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THE STRUCTURE OF $(C_5H_5)_2W(CO)_2$, A COMPOUND CONTAINING A BENT *trihapto*-CYCLOPENTADIENYL LIGAND

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Summary

The crystal and molecular structure of the complex $(C_5H_5)_2W(CO)_2$ has been determined by X-ray analysis ($R_1 = 0.063$). The structure contains a *trihapto*-cyclopentadienyl ligand, bent along its 1,3-axis by 20° . By this unusual structure, a 20-electron valence configuration of the central metal is avoided.

Introduction

The stability of carbocyclic aromatic 6- π systems is intimately connected to a planar nuclear geometry. Any severe deviation from planarity is necessarily accompanied by a substantial loss of stability and will hence only be brought about by strong perturbations.

Bent benzene ligands have been observed in a number of transition metal complexes, for which a *hexahapto* arrangement with planar rings would lead to an energetically unfavourable 20-electron configuration for the metal atom [1]. One bent and one planar hexamethylbenzene ligand, for example, have been observed in bis(hexamethylbenzene)ruthenium(0); the bending of one ring by 42.8° results in a *tetrahapto*-coordination and hence in a stable 18-electron configuration of the central metal atom [1]. Bent *tetrahapto*-coordination geometries have also been observed in vinyl benzene derivatives to which two metal atoms are coordinated [2]. Structures with similarly bent *trihapto*-cyclopentadienyl ligands on the other hand have not yet been reported*. Even in cyclopentadienyl compounds in which the 18-electron configuration of the

* A bent *trihapto* structure for the central five-membered ring of a fluorene ligand, observed in dichlorodifluorenylzirconium(IV), has been related to steric crowding in this molecule [3].

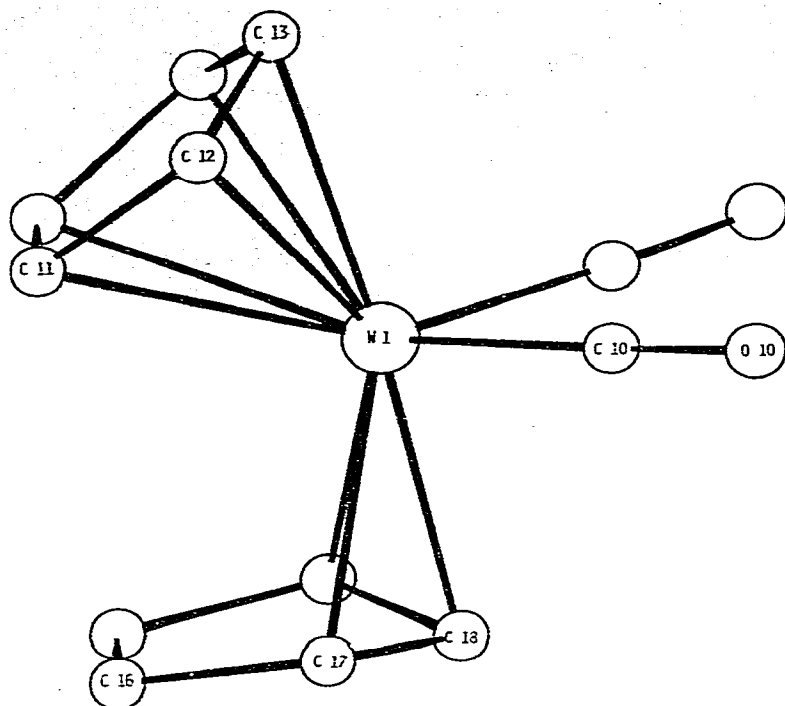


Fig. 1. Molecular structure of $(C_5H_5)_2W(CO)_2$.

metal atom is exceeded, no severe deviation from planarity has yet been found for a C_5H_5 ligand. The largest deviation from planarity observed to date appears to exist in $(C_5H_5)_2VNN[Si(CH_3)_3]_2$ [4], where a bending along the 1,3-axis of a C_5H_5 ligand by about 6° has been reported; even here, however, all five C atoms are still within bonding distance from the metal center. Definitely planar rings, albeit acentrally bonded to the metal atom, have been found to persist even in formal 20-electron complexes of the type $(C_5H_5)_2Mo(NO)R$ [5]. The hitherto consistent lack of definite structural examples of bent *trihapto*-cyclopentadienyl ligands might lead to the impression that such a coordination geometry is unavailable for cyclopentadienyl ligands [6]. In this paper we report on the first definite example of a structure containing a bent *trihapto*- C_5H_5 ligand.

Results and discussion

The structure of $(C_5H_5)_2W(CO)_2$, the synthesis and reactions of which have been described previously [7], has been determined by a single crystal X-ray study*. Crystal data were obtained on a Syntex four-circle diffractometer at $-80^\circ C$ (orthorhombic, space group $Prma$, $Z = 4$, $d_{calc} 2.38 \text{ g cm}^{-3}$, $a 1536.1(8)$, $b 1090.0(7)$, $c 1241.3(8) \text{ pm}$). A total of 933 independent nonzero reflexion data ($I \geq 3\sigma(I)$, $T = -80^\circ C$, ω -scan $0.9 \leq \dot{\omega} \leq 29.7^\circ \text{ min}^{-1}$, graphite monochro-

* Black crystals of this compound were obtained by crystallization from a saturated diethyl ether solution at $-80^\circ C$; the material is clearly different from the light-orange compound $(C_5H_5)(C_5H_7)W(CO)_2$ [7].

mator, $\lambda(\text{Mo-K}\alpha)$ 71.069 pm) were collected using the same instrumentation. The structure has been solved and refined by conventional procedures to an agreement factor of $R_1 = 0.063$ (Structure solving system Syntex XTL). The asymmetric unit of the crystal cell contains two independent half-molecules; the tungsten atoms are situated on a mirror plane in space group $Pnma$; the individual molecules therefore show crystallographic mirror symmetry. Both molecules have identical geometry within the limits of error. The observed molecular structure is presented in Fig. 1; the most pertinent numerical data are

TABLE 1
STRUCTURAL PARAMETERS OF $(\text{C}_5\text{H}_5)_2\text{W}(\text{CO})_2^a$

Atom	x/a	y/b	z/c	B		
W1	0.30957(7)	0.25000(0)	0.22882(8)			
W2	0.02202(7)	0.25000(0)	0.75131(7)			
C10	0.295(1)	0.355(2)	0.109(1)		2.4(4)	
O10	0.282(1)	0.426(1)	0.035(1)		3.5(3)	
C20	-0.049(1)	0.142(2)	0.833(1)		2.4(3)	
O20	-0.100(1)	0.075(1)	0.880(1)		3.2(3)	
C11	0.265(1)	0.316(2)	0.406(2)		2.9(4)	
C12	0.203(1)	0.355(2)	0.324(2)		2.7(4)	
C13	0.164(2)	0.250(0)	0.286(2)		3.0(6)	
C16	0.464(1)	0.312(2)	0.364(1)		2.3(3)	
C17	0.446(1)	0.353(2)	0.255(1)		1.6(3)	
C18	0.454(1)	0.250(0)	0.186(2)		0.8(4)	
C21	0.063(1)	0.314(2)	0.568(1)		2.7(4)	
C22	-0.021(1)	0.145(2)	0.595(2)		2.7(4)	
C23	-0.073(1)	0.250(0)	0.606(2)		3.5(6)	
C26	0.210(2)	0.314(2)	0.746(2)		3.5(5)	
C27	0.146(1)	0.361(2)	0.829(2)		2.9(4)	
C28	0.124(2)	0.250(0)	0.890(2)		2.7(5)	

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W1	2.48(7)	1.92(7)	0.18(6)	0.00(0)	0.12(3)	0.00(0)
W2	2.68(8)	2.06(7)	0.34(6)	0.00(0)	-0.02(3)	0.00(0)

Relevant interatomic distances

W1—C10	188(2)	W2—C20	190(2)
W1—C11	242(2)	W2—C21	247(2)
W1—C12	231(2)	W2—C22	235(2)
W1—C13	234(3)	W2—C23	232(3)
W1—C16	298(2)	W2—C26	297(3)
W1—C17	240(2)	W2—C27	245(2)
W1—C18	228(2)	W2—C28	232(3)
C11—C12	146(3)	C21—C22	141(3)
C12—C13	137(3)	C22—C23	141(3)
C11—C11 _m	145(3)	C21—C21 _m	140(3)
C16—C17	145(2)	C26—C27	151(3)
C17—C18	142(2)	C27—C28	147(3)
C16—C16 _m	135(3)	C26—C26 _m	140(4)

^a Numbers given in parentheses give the standard deviations in units of the last significant digit. Thermal parameters are given in 10^4 pm^2 . Anisotropic parameters refer to the expression $T = \exp(-\frac{1}{4}(h^2a^*{}^2B_{11} + \dots + 2hka^*b^*B_{12} + \dots))$.

given in Table 1. Tables of structure factors will be supplied by the author on request.

$(C_5H_5)_2W(CO)_2$ is a mirror-symmetric molecule containing one planar (C11, C12, C11m, C12m, C13; C21, C22, C21m, C22m, C23) ** and one bent (C16, C17, C16m, C17m, C18; C26, C27, C26m, C27m, C28) cyclopentadienyl ligand. In addition, two carbonyl groups are bound to the metal, sustaining an angle of $74.5(8)^\circ$ (C10—W1—C10m) and $76.6(8)^\circ$ (C20—W2—C20m), respectively.

The *pentahapto*- C_5H_5 group is planar within the limits of error (3 pm). The relevant metal—carbon distances have a mean value of 237 pm and range from 231(2) to 247(2) pm. The observed variation of these bond lengths is within the range typically found for metal carbon distances in $\eta^5-C_5H_5$ metal complexes.

The *trihapto*-cyclopentadienyl moiety is best regarded as composed of an allylic (C17, C18, C17m; C27, C28, C27m) and an olefinic (C16, C16m; C26, C26m) fragment. The planes defined by these two ring segments (C17, C18, C17m; C27, C28, C27m and C17, C16, C16m, C17m; C27, C26, C26m, C27m) intersect at an angle of 20° (19.6°). The carbon atoms of the allylic fragment are bonded to the metal at distances typical for η^3 -allyl—metal interactions [8], with the central carbon atom somewhat nearer to the metal (W1—C18) 228(2) pm; W2—C28 232(3) pm) than the terminal ones (W1—C17 240(2) pm; W2—C27 245(2) pm). The angle spanned by the coordinated allylic and $\eta^5-C_5H_5$ planes is 53° (52.6°) for the two independent molecules.

The olefinic carbon atoms (C16 and C16m; C26 and C26m) of the bent C_5H_5 ring are separated from the metal by distances of 298(3) pm in both independent molecules. These distances are definitely outside the range generally accepted for tungsten—carbon bonding interactions. The olefinic segment cannot therefore be considered as coordinatively bonded to the tungsten atom.

The observed *trihapto*-coordination of one C_5H_5 ligand satisfies an 18-electron valence configuration of the central metal. It is noteworthy that this stable electron configuration is arrived at by distorting part of the C_5H_5 π -system out of the coordination sphere of the metal and not simply by eliminating one of the CO ligands.

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* The m refers to the mirror related atom, the numbers 1—18 relate to one of the two independent molecules, the numbers 2—28 to the other molecule.

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