14] Electrochemical studies of I were originally interpreted in terms of a two-electron reduction process,[15] although very recently a one-electron-transfer mechanism has been suggested.[16] Reduction by sodium amalgam of II was reported to give a green solution with infrared carbonyl bands, indicating formation of an anionic materia, but only IV was isolated.[17] In view of the above conflicting interpretations of the electrochemical reduction of I and the suggestion of the formation of an anionic species from II, we decided to reinvestigate the reduction of I−III using potassium naphthalenide as reducing agent.

Results and Discussion

In the present study, dropwise addition (2:l molar ratio) of potassium naphthalenide to a slurry of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ (II) in THF at −78 °C gave a dark green solution with infrared carbonyl absorptions at 1983, 1917, 1892, 1798, and 1744 cm$^{-1,}$ corresponding to a mixture of the neutral dimer V and the dianion $[\{Mo(CO)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_7H_7C_7H_7)]^{2-}$ (VIIIa). After 2 h, the solution turned yellow and the infrared spectrum showed only the carbonyl absorptions at 1893, 1798, and 1744 cm^{-1} due to VIIIa. However, direct workup gave only the neutral dimer V, but if [PPN]Br was added after the solution turned yellow, subsequent workup gave the yellow complex VIII, $[\{Mo(CO)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_7H_7\text{-}C_7H_7)][PPN]_2$, which is stable in air for several minutes and for 3−4 days under N$_2$ at −20 °C. Satisfactory microanalysis was obtained for VIII. Exposure to air results in rapid oxidation of VIII to V. The ^{1}H NMR (270 MHz) spectrum of VIII measured at −60 °C in acetone-d_6 shows a triplet at δ 5.00 assigned to H_4 ($H_4{}^1$) (for numbering see Scheme 1) with J_{34} = 6.23 Hz, a double doublet at δ 4.83 ($H_{3,5}$) with coupling to H_4 and the equivalent H_2 and H_6 (J_{23} = 10.2 Hz), and a doublet at δ 3.46 (H_2, J_{23} = 10.2 Hz). The broad singlet at δ 1.89 is assigned to H_1 and H_7, which do not couple because of the estimated dihedral angle of ca. 90°

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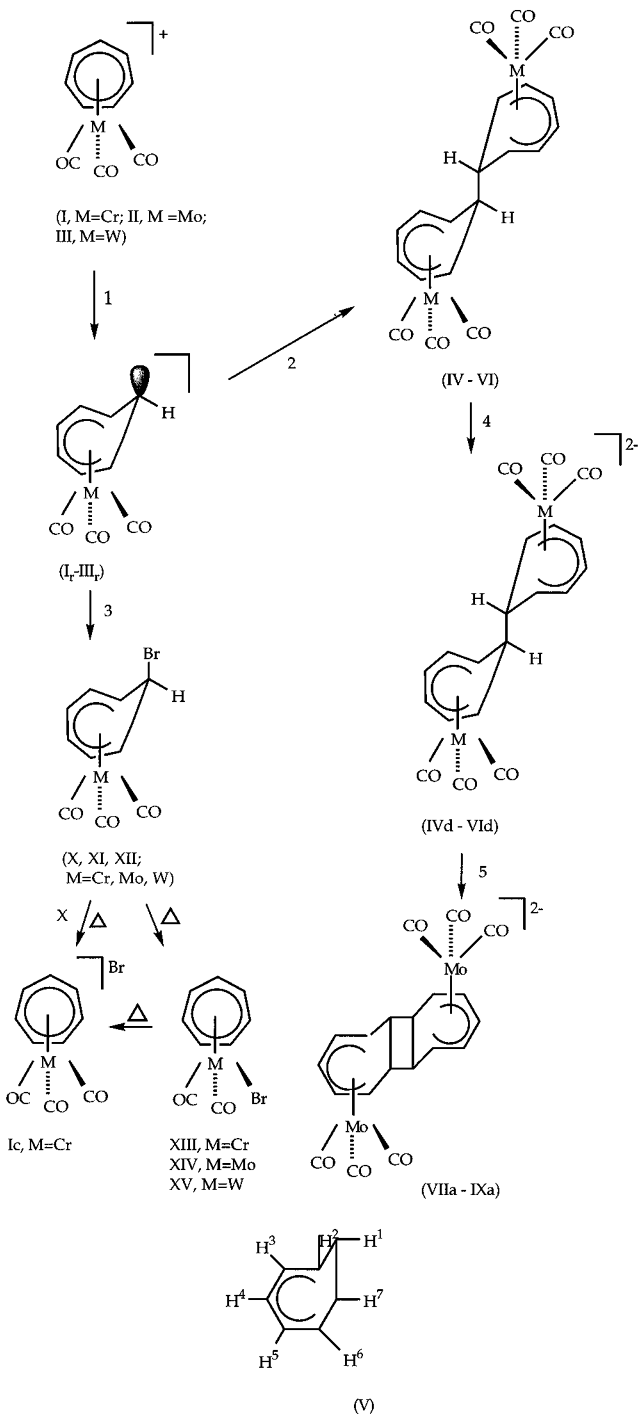
Scheme 1[a]



[a] Legend: (1) potassium naphthalenide/THF, −78 °C, one-electron reduction; (2) dimerization; (3) CBr_4; (4) two-electron reduction; (5) cyclodimerization.

between the two carbon−hydrogen bonds in the dimer. In the case of a monomeric product such as $[(\eta^5\text{-}C_7H_7)Mo(CO)_3]^-$, coupling between H_1 and H_7 would be expected. The upfield shifts of the proton spectra of VIII relative to those of V are also consistent with formation of an anionic species. The phenyl protons of PPN occur as a multiplet at δ 7.5−7.8 ppm. Unfortunately, we were not able to obtain crystals of VIII suitable for X-ray crystallography.

Further support for the dimeric nature of VIII is provided by its formation from the neutral dimer V on treatment of the latter with potassium naphthalenide in THF at −78 °C, which again, after 30 min, gave a yellow solution that on addition of [PPN]Br and workup produced a pure sample of VIII.

If the above reduction of II is carried out at −78 °C in the presence of the radical inhibitor CBr_4 and the reaction monitored by means of a low-temperature infrared cell, three strong bands are observed at 1991, 1925, and 1896 cm^{-1} and attributed to the bromo ring addition product $[(\eta^6\text{-}C_7H_7\text{-}\textit{exo}\text{-}Br)Mo(CO)_3]$ (XI) by analogy with the infrared carbonyl bands of the corresponding phosphine adducts.[18] The two weaker bands observed at 2011 and 1967 cm^{-1} are due to the normal bromide $[(\eta^7\text{-}C_7H_7)Mo(CO)_2Br]$ (XIV). The intensities of the ring adduct XI decreased on standing, while those of XIV increased. Similar results were obtained for the W complex III; however, in the case of the Cr complex I, the peaks due to the ring adduct $[(\eta^6\text{-}C_7H_7\text{-}\textit{exo}\text{-}Br)Cr(CO)_3]$ (X) which occurred at 1985, 1921, and 1896 cm^{-1} predominated and persisted up to −20 °C, at which point they were replaced by those of the starter cation Ic and two peaks at 2036 and 1990 cm^{-1}. By analogy with peaks for the corresponding Mo and W bromides (XIV and XV), these are assigned to the hitherto unreported Cr bromide $[(\eta^7\text{-}C_7H_7)Cr(CO)_2Br]$ (XIII), although subsequent workup gave only $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]Br$.

Probable mechanisms for these reactions are shown in Scheme 1. Since molecular orbital calculations of the complexes I−III show the LUMO to be ring-centered in all three cases,[19] it is suggested that initial one-electron reduction occurs with potassium naphthalenide to give the radicals Ir−IIIr, with a SOMO which is ring-centered. In the absence of CBr_4, these radicals dimerize to give the corresponding neutral dimers IV−VI, which undergo two-electron reduction to form the diradical intermediates IVd−VId (M = Cr, Mo, W), these in turn undergo cyclodimerization to form the dianions $[\{M(CO)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_7H_7\text{-}C_7H_7)]^{2-}$ (VIIa−IXa; M = Cr, Mo, W). Attempts to isolate the PPN derivatives of VIIa and IXa were unsuccessful, although the infrared carbonyl bands were consistent with their formation; however, workup in the Cr case gave mainly the neutral dimer IV and in the W case mainly $W(CO)_6$. Only in the Mo case could we isolate and characterize the PPN salt of VIIIa.

In the presence of CBr_4, II_r combines with a bromine atom to give the unstable ring adduct $[(\eta^6\text{-}C_7H_7\text{-}\textit{exo}\text{-}Br)Mo(CO)_3]$ (XI), which decomposes heterolytically on raising the temperature to re-form the starting compound II and bromide ion, which then form the normal carbonyl substitution product $[(\eta^7\text{-}C_7H_7)Mo(CO)_2Br]$ (XIV).

Previous studies of the photochemical dimerization of cycloheptatriene have yielded only the stable nonplanar bicyclo[3.2.0]heptadiene.[20] The cyclodimerization reported here is analogous to that observed recently for benzene in $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]^+$.[21] Protonation of VIII in THF at −78 °C with glacial acetic acid gave an

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immediate color change from yellow to reddish orange and infrared carbonyl peaks corresponding to those of the neutral dimer V; however, workup gave only [(η^6-C_7H_8)Mo(CO)$_3$], arising from C−C bond cleavage of V. Formation of this monomeric species on protonation of the dimer VIII suggests that caution is necessary in inferring that formation of a monomeric species such as [(η^5-C_6H_7)Mn(CO)$_3$] necessarily occurs by protonation of another monomeric species, [(η^4-C_6H_6)Mn(CO)$_3$]$^-$.[22]

Experimental Section

All solvents were freshly dried by standard methods. All reactions and workup were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Infrared spectra were measured using a 0.1 mm CaF_2 cell on a Perkin-Elmer 1720 Fourier Transform Spectrometer linked to a 3700 data station. Low-temperature spectra were obtained with a Specac variable-temperature cell P/N 21,500. ^{1}H NMR spectra were recorded on a JEOL GX 270 spectrometer. Analyses were performed by the Microanalytical Laboratory of the Chemical Services Unit of University College Dublin. The complexes [(η^7-C_7H_7)M(CO)$_3$]BF_4 (Cr, Mo, W) were synthesized by previously well-established methods.[23] Potassium naphthalenide was standardized by titration with standard 0.1 M HCl.

Synthesis of VIII. To a slurry of [(η^7- C_7H_7)Mo(CO)$_3$]BF_4 (0.23 g, 0.64 mmol) in THF (50 mL) precooled to −78 °C was added K[$C_{10}H_8$] (6.5 mL, 1.3 mmol) under argon. After 2 h the solution turned from dark green to yellow, whereupon [PPN]Br (0.8 g, 1.28 mmol) was added as a slurry in THF precooled to −78 °C. This mixture was stirred for 90 min and filtered cold and the volume reduced to 15 mL. On storage overnight at −20 °C, yellow crystals of [{Mo(CO)$_3$}$_2$(μ-η^5:η^5-C_7H_7-C_7H_7)][PPN]$_2$ (IV) formed and were dried under vacuum. Anal. Calcd for $C_{46}H_{37}NO_3P_2Mo$: C, 68.2; H, 4.60; N, 1.73. Found for VIII: C, 68.7; H, 4.93; N, 1.43.

Reduction of [(η^7-C_7H_7)M(CO)$_3$]BF_4 (M = Cr, Mo, W) using Potassium Naphthalenide in the Presence of CBr_4. To a slurry of [(η^7-C_7H_7)Mo(CO)$_3$]BF_4 (0.23 g, 0.64 mmol) and CBr_4 (0.21 g, 0.64 mmol) in THF (50 mL) at −78 °C was added an equimolar amount of 0.2 M potassium naphthalenide (3.2 mL, 0.64 mmol). Samples were removed by syringe every 5 min for IR analysis using the low-temperature cell. After it was stirred for 1 h or until no further change was observed in the IR spectrum, the solution was filtered and concentrated to 10 mL under vacuum. Recrystallization from acetone/ether yielded the dark green monocarbonyl substitution product [(η^7-C_7H_7)Mo(CO)$_2$Br] (62 mg, 32%). The reduction of [(η^7-C_7H_7)W(CO)$_3$]BF_4 in the presence of CBr_4 using the identical procedure yielded [(η^7-C_7H_7)W(CO)$_2$Br] (71 mg, 28%), while reduction of [(η^7-C_7H_7)Cr(CO)$_3$]BF_4 in the presence of CBr_4 yielded only the starting cation [(η^7-C_7H_7)Cr(CO)$_3$]Br.

Reaction of [{Mo(CO)$_3$}$_2$$\mu$-$\eta^5$:$\eta^5$-$C_7H_7$-$C_7H_7$)][PPN]$_2$ with Glacial Acetic acid. To [{Mo(CO)$_3$}$_2$(μ-η^5:η^5-C_7H_7-C_7H_7)]-[PPN]$_2$ (2.8 mmol) in THF at −78 °C was added glacial acetic acid (160 mL, 2.8 mmol) at −78 °C, upon which an immediate color change occurred from yellow to red. The solution was filtered, concentrated to 10 mL, and stored overnight at −20 °C to yield [(η^6-C_7H_8)Mo(CO)$_3$].

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