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Synthesis, Structure, and Haptotropic Interconversions of Tungsten Cycloheptatrienyl–Acetonitrile–Carbonyl Complexes

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Abstract—Tungsten cycloheptatrienyl complexes $(\eta^7\text{-}C_7H_7)W(CO)_2I$ (**I**), $[(\eta^3\text{-}C_7H_7)W(CO)_2(CH_3CN)_3]PF_6$ (**II**), and $[(\eta^7\text{-}C_7H_7)W(CO)_2(CH_3CN)]PF_6$ (**III**) (CIF files CCDC nos. 1875096 (**I**), 1875097 (**II**), 1875098 (**III**)), characterized earlier only by spectroscopic methods, were prepared and studied by X-ray diffraction. The tris(acetonitrile) complex **II** can lose two acetonitrile ligands in both coordinating and non-coordinating solvents with the $\eta^3 \to \eta^7$ change in the hapticity of the cycloheptatrienyl ring to be converted to **III**. The reverse ligand attachment process with the $\eta^7 \to \eta^3$ change in the hapticity of the cycloheptatrienyl ring takes place upon the dissolution of monoacetonitrile complex **III** in acetonitrile. The electron-compensating $\eta^3 \leftrightarrow \eta^7$ change in the hapticity of the tropylium ligand is reversible.

Keywords: cycloheptatrienyl complexes, tungsten complexes, haptotropic transformations, X-ray diffraction

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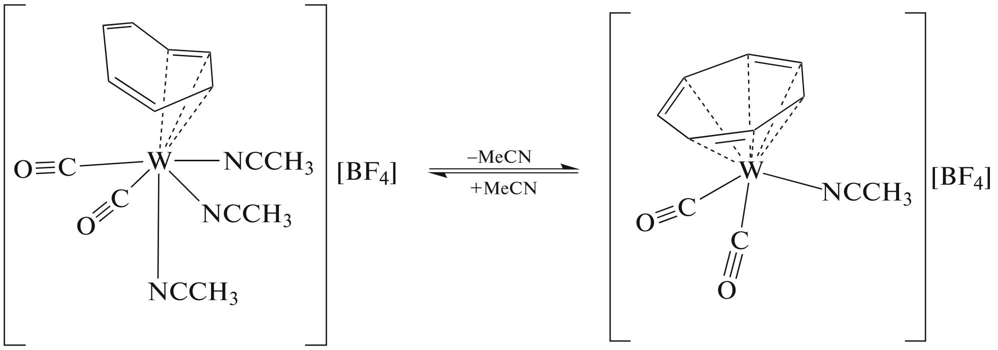
INTRODUCTION

The problem of hapticity change of π-coordinated cyclic ligands is a part of the coordination chemistry topic of ligand denticity change depending on the population of vacant orbitals and on the steric details of ligand–ligand interactions. In particular, complexes with η^7-, η^5-, η^3-, and η^1-coordination modes have been observed for the cycloheptatrienyl ligand (C_7H_7) [1]. Primary attention was given to $\eta^7 \to \eta^3$ transitions [2–4] for the tungsten complexes $[(\eta^7\text{-}C_7H_7)]$+ $W(MeCN)(CO)_2$ (Scheme 1).



Scheme 1.

In particular, it was shown [3] that the transformation of $[(\eta^7\text{-}C_7H_7)W(MeCN)(CO)_2]^+$ requires L = CO, i.e., a potent π-acceptor ligand; the attachment of two L' = MeCN molecules induces a color change from dark green to orange-yellow, a sharp decrease in the CO stretching frequencies (from 2022 and 1969 to 1956 and 1880 cm^{-1}), and a characteristic change in the ^{1}H NMR spectrum, with the shifts of cycloheptatrienyl proton signals from 5.68 to 5.08 ppm and the coordinated acetonitrile signal from 2.50 to 2.30 and 2.26 ppm [3].

In this study, we prepared single crystals of $(\eta^7\text{-}C_7H_7)W(CO)_2I$ (**I**), $[(\eta^3\text{-}C_7H_7)W(CO)_2(CH_3CN)_3]$-

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† Deceased.

PF_6 (**II**), and $[(\eta^7\text{-}C_7H_7)W(CO)_2(CH_3CN)]PF_6$ (**III**) and studied the interconversions of these complexes in solutions.

EXPERIMENTAL

All operations for the synthesis and isolation of complexes **I**–**III** were carried out in a pure argon atmosphere in anhydrous solvents. Complex **I** was synthesized by a reported procedure [5].

The reaction involving silver compounds was carried out at room temperature away from light in order to avoid contamination of the reaction mixture with silver iodide decomposition products. Elemental analysis was carried out using an EA3000 CHNS EuroVector analyzer. IR spectra were recorded on a BrukerAlpha FT IR spectrometer with a Platinum ATR attachment. ^1H and ^{13}C NMR spectra were run on a Bruker AV 400 spectrometer operating at 400.13 and 75.4 MHz, respectively, with deuterium lock at 303 K. The ^1H and ^{13}C chemical shifts are referred to TMS.

Synthesis of $[(C_7H_7)W(CO)_2(CH_3CN)_3]PF_6$ (II). A solution of $AgPF_6$ (0.424 g, 1.67 mmol) in acetonitrile (9 mL) was added to a green solution of $(C_7H_7)W(CO)_2I$ (**I**) (0.229 g, 0.50 mmol) in acetonitrile (13 mL). The reaction mixture was stirred for 20 min. The resulting orange solution was filtered to remove the precipitated AgI, concentrated under reduced pressure without heating to half of the volume, and diethyl ether (3 mL) was added dropwise. The orange precipitate that formed within 4 days at –25°C was separated by decantation, washed with diethyl ether (5 mL), and dried in vacuum. The yield was 0.26 g (86%).

For $C_{15}H_{16}F_6N_3O_2PW \cdot 0.5(C_2H_5)_2O$ ($M = 636$)

Anal calcd., %	C, 32.10	H, 3.33	N, 6.61
Found, %	C, 32.41	H, 2.18	N, 6.94

IR (ν, cm $^{-1}$): 3027 w.br, 2950 w, 2931 vw, 2319 w, 2290 w, 1944 m, 1872 s, 1434 vw, 1409 w.br, 1367 vw, 1030 vw, 881 vw, 831 vs.br, 725 m, 625 w, 556 s, 519 w, 477 w, 469 w, 435 w, 416 vw. ^1H NMR (CD_3CN; δ, ppm): 1.98 (s, 9H, $MeCN_{uncoord}$, 5.18 (s, 7H). ^1H NMR (d^6-acetone; δ, ppm): 2.69 (s, 3H, CH_3CN) 6.00 (s, 7H C_7H_7). ^{13}C NMR (d^6-acetone, δ, ppm): 94.9 (C_7H_7), 210.0 (CO).

Synthesis of $[(C_7H_7)W(CO)_2(CH_3CN)]PF_6$ (III). (A) Dichloromethane (10 mL) was added to the orange powder of $[(C_7H_7)W(CO)_2(CH_3CN)_3]PF_6$ (0.26 g, 0.43 mmol), and the mixture was kept for 1 h without stirring until the color changed to green. The solvent was removed in vacuum, the green residue was dissolved in dichloromethane (15 mL), the solution was filtered, toluene (5 mL) was added dropwise, and the solution was concentrated under reduced pressure until it became turbid. The dark green precipitate that formed within a week at –25°C was separated by decantation, washed with toluene (5 mL), and dried in vacuum. The yield was 91 mg (41%).

For $C_{11}H_{10}F_6NO_2PW$ ($M = 517$)

Anal calcd., %	C, 25.55	H, 1.95	N, 2.71
Found, %	C, 26.01	H, 2.24	N, 2.53

IR (ν, cm $^{-1}$): 3077 vw, br, 3010 vw, 2943 vw, 2442 vw, br, 2322 vw, 2002 m, 1954 s, 1475 w, 1433 w, 1415 vw, 1361 vw, 1249 vw, 1056 vw, 1033 vw, 955 vw 897 vw, 877 vw, 864 w, 822 vs, br, 808 vs, 554 s, 517 w, 503 w, 491 w, 464 w, 423 s.

(B) Toluene (6 mL) was added to complex **II** (0.104 g, 0.2 mmol)) and the mixture was heated at reflux for 30 min until the precipitate color changed to green. Then the solution was kept at –25°C for 10 min and decanted, and the black-green crystals were washed with heptane (5 mL) and dried in vacuum. The yield was 0.027 g (30%).

The IR spectrum completely coincided with that of the sample obtained in synthesis A.

Transformation of III into II. Acetonitrile (6 mL) was added to green powder of **III** (0.091 g, 0.2 mmol) and the mixture was kept for 1 h without stirring. This was accompanied by complete dissolution of the compound and change of the solution color from green to orange. The reaction mixture was concentrated under reduced pressure to half of the volume. Diethyl ether (~3 mL) was added dropwise until the solution became turbid. The solution was kept for a week at –25°C and decanted, and the orange precipitate was washed with diethyl ether (5 mL) and dried in vacuum. The yield was 0.048 g (46%).

The IR and NMR data fully coincided with the data for compound **II**.

X-ray diffraction analysis was performed on a Bruker APEX II CCD diffractometer. The absorption corrections were applied by multiple measurement of equivalent reflections using the SADABS program [6]. The structures of **I**–**III** were solved by the direct method and refined by the least-squares method on F^2 in the anisotropic approximation for non-hydrogen atoms using SHELX-2014 [7] and OLEX2 [8] program packages. The crystallographic data and structure refinement parameters for **I**–**III** are summarized in Table 1. Selected bond lengths and bond angles of **I**–**III** are presented in the captions to Figs. 1–3.

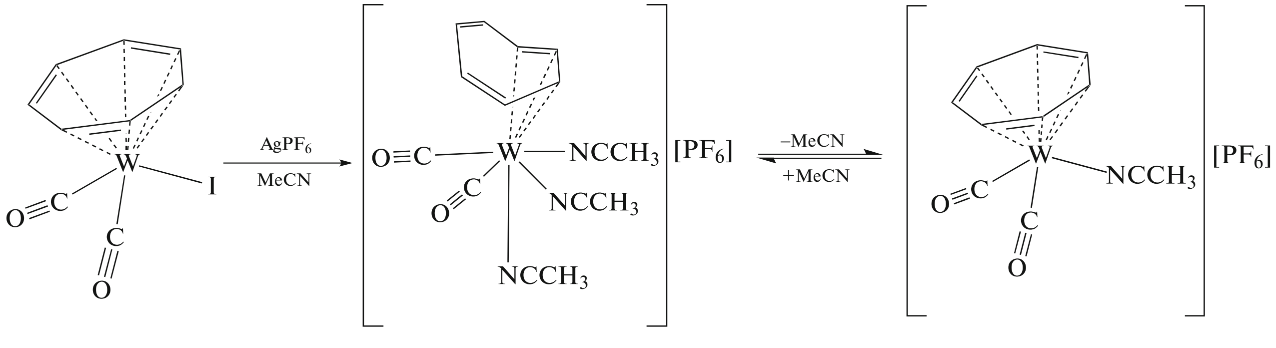
The atom coordinates and other structure parameters are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1875096 (**I**), 1875097 (**II**), 1875098 (**III**); http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystallographic data and structure refinement details for complexes **I–III**

Parameter	Value		
	I	**II**	**III**
Molecular formula	$C_{18}H_{14}I_2O_4W_2$	$C_{15}H_{16}F_6N_3O_2PW$	$C_{11}H_{10}F_6NO_2PW$
M	915.79	599.13	517.02
Radiation (λ, Å)	MoK_α (λ = 0.71073)		
Measurement temperature, K	150	120	150
System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/c$	$P2_1/c$
a, Å	7.2133(8)	14.7893(7)	11.4294(4)
b, Å	10.514(1)	8.3359(4)	10.8123(4)
c, Å	13.780(1)	16.0951(7)	11.9302(4)
β, deg	104.324(2)	90.6202(7)	100.3769(5)
V, Å^3	1012.6(2)	1984.1(2)	1450.20(9)
Z	2	4	4
ρ(calcd.), g/cm^{-3}	3.004	2.006	2.368
μ, mm^{-1}	14.420	5.972	8.147
F(000)	816.0	1144.0	968.0
Scanning range θ, deg	4.932–59.158	5.062–61.016	3.622–63.984
Scan mode	ω		
Number of unique reflections (N_1)	2958	6051	4935
R_{int}	0.0265	0.0279	0.0206
Number of reflections with $I > 2\sigma(I)$ (N_2)	2664	5358	4620
Number of refined parameters	127	256	200
GOOF (F^2)	1.051	1.040	1.065
R_1 for N_2	0.0206	0.0164	0.0163
wR_2 for N_1	0.0430	0.0349	0.0405
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.90/–1.02	0.68/–0.49	0.71/–1.11

RESULTS AND DISCUSSION

The reaction of green 18-electron complex **I** [5] with excess silver hexafluorophosphate in acetonitrile involved elimination of silver iodide to give cationic 18-electron complex **II**, which was isolated as orange crystals from an acetonitrile–diethyl ether mixture (1 : 2) (Scheme 2).



Scheme 2.

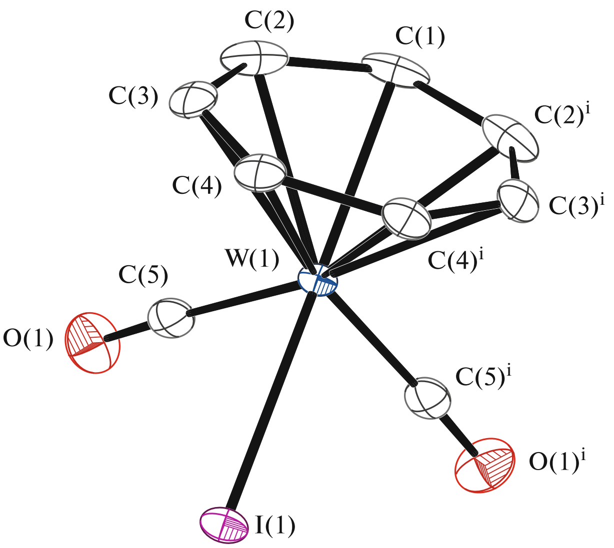


Fig. 1. Molecular structure of complex **I**. Selected distances: W(1)–I(1), 2.8191(4); W(1)–(5), 2.003(4); C(1)C(2)^i, 1.403(5); C(1)–C(2), 1.403(5); C(2)–C(3), 1.432(5); C(3)–C(4), 1.381(5); C(4)–C(4)^i, 1.439(7); O(1)–C(5), 1.144(4) Å.

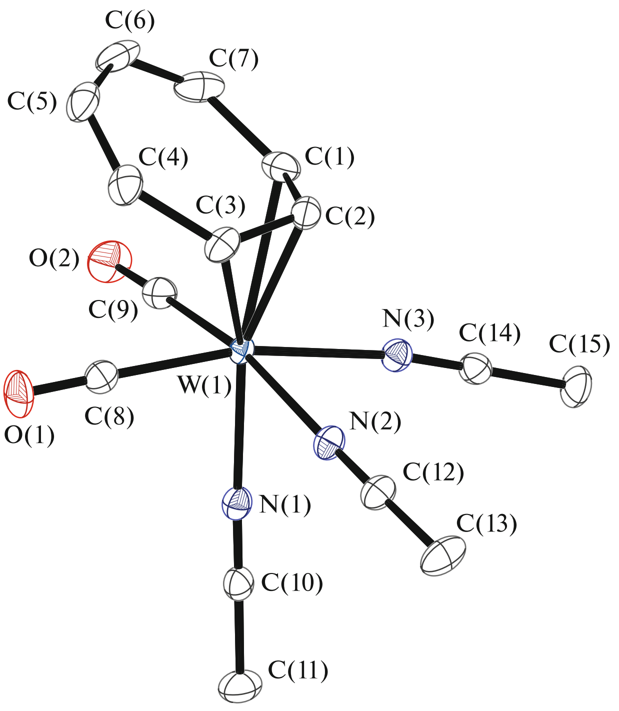


Fig. 2. Molecular structure of the cation of complex **II**. Selected distances and angles: W(1)–N(1), 2.149(2); W(1)–N(2), 2.193(2); W(1)–N(3), 2.202(2); W(1)–C(1), 2.367(2); W(1)–C(2), 2.193(2); W(1)–C(3), 2.367(2); W(1)–C(4), 3.380(2); W(1)–C(5), 4.032(2); W(1)–C(6), 4.033(2); W(1)–C(7), 3.387(2); W(1)–C(8), 1.968(2); W(1)–C(9), 1.972(2); O(1)–C(8), 1.151(2); O(2)–C(9), 1.154(2); C(1)–C(7), 1.466(3); C(2)–C(3), 1.423(3); C(3)–C(4), 1.462(3); C(4)–C(5), 1.346(3); C(5)–C(6), 1.436(3); C(6)–C(7), 1.339(3); C(1)–C(2), 1.425(3); N(1)–C(10), 1.136(2); N(2)–C(12), 1.136(2); N(3)–C(14), 1.134(3) Å; and C(8)W(1)C(9), 84.21(8)°; N(1)W(1)N(2), 80.17(6)°; N(1)W(1)N(3), 78.26(6)°; N(2)W(1)N(3), 81.27(6)°.

This was accompanied by shifts of two intense CO bands (1995, 1939 cm^{-1}) to lower frequency (1944, 1872 cm^{-1}).

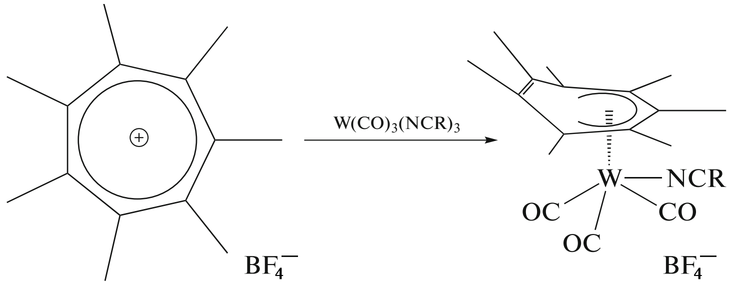
According to X-ray diffraction data, the cation of complex **II** contains three acetonitrile ligands. The tropylium ligand geometry and the W–C(C_7H_7) bond lengths considerably change. Unlike complex **I**, which has a planar C_7H_7 moiety (Fig. 1), in complex **II**, four carbon atoms deviate from the plane and are located at non-bonding distances from the W atom (W–C, 4.032(2) and 4.033(2) Å), i.e., during the reaction, the $\eta^7 \to \eta^3$ hapticity change takes place. The geometry of the complexes also changes: **II** has a pseudo-octahedral geometry and **III** has a three-legged stool configuration.

The dissolution of **II** in dichloromethane, acetone, or THF or refluxing in toluene induces a change in the solution color from orange to green, with a cherry tint (dichroism) being visible at higher concentrations. As this takes place, the cation in complex **II** loses two acetonitrile molecules to give 18-electron complex **III** (Scheme 2) containing, apart from two CO ligands, one acetonitrile ligand and a η^7-coordinated tropylium ligand. The reverse reaction, in which the monoacetonitrile complex is again converted to triacetonitrile complex **II**, takes place on dissolution in acetonitrile. According to IR spectroscopy data, the CO stretching frequency increases.

The ^{1}H NMR spectrum of a solution of triacetonitrile complex **II** (in CD_3CN) exhibits only signals for uncoordinated acetonitrile (1.98 ppm), while in the range of aromatic protons, a broadened singlet is present at 5.18 ppm, apparently, due to fast sliding of the η^3-coordinated tropylium with respect to tungsten. For the same reason, the corresponding signal cannot be detected in the ^{13}C NMR spectrum. When complex **II** is dissolved in d^6-acetone, the color changes to green, probably, due to elimination of some of the acetonitrile ligands to give cation **III**. This induces a substantial shift of the ^{1}H NMR signal for the tropylium moiety (6.00 ppm); the ^{13}C NMR spectrum exhibits signals corresponding to the tropylium (94.9 ppm) and CO groups (210 ppm).

The X-ray diffraction data for **I–III** provide the conclusion that the cycloheptatrienyl ligand undergoes an electron-compensating hapticity change $\eta^7 \leftrightarrow \eta^3 \leftrightarrow \eta^7$. The distances between the cycloheptatrienyl carbon atoms also change. For example, the C(1)–C(7) and C(3)–C(4) bond lengths in **II** and **III** differ by ~0.6 Å, as a result of changed coordination mode of the tropylium ligand. However, the $W(CO)_2$ structure and bond lengths in **II** and **III** are similar; the W bond lengths with carbon atoms of the tropylium ligand in molecules **I**–**III** also differ insignificantly.

It is noteworthy that the permethylated tricarbonyl complexes η^5-$Me_7C_7W(CO)_3(MeCN)^+$ (**IV**) and η^5-$Me_7C_7W(CO)_3I$ (**V**) exhibit the electron-compensating $\eta^7 \leftrightarrow \eta^5$ hapticity transition [9] (Scheme 3).



Scheme 3.

This apparently means that the loss of aromaticity of the seven-membered ring is not a significant factor. From this standpoint, it is of interest to compare tropylium complexes with the heterometallic tetrahedral clusters $Cp_3Cr_3S_4ML$ containing a $Cp_3Cr_3(\mu^3\text{-}S)(\mu\text{-}S)_3$ moiety, which is bound to the metal-containing groups, ML = CpCr, CpV$^\bullet$, CpNb$^\bullet$ [10] and Co(CO) [11], as a seven-electron ligand donating four electrons from three μ-S-bridges and three electrons from the Cr–M bonds. For example, in the electron-saturated $Cp_3Cr_3S_4Co(CO)$ cluster, all Co–Cr and Co–S bonds are single (on average, 2.658 and 2.163 Å) [11],

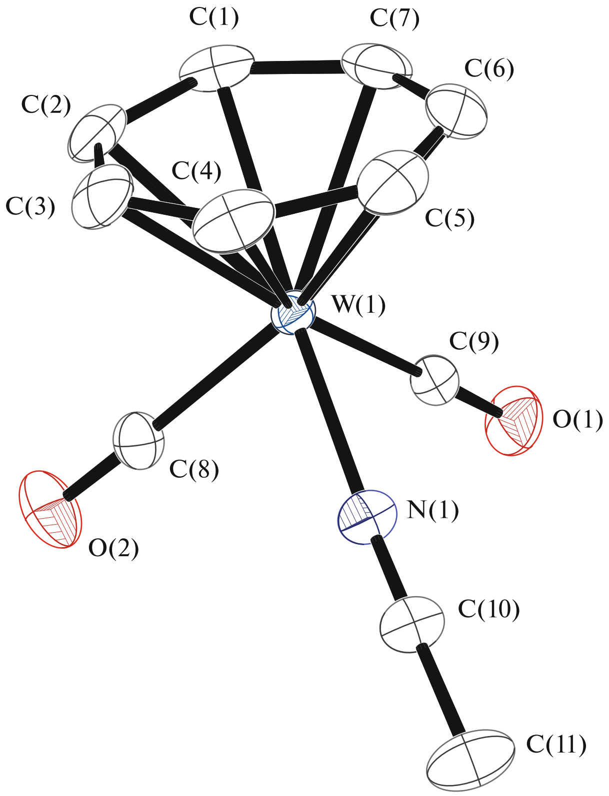


Fig. 3. Molecular structure of the cation of complex **III**. Selected distances and angles: W(1)–N(1), 2.121(2); W(1)–C(1), 2.320(2); W(1)–C(2), 2.277(2); W(1)–C(3), 2.337(2); W(1)–C(4), 2.332(2); W(1)–C(5), 2.327(2); W(1)–C(6), 2.336(2); W(1)–C(7), 2.278(2); W(1)–C(8), 2.012(2); W(1)–C(9), 2.011(2); O(2)–C(8), 1.137(3); O(1)–C(9), 1.138(2); C(1)–C(7), 1.403(4); C(2)–C(3), 1.424(3); C(3)–C(4), 1.391(4); C(4)–C(5), 1.429(4); C(5)–C(6), 1.395(4); C(6)–C(7), 1.430(4); C(1)–C(2), 1.409(3); N(1)–C(10), 1.137(3) Å; and C(9)W(1)C(8), 81.60(8)°; C(8)W(1)N(1), 89.38(7)°; C(9)W(1)N(1), 86.22(7)°.

whereas the introduction of two additional CO ligands in the solvated cluster $Cp_3Cr_3(\mu^3\text{-}O)(\mu^3\text{-}S)_3Co(CO)_3 \cdot CH_3COOH \cdot 0.5C_6H_6$ sharply loosens both the Co–Cr bonds (to 3.216(6), 3.238(6), and 2.892(6) Å) and the Co–S bonds (to 2.48 Å) [12]. It should be emphasized that this effect is observed only if extra electrons of the additional CO molecules get to the antibonding orbitals of the bonds between cobalt and the chromium sulfide core, as is also the case for the tungsten–tropylium bonds of **II**, **IV**, and **V**.

Thus, the tungsten cycloheptatrienyl complexes $[(\eta^7\text{-}C_7H_7)W(CO)_2I$, $[(\eta^3\text{-}C_7H_7)W(CO)_2(CH_3CN)_3]PF_6$, and $[(\eta^7\text{-}C_7H_7)W(CO)_2(CH_3CN)]PF_6$, characterized earlier only by spectroscopic methods, were prepared and studied by X-ray diffraction. It was found that tris(acetonitrile) complex $[(\eta^3\text{-}C_7H_7)W(CO)_2(CH_3CN)_3]PF_6$ loses two acetonitrile ligands in both coordinating and noncoordinatng solvents with the $\eta^3 \to \eta^7$ change in the hapticity of the cycloheptatrienyl ring. The reverse ligand attachment process accompanied by the $\eta^7 \to \eta^3$ change in the hapticity of the cycloheptatrienyl ring takes place upon the dissolution of monoacetonitrile complex $[(\eta^7\text{-}C_7H_7)W(CO)_2(CH_3CN)]PF_6$ in acetonitrile. Thus, the tropylium ligand undergoes the electron-compensating $\eta^3 \leftrightarrow \eta^7$ hapticity change, comparable with similar changes of bonds between the Co(CO) and $Co(CO)_3$ moieties and the chromium sulfide core in heterometallic tetrahedral clusters.

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