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Complexes containing the heptadentate cogwheel C_7Me_7: synthesis and structural characterization of heptamethylcycloheptatrienyl (CHT*) tungsten complexes

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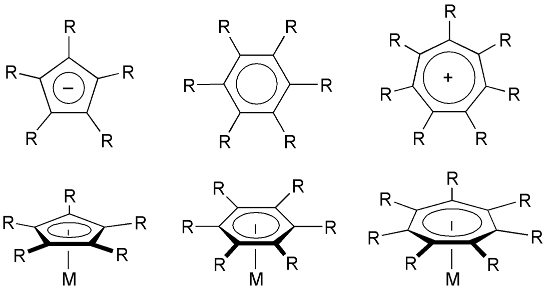
The first heptamethylcycloheptatrienyl (CHT*) complexes $[(\eta^5\text{-}C_7Me_7)W(CO)_3(NCR)][BF_4]$ (R = Me, Et) and $[(\eta^5\text{-}C_7Me_7)W(CO)_3I]$ have been prepared from $[(C_7Me_7)BF_4]$.

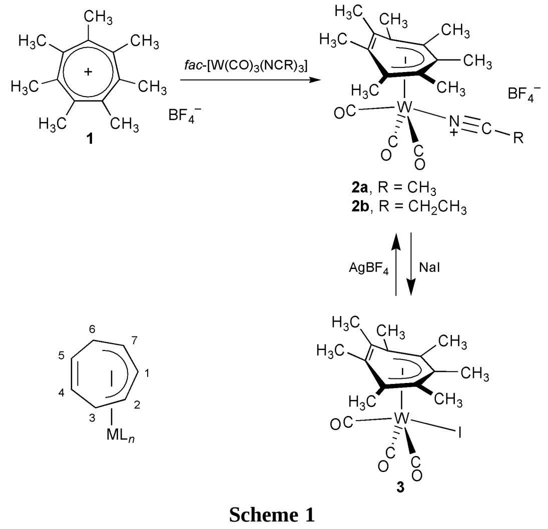
In contrast to complexes with sterically demanding peralkylated or perarylated cyclopentadienyl (η-C_5R_5) and arene (η-C_6R_6) groups (R ≠ H),[1] the corresponding cycloheptatrienyl complexes, (η-C_7R_7)M, are unknown despite the fact that the aromatic cycloheptatrienyl cations $C_7Me_7^+$ and $C_7Ph_7^+$ have been known for decades.[2,3] The molecular structures of $C_7Me_7^+$ and $C_7Ph_7^+$, however, have been determined only recently and represent the first structurally characterized cycloheptatrienyl cations with seven substituents to date.[4,5] Attempts to coordinate transition metals to the central seven-membered ring of these persubstituted π-perimeters have not been succesful so far.[6]



In continuation of our work on transition metal complexes with novel cycloheptatrienyl ligands,[7] we became interested in the synthesis of salts containing the heptamethylcycloheptatrienyl cation, $C_7Me_7^+$, and in the use of these compounds as ligands in organotransition metal chemistry. Thus, we have recently reported an improved protocol for the synthesis of heptamethylcycloheptatriene, C_7Me_7H, from hexamethylbenzene together with the synthesis and structural characterization of $[(C_7Me_7)BF_4]$ **1**,[4] which revealed a non-planar, boat-like geometry of the seven-membered ring owing to steric congestion caused by the seven methyl substituents. Consequently, we had stated that this strong distortion might impede applications of the C_7Me_7 ligand to the synthesis of organometallic derivatives. In the meantime, however, we have observed that coordination of this sterically demanding cation to transition metal centers is surprisingly easy, and with this contribution, we present the first transition metal complexes containing this molecular cogwheel.

The reaction of tropylium salts with complexes of the type *fac*-$[M(CO)_3(NCR)_3]$ (M = Mo, W; R = Me, Et) can result in the formation of cationic cycloheptatrienyl complexes $[(\eta^7\text{-}C_7R_7)M(CO)_3]^+$ by substitution of the three nitrile ligands,[8,9] *e.g.* 1,2,4,6-tetramethylcycloheptatrienyl hexafluorophosphate gives $[(\eta^7\text{-}1,2,4,6\text{-}C_7Me_4H_3)W(CO)_3][PF_6]$ upon treatment with *fac*-$[W(CO)_3(NCEt)_3]$ in the presence of a catalytic amount of ferricenium ion. This cationic tungsten complex reacts further with halides to form neutrally charged complexes $[(\eta^7\text{-}1,2,4,6\text{-}C_7Me_4H_3)W(CO)_2X]$ (X = Br, I),[9] which agrees with the reactivity observed for related cationic molybdenum and tungsten tricarbonyl complexes.[8,10]

In view of the observations described above, the reaction of $[(C_7Me_7)BF_4]$ **1** with *fac*-$[W(CO)_3(NCEt)_3]$ appeared to be a promising method for the preparation of the first CHT* complex (CHT* = C_7Me_7).[11] Hence, a thf–dichloromethane solution of **1** was treated with an equimolar amount of the nitrile complex in the presence of a catalytic quantity of $[Cp_2Fe][PF_6]$. After stirring for 2 h and evaporation of the solvents, the intermediate product (presumably **2b**, *vide infra*) was redissolved in acetone, and a large excess of sodium iodide was added (Scheme 1). Surpringly, no CO evolution could be observed, which is inconsistent with the formation of a complex $[(\eta^7\text{-}C_7Me_7)W(CO)_2I]$, which we had expected arguing from analogy with the 1,2,4,6-tetramethylcycloheptatrienyl system (*vide supra*). Instead, a stable, purple–red crystalline solid could easily be separated by column chromatography, of which the spectroscopic characterization indicated a C_7Me_7 ring not coordinated in a symmetric η^7-fashion. Its ^1H NMR spectrum exhibits four different resonances for the methyl protons in a 6:6:6:3 ratio. Consistently, in the ^{13}C NMR spectrum the methyl and the ring carbon atoms give rise to four resonances each, in addition to two signals for the carbonyl carbon atoms.† These results together with the observation of three carbonyl stretching frequencies in the IR spectrum suggest the formation of $[(\eta^5\text{-}C_7Me_7)W(CO)_3I]$ **3**, in which the C_7Me_7 ligand is only η^5-coordinated (Scheme 1).



Scheme 1

In order unambiguously to confirm this conclusion, the molecular structure of **3** was established by X-ray diffraction analysis.‡ The asymmetric unit contains two independent, almost identical molecules, and the structure of molecule A is shown in Fig. 1. The complex is almost C_s symmetric with the pseudo mirror plane including I, W, C1, C15 and O1. The η^5-coordinated ring is strongly distorted from planarity and rather adopts a boat conformation with its uncoordinated part strongly bending back from the rest of the molecule.[12] Furthermore, the distance between the two uncoordinated carbon atoms [C4A–C5A 1.312(10) Å, C4B–C5B 1.310(10) Å] clearly corresponds to a C(sp^2)–C(sp^2) double bond, and hence the solid state structure of **3** is best described as a pentadienyl complex as shown in Scheme 1. In fact, the structural features compare well with those of other complexes containing 'true' pentadienyl ('open Cp')[13] or related cycloheptadienyl ligands.[14]

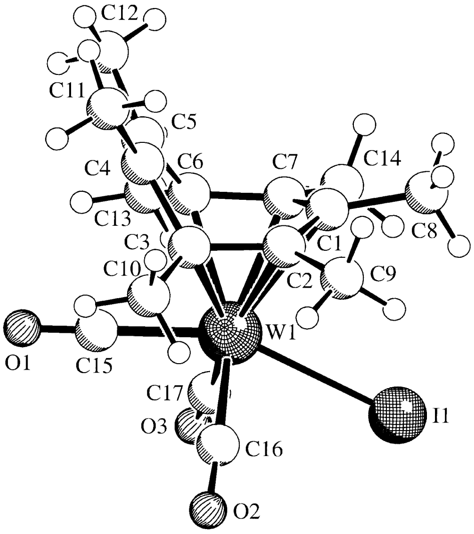


Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): molecule A [molecule B] C1–C2 1,447(9) [1.428(9)], C1–C7 1.427(10) [1.432(10)], C2–C3 1.429(9) [1.451(9)], C3–C4 1.497(9) [1.503(9)], C4–C5 1.312(10) [1.310(10)], C5–C6 1.506(9) [1.496(9)], C6–C7 1.440(10) [1.442(9)], W1–I1 2.8425(6) [2.8659(5)], W1–C1 2.440(7) [2.425(6)], W1–C2 2.308(7) [2.303(7)], W1–C3 2.332(7) [2.335(6)], W1–C6 2.346(6) [2.329(6)], W–C7 2.323(6) [2.292(6)], W1–C15 2.008(10) [1.984(8)], W1–C16 1.988(8) [1.991(9)], W1–C17 2.000(8) [1.995(7)]; C15–W1–I1 153.2(2) [154.2(2)], C16–W1–C17 93.1(3) [93.7(3)].

Nevertheless, this η^5-bonding mode is quite unique for a cycloheptatrienyl ligand,[15] and only very few examples have been reported in the older literature[16] in addition to proposed intermediates containing an η^5-cycloheptatrienyl ring.[17] In contrast, the η^7–η^3 hapticity interconversion in cycloheptatrienyl complexes has been studied in great detail.[18] It appears that the constrained geometry of the uncoordinated heptamethylcycloheptatrienyl cation[4] accounts for the unusual reactivity observed here as the C_7Me_7 ring tries to retain its boat conformation.

In order to prove the intermediacy of **2b** in the formation of **3** from **1**, the iodine in **3** was removed by treatment of **3** with [AgBF$_4$] in acetonitrile solution. The IR and NMR spectroscopic characterization of the red crystalline compound reveals that the η^5-bound cycloheptatrienyl complex **2a** must have formed.† Even after one week in CD_2Cl_2 solution, the NMR spectrum gave no indication for a η^5–η^7 hapticity interconversion by intramolecular substitution of the coordinated acetonitrile by the pendent double bond. Thus, a η^7-C_7Me_7 complex still remains elusive.

With this contribution, we have demonstrated that η^5-bound heptamethylcycloheptatrienyl complexes are surprisingly stable and easy to prepare. These are very promising candidates for further reactions, *e.g.* for the preparation of bimetallic complexes[19] by specifically utilizing the pendant double bond for the coordination of an additional metal center. Future work in this area will also elucidate the possibility to prepare (η^7-C_7Me_7)M complexes which can be expected to be very reactive due to the permethylated ligand being in an 'entatic' state.

Notes and references

† *Spectroscopic data* for **2a** and **3**; all resonances have been unambiguously assigned by two-dimensional NMR spectroscopy (COSY experiments); for the numbering, see Scheme 1.

2a: IR (CH_2Cl_2): $\tilde{\nu}$ 2042, 2000, 1954 cm^{-1} (CO). δ_H(600 MHz, CD_2Cl_2): 2.71 (s, 3H, CH_3CN), 2.46 (s, 3H, 1-CH_3), 2.41 (s, 6H, 2,7-CH_3), 2.40 (s, 6H, 3,6-CH_3), 1.46 (s, 6H, 4,5-CH_3). δ_C(150 MHz, CD_2Cl_2): 212.7 (2 × Mo–CO), 211.7 (1 × Mo–CO), 137.0 (C-4,5), 134.0 (C-1), 132.4 (CN), 110.8 (C-2,7), 102.9 (C-3,6), 27.1 (3,6-CH_3), 20.6 (2,7-CH_3 + 1-CH_3), 17.4 (4,5-CH_3), 4.7 (CH_3CN).

3: IR (CH_2Cl_2): $\tilde{\nu}$ 2018, 1976, 1930 cm^{-1} (CO). δ_H(600 MHz, CD_2Cl_2): 2.74 (s, 3H, 1-CH_3), 2.25 (s, 6H, 3,6-CH_3), 2.16 (s, 6H, 2,7-CH_3), 1.41 (s, 6H, 4,5-CH_3). δ_C(150 MHz, CD_2Cl_2): 213.8 (1 × Mo–CO), 209.3 (2 × Mo–CO), 135.1 (C-4,5), 131.4 (C-1), 106.0 (C-2,7), 97.0 (C-3,6), 26.5 (3,6-CH_3), 22.0 (2,7-CH_3), 21.0 (1-CH_3), 17.3 (4,5-CH_3).

‡ *Crystal data* for $C_{17}H_{21}IO_3W$ **3**: M = 584.09, a = 7.515(1), b = 29.376(1), c = 16.328(1) Å, β = 90.13(1)°, V = 3604.6(5) Å^3, μ = 81.31 cm^{-1}, Z = 8, monoclinic, space group $P2_1/n$ (no. 14), T = 198 K, 28135 reflections collected ($\pm h, \pm k, \pm l$), 8237 independent (R_{int} = 0.087) and 5361 observed reflections [$I \geqslant 2\sigma(I)$], R = 0.044, wR^2 = 0.064, two chemically identical molecules with different conformation in the asymmetric unit. CCDC 182/1735.

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