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INDENYL AND FLUORENYL TRANSITION ELEMENT COMPLEXES

II *. SYNTHESIS AND X-RAY STUDY OF (η^3-INDENYL)(η^5-INDENYL)TUNGSTEN DICARBONYL

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Summary

Heating of $W(CO)_6$ with indene in diglyme at 175°C gives a mixture of $(C_9H_7)_2W(CO)_2$ (I) and $[(\eta^5\text{-}C_9H_7)W(CO)_3]_2$ in low yields; A single crystal X-ray study of I has shown it to contain indenyl ligands differently bonded to tungsten: the planar η^5-ligand with all five-membered ring atoms equidistant from the metal (~2.3 Å), and the π-allyl η^3-ligand. The latter is bent across the C(13)—C(15) axis by 26°, its nodal carbon atoms C(12) and C(16) which do not participate in bonding with the metal being at distances of ca. 3.2 Å from W. Complex I is the first η^3-indenyl compound studied by X-ray diffraction. The possibility of fast on the NMR time scale for intramolecular exchange of indenyl ligands is discussed.

Introduction

The electronic structures of the overwhelming majority of stable chromium family metal π-complexes conform to the Sidgwick rule. A large number of these compounds containing two to four cyclopentadienyl ligands per molecule have been described. In order that the outer metal 18-electron shell be filled, some of these complexes should contain cyclopentadienyl ligands differently bonded to the central metal. Detailed ^{1}H NMR studies have shown tetracyclopentadienylmolybdenum to contain two η^5- and two η^1-rings [1], $(C_5H_5)_2Cr(NO)_2$ [2] and $(C_5H_5)_2Mo(NO)S_2CN(CH_3)_2$, and $[(C_5H_5)_2Mo(NO)S_2C_2(CN)_2][P(C_6H_5)_4]$ [3]

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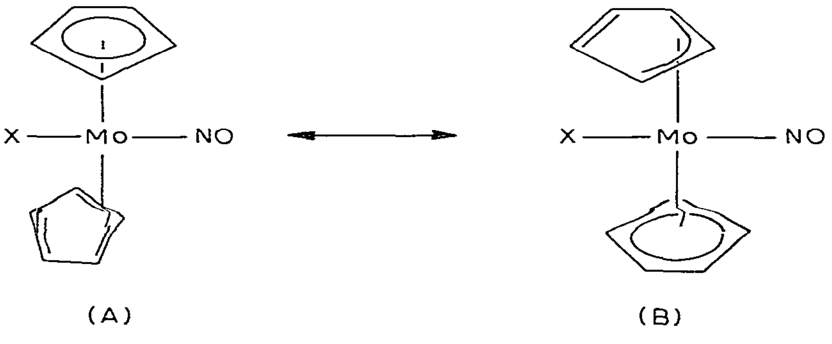
* For part I see ref. 14.

one η^5- and one η^1-C_5H_5 ligand. The compounds $(C_5H_5)_2Mo(NO)X$ where X is I, CH_3, C_5H_5 studied by King [4] and Cotton [5] and $(C_5H_5)_2W(CO)_2$ described by Brintzinger et al. [6,7] deserve special attention. If Sidgwick's rule holds with these complexes, both cyclopentadienyl ligands should participate in bonding with 8 of their 10 electrons. $(C_5H_5)_3Mo(NO)$ was first suggested by Cotton [8] to contain cyclopentadienyl ligands of three different types of which two (η^5- and η^1-ones) are well known and have been studied with other compounds. The third ligand was supposed to behave as a π-allyl one donating 3 π-electrons to the metal. The proton NMR spectrum of the complex [5] measured at —110°C does not contradict the suggested structure. In fact, it contains two singlet signals from polyhapto-cyclopentadienyl ligands and an $AA'BB'X$ spectrum from the monohapto-ring protons. The single crystal X-ray study has however shown that one of the ligands is actually η^1-bonded to the metal while two other ligands do not differ significantly from each other. All their carbon atoms lie close enough to the metal to participate in the bonding, though two Mo—C bonds are "short" (2.33—2.34 Å), two "long" (ca. 2.6 Å), and one is "intermediate" (2.43 Å) [9]. A similar distribution of Mo—C bond lengths was observed by Cotton in $(C_5H_5)_2Mo(NO)CH_3$ [10] containing two polyhapto rings. Cotton has therefore discarded the idea of η^3-coordination and treats these compounds as non-perfect η^5-complexes. King [11] has put forward the concept of "interligand resonance" and "fluxional" behaviour: in his view, non-perfect η^5-complexes may be described as resonance hybrides of two canonical structures (A and B). The resonance results in a displacement of molybdenum with respect to the ring centre which makes the Mo—C bond lengths different.



Fluxional behaviour of non-perfect η^5-complexes manifests itself by equivalence of the cyclopentadienyl ring protons in the proton NMR spectra irrespective of the differences in the Mo—C distances. According to King, the η^3-cyclopentadienyl ring cannot be detected, e.g. by X-ray diffraction, because the canonical structures do not correspond to physically plausible molecular states.

Up to now, among the transition metal π-complexes studied by X-ray analysis no compounds containing an η^3-cyclopentadienyl ring have been established. Among nontransition metal compounds, $(CH_3)_2AlC_5H_5$ was first suggested by Drew and Haaland, from the electron diffraction data, to involve η^3-metal—ligand bonding [12]. More detailed study [13] has however shown that the complex structure may be described in terms of polyhapto bonding with the metal displaced by 0.9 Å with respect to the centre of the C_5H_5 ligand retaining D_{5h} effective symmetry.

The possibility of participation of one of the cyclopentadienyl double bonds in coordination bonding may only be excluded when the ligand is nonplanar. Such distortion of the rigid cyclopentadienyl ring structure would be unfavourable energetically. At the same time, one may expect that the energy difference between structures containing two identical ligands bonded as in non-perfect η^5-complexes such as $(C_5H_5)_3Mo(NO)$ and those containing η^5- and η^3-ligands should be significantly smaller than with the corresponding complexes of the indenyl series. In that case, deviation from planarity should not lead to any considerable energy loss because the released π-electron pair is involved in the benzene nucleus sextet. In the present work, we describe the synthesis of $(C_9H_7)_2W(CO)_2$ (I) which is the first compound proved by X-ray diffraction to contain an η^3-bonded indenyl ring.

Results and discussion

In order to obtain $[\eta^5\text{-}C_9H_7(CO)_3W]_2$ (II), a convenient starting material for the synthesis of the anion $\eta^5\text{-}C_9H_7(CO)_3W^-$ [14], we studied the reaction between $W(CO)_6$ and indene in diglyme at 175°C. Compound II has not previously been described in the literature. Unlike a similar reaction of $Mo(CO)_6$ [14,15] yielding $[\eta^5\text{-}C_9H_7(CO)_3Mo]_2$ (III), the process gave a mixture of dimer II and complex I in yields of 1.5 and 1.1%, respectively. The main portion of tungsten hexacarbonyl remained unreacted.

$$C_9H_8 + W(CO)_6 \rightarrow \underset{\text{(II)}}{[\eta^5\text{-}C_9H_7(CO)_3W]_2} + \underset{\text{(I)}}{(\eta^3\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)W(CO)_2}$$

The structure II was proven by the IR and proton NMR spectra: $\nu(C{\equiv}O)$ $(CHCl_3)$ = 1905, 1955 cm^{-1}; ^1H NMR $(CDCl_3)$: A_2X spectrum, $\delta_A = 5.73$ ppm, $\delta_X = 5.39$ ppm, $J(AX) = 2.8$ Hz (the five-membered ring); $AA'BB'$ spectrum at 7.07 and 7.45 ppm (the six-membered ring). The IR and proton NMR parameters of II practically coincide with those of III.

The mass spectrum of I having the composition $C_{20}H_{14}O_2W$ (according to elemental analysis) contains a low intensity molecular ion and intense ions $(C_9H_7)_2W(CO)^+$ ($M^+ - CO$) and $(C_9H_7)_2W^+$ ($M^+ - 2CO$) with intensities of multiplet components corresponding to natural abundances of tungsten isotopes. The base ion is $C_9H_7^+$. The IR spectrum of I in chloroform solution contains two carbonyl bands of approximately equal intensities, 1871 and 1949 cm^{-1}. IR patterns of this type are characteristic for Group VI metal cyclopentadienyl-allyl complexes $(\eta^5\text{-}C_5H_5)M(CO)_2(\eta^3\text{-allyl})$. Thus, $\eta^5\text{-}C_5H_5W(CO)_2(\eta^3\text{-}C_5H_7)$ shows $\nu(C{\equiv}O)$ at 1872, 1950 cm^{-1} [6]. After consideration of the combined mass spectral and IR evidence and bearing in mind Sidgwick's rule, we have suggested the structrue $(\eta^3\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)W(CO)_2$ for complex I.

In order to prove this suggestion we carried out a single crystal X-ray study of the compound.

The molecular geometry together with bond lengths is shown in Fig. 1. The bond angles are listed in Table 1. The W atom is linked with two carbonyl

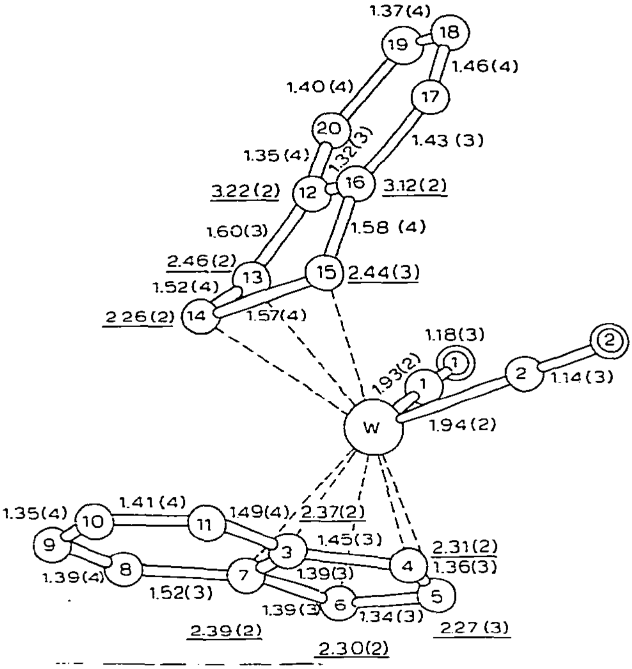


Fig. 1. The structure of complex I with interatomic distances.

groups and two indenyl ligands one of which is bonded as η^3-(π-allyl) ligand and the other one as η^5-ligand. That completes the outer 18-electron shell of the W atom. Assuming that the allyl fragment which donates three electrons occupies two coordination sites while the cyclopentadienyl ring donating five electrons occupies three sites one can treat I as usual seven-coordinate Group VI transition metal complex.

Of the compounds studied by X-ray diffraction, two molybdenum complexes are analogous to I by the type of coordination of the central atom. These are (η^3-*p*-methylbenzyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum (IV) [16] and (η^3-1,1′,2′-(oxo-5′-cyclopentene-1′)-yl-1′-ethyl)-(η^5-cyclopentadienyl)dicarbonylmolybdenum [17]. Unfortunately, no structural parameters have been reported for the latter compound. Therefore only the structural data on I and IV can be compared. Similarly to other seven-coordinate complexes, the η^5-cyclopenta-

TABLE 1

BOND ANGLES (°)

C(1)—W—C(2)	80.6(1.0)	C(3)—C(7)—C(8)	119(2)	C(14)—C(15)—C(16)	101(2)
W—C(1)—O(1)	176(2)	C(7)—C(8)—C(9)	115(2)	C(15)—C(16)—C(12)	115(2)
W—C(2)—O(2)	177(2)	C(8)—C(9)—C(10)	125(2)	C(16)—C(12)—C(13)	107(2)
C(3)—C(4)—C(5)	107(2)	C(9)—C(10)—C(11)	123(2)	C(12)—C(16)—C(17)	122(2)
C(4)—C(5)—C(6)	110(2)	C(10)—C(11)—C(3)	115(2)	C(16)—C(17)—C(18)	115(2)
C(5)—C(6)—C(7)	109(2)	C(11)—C(3)—C(7)	122(2)	C(17)—C(18)—C(19)	118(2)
C(6)—C(7)—C(3)	107(2)	C(12)—C(13)—C(14)	104(2)	C(18)—C(19)—C(20)	124(2)
C(7)—C(3)—C(4)	106(2)	C(13)—C(14)—C(15)	106(2)	C(19)—C(20)—C(12)	116(2)
				C(20)—C(12)—C(16)	124(2)

dienyl ligand in I is not bonded to the metal completely symmetrically, the W—C(C_5H_5) bond lengths ranging from 2.27 to 2.37(2) Å. Because of the closeness of Mo and W atomic radii, the distances in IV are nearly the same (2.290—2.382 Å). Such bond lengths are typical for molybdenum and tungsten monocyclopentadienyl complexes, e.g. 2.31—2.36 Å in $[(\eta^5\text{-}C_5H_5)W(CO)_3(AlMe_2)]_2$ [18] and 2.305—2.377 Å in $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ [19]. The η^5-indenyl ligand is planar on the whole, the largest deviation of carbons from the ligand least squares plane not exceeding 0.03 Å. The scatter of the C—C bond lengths around their mean (1.41(3) Å) are such that the π-electrons may be thought to be fully delocalized over the aromatic ligand system.

The other indenyl ligand loses planarity because of the η^3-type coordination to the metal. This ligand is bent about the C(13)—C(15) direction by 26°. The tungsten to C(12) and C(16) distances are apparently nonbonded (3.22(2) and 3.12(2) Å, respectively) and the benzene ring together with its *exo*-cyclic atoms C(13) and C(15) makes a planar system to within 0.02 Å. Unlike IV where the Mo—C bond between the metal and the *exo*-cyclic CH_2 group is shorter than the other two ones, the distribution of the M—C(allyl) bonds observed in I is usual for transition metal π-allyl complexes, the central C(14) atom forming a far shorter W—C bond (2.26(2) Å) than the terminal C(13) and C(15) atoms (2.46(2) and 2.44(2) Å, respectively).

The unusual relative arrangements of the allyl ligand and the metal—carbonyl fragment is to be noted. In fact, apexes of the C(13)C(14)C(15) and C(1)WC(2) angles have the same direction, contrary to that found in IV. Apart from this, the allyl group and C(1)WC(2) planes are almost parallel and make a dihedral angle as small as 5°, whereas in IV the dihedral angle amounts to 34° *. At the same time, the relative arrangement of the metal—carbonyl fragment and the η^5-C_5H_5 ligand and the dihedral angles between them are essentially the same in both two compounds; 38° in I and 40.7° in IV.

The difference in the metal coordination between I and IV corresponds to rotation of the allyl fragment about its centre of gravity by 180° in its own plane. This difference can be caused by steric interactions. In fact, unlike IV, the allyl and cyclopentadienyl-type ligands in I are bulky indenyl systems. As is seen from Fig. 2, rotation of the η^3-ligand as indicated by dashed lines would lead to an extremely close approach of the indenyl rings to each other.

The metal—carbonyl groups W—C—O are linear and have the usual bond lengths W—C (1.94(2) Å) and C—O (1.16(3) Å) (see, e.g., the list of bond lengths in [18]).

C—C bond lengths do not deserve a special discussion because of their rather low precision caused by neglect of absorption and the large tungsten atomic number.

The procedure for the preparation of I described above gives low yields. We have studied other routes to this compound. For that prupose, $[\eta^5\text{-}C_9H_7(CO)_3W]_2Hg$ described by us previously [14] has been reduced with a Na/K alloy in THF solution to the corresponding anion. This was converted to the halo compounds V—VII unknown earlier by the reactions shown in Scheme 1.

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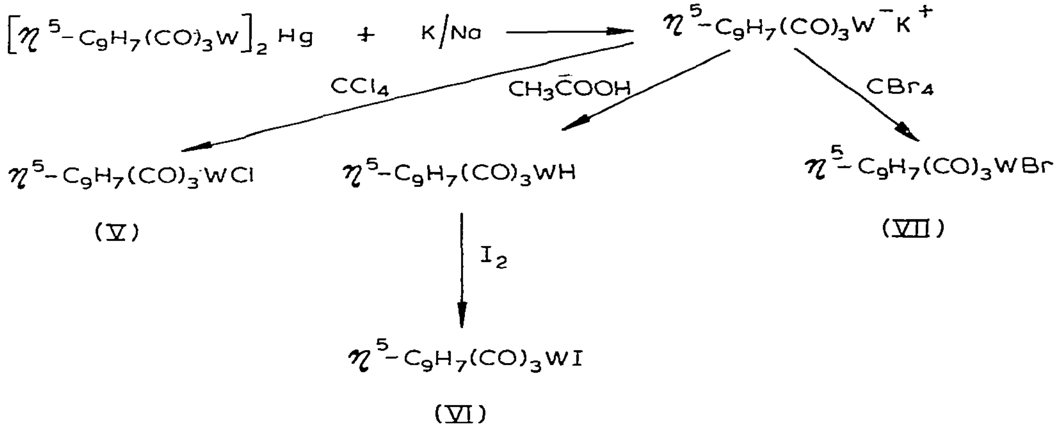
* The angles have been calculated from the atomic coordinates reported in [16].

SCHEME 1



Compounds V—VII should react with aluminium chloride in the presence of excess indene to give the cationic complex $[\eta^5\text{-}C_9H_7(CO)_3W(\eta^2\text{-}C_9H_8)][AlCl_3X]$ (VIII) by analogy to what occurs in similar reactions of compounds of the η^5-cyclopentadienyl series [20]. In VIII, the indene ligand is bonded to the metal through the double bond. Without isolating VIII, we added excess potassium t-butoxide to the reaction mixture to obtain I in yields of 4—7%. The latter procedure has little advantages over the direct synthesis from indene and

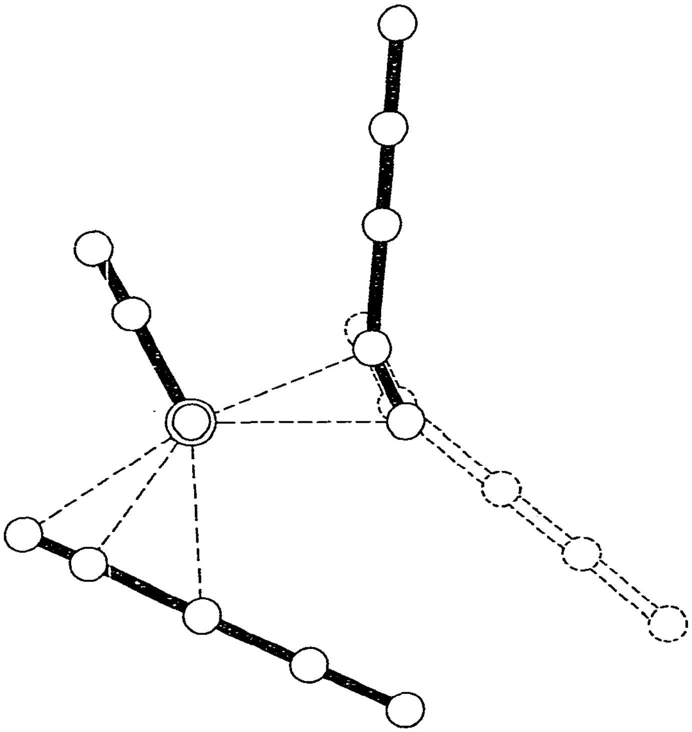


Fig. 2. Mutual arrangement of indenyl ligands in complex I.

$W(CO)_6$ after all. Studies in this direction are under way in this laboratory.

The proton NMR spectrum of I in benzene-d_6 contains signals at δ 6.6, 4.78 and about 3.4 ppm with intensity ratio of 4 : 2 : 1. The first signal may therefore be assigned to the benzene rings protons, the second one to the protons at the C(13), C(15) and C(6), C(4) carbon atoms, and the third one to the protons at C(5) and C(14). The spectrum may only be explained on the assumption that the exchange of nonequivalent indenyl ligands is fast on the NMR time scale. Unfortunately, the low solubility of the complex in organic solvents even at room temperature hinders low-temperature NMR studies. To increase the product solubility, we are now working on the synthesis of its analogues containing alkyl substituents in the indenyl ligand.

In view of the results obtained, it would be interesting to discuss the data reported by Brintzinger et al. who have synthesized $(C_5H_5)_2W(CO)_2$ (IX) and studied it in solution [6,7]. The IR frequencies reported for $\nu(C\equiv O)$ in IX coincide with those observed in I; the proton NMR spectrum of IX contains a singlet from protons of both C_5H_5 rings and does not change in the temperature range +20 to −100°C. The special characteristics of IX are thus analogous to those of I. An X-ray diffraction study is needed to solve the problem of the molecular structure of IX unambiguously.

Important additional information about the structure of compounds of this type may be determined from their ^{13}C NMR spectra. In particular, the data that allowed Köhler [21] to prove the η^3-type of bonding between the metal and the indenyl ligands in bis(indenyl)nickel were those obtained from ^{13}C NMR studies *.

The higher probability for η^3-bonding of indenyl ligands compared with cyclopentadienyl ones and the possibility of fast processes with change of the type of bonding (interconversions $\eta^3 \rightleftharpoons \eta^5$) are compatible with the suggestion that the formation of η^3-indenyl intermediates in certain reactions may be one of the reasons explaining differences in reactivities of indenyl and cyclopentadienyl compounds. Thus, Mawby and Hart-Davis [24] attributed the difference in the rates of the reactions of η^5-$C_9H_7(CO)_3MoCH_3$ and η^5-$C_5H_5(CO)_3MoCH_3$ with phosphines and phosphites to easy conversion of the η^5-C_9H_7 ring to the η^3-one with the formation of a free coordination site on the metal which facilitates further interaction with nucleophiles. For that reason studies of new η^3-indenyl transition metal derivatives are of general importance.

Experimental

The procedures described were carried out under argon. Tetrahydrofuran and diglyme were distilled in inert atmosphere prior to use after prolonged refluxing

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* The criteria for the determination of the type of bonding of C_5H_5 ligands in metal complexes from NMR data are discussed by Sergeev in the review [22]. The use of these data in combination with IR data provides a diagnostic tool for distinguishing between complex structures. Application of this approach to the compound of composition $C_{22}H_{20}O_2Mo$ reported by Brunner and Lucas and claimed by these authors to have the structure $(\eta^5$-$C_5H_5)(CO)_2Mo(\eta^1$-$C_5H_5)_3$ seems to indicate that this complex contains a polycyclic system incorporating three cyclopentadiene units η^3-bonded to the metal at one of the rings. At any rate, the ^1H NMR and IR ($\nu(C\equiv O)$) data agree with that structure.

over Na/K and Na, respectively. The II activity grade alumina was used. The IR spectra were obtained on UR-20 and the proton NMR spectra on Varian Xl-100-15 instruments.

Compound I forms monoclinic crystals, $a = 21.938(6)$, $b = 6.724(2)$, $c = 11.000(3)$ Å, $\beta = 109.12(2)°$, $V = 1533.1(7)$ Å^3, M = 474.2, $d_{exp} = 2.03$, $d_{calc} = 2.05$ g/cm^3 for $Z = 4$, space group $P2_1/a$. Unit cell parameters and reflection intensities (2319 reflections with $I \geqslant 2\sigma$) were measured with a Syntex $P2_1$ four-circle diffractometer (Mo-K_α radiation, graphite monochromator, $\theta/2\theta$ scan, $2\sigma \leqslant 52°$). Absorption corrections were neglected. The structure was solved by the heavy atom technique and refined by the least squares procedure in a full-matrix anisotropic approximation to a final R value of 0.067. The computations were performed on a mini-computer Eclipse S/200 using the EXTL programs. The atomic coordinates and their temperature factors are listed in Table 2.

Reaction of indene with W(CO)$_6$

A mixture of tungsten hexacarbonyl (10 g) and freshly distilled indene (20 ml) was heated in 40 ml diglyme at 175°C for 11 h. After cooling to room temperature, the solution was decanted from $W(CO)_6$ precipitate and all volatiles (diglyme, indene, and dissolved $W(CO)_6$) were removed under vacuum. The residue was extracted with chloroform, evaporated to a minimal volume and chromatographed on an Al_2O_3 column (3 X 20 cm). The first dark red band was eluted with benzene/petroleum ether (1 : 1). The solvents were then distilled off and the product was recrystallized from CH_2Cl_2/heptane to give $[\eta^5\text{-}C_9H_7(CO)_3W]_2$ (0.3 g, 1.5%), m.p. 204—5°C (dec.). Analysis found: C, 37.62, 37.66; H, 1.94, 2.02; W, 47.29, 47.29. $C_{24}H_{14}O_6W_2$ calcd.: C, 37.63; H, 1.84; W, 47.99%.

The remaining orange-yellow band was eluted with benzene containing 5% methanol. After the removal of the solvents under vacuum and recrystallization of the residue from CH_2Cl_2/heptane, the product was orange crystals of $(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_9H_7)W(CO)_2$ (0.15 g), m.p. 170°C (dec. above 155°C). Analysis found: C, 51.30; 51.07; H, 3.22, 3.07; W, 38.44, 38.66. $C_{20}H_{14}O_2W$ calcd.: C, 51.09; H, 3.00; W, 39.10%.

Synthesis of $\eta^5\text{-}C_9H_7(CO)_3W^-K^+$

Solutions of $\eta^5\text{-}C_9H_7(CO)_3W^-K^+$ were made from $[\eta^5\text{-}C_9H_7(CO)_3W]_2Hg$ (0.5 g) and Na/K alloy (0.15—0.25 ml) in 30 ml of THF by stirring the reaction mixture at 25°C for 30 min as described earlier [14]. The extent of reduction was determined from IR spectra. The solutions were filtered through a G3 filter before use.

Synthesis of $\eta^5\text{-}C_9H_7(CO)_3WCl$

CCl_4 (5 ml) was added to a solution of $\eta^5\text{-}C_9H_7(CO)_3W^-K^+$ at 0°C, and the mixture was stirred and allowed to warm up to 25°C. After that, the reaction was complete. After the removal of the solvent under vacuum, the residue was extracted with CH_2Cl_2, the extract was filtered, and diluted to twice its initial volume with heptane. Methylene chloride was then removed under vacuum. Compound V was obtained in the form of red crystals (0.2 g, 46%). $\nu(C\equiv O)$ (THF): 1945, 1967, 2050 cm^{-1}. Proton NMR ($CDCl_3$): A_2X spectrum, $\delta_A =$

TABLE 2

ATOMIC COORDINATES (X 10^5 FOR W AND X 10^4 FOR THE OTHER ATOMS) AND THEIR ANISOTROPIC TEMPERATURE FACTORS (X 10^2 FOR W AND X 10 FOR THE OTHER ATOMS) IN THE FORM $T = \exp[-1/4 \times 10^{-2}(B_{11}h^2a^{*2} + \ldots 2B_{23}klb^*c^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	15337(4)	27703(12)	26683(8)	106(4)	258(4)	175(3)	2(4)	−13(2)	−13(4)
O(1)	1416(9)	−1449(26)	3715(16)	45(10)	36(8)	37(8)	−7(7)	4(7)	4(7)
O(2)	1412(8)	3942(26)	5287(16)	35(7)	49(9)	27(8)	2(7)	3(7)	−7(7)
C(1)	1452(11)	177(32)	3345(22)	18(11)	22(10)	32(11)	2(8)	2(8)	−1(8)
C(2)	1449(12)	3547(34)	4300(21)	31(12)	36(10)	20(10)	19(9)	10(9)	4(8)
C(3)	2058(11)	4990(36)	1666(22)	10(10)	46(12)	28(11)	3(9)	0(8)	−6(9)
C(4)	2395(12)	4927(39)	3042(21)	19(11)	61(14)	16(9)	−10(10)	5(8)	1(9)
C(5)	2616(11)	3050(32)	3319(30)	18(9)	14(8)	13(18)	−8(8)	0(10)	3(11)
C(6)	2464(11)	1952(36)	2242(21)	12(9)	44(12)	29(10)	13(9)	5(8)	4(9)
C(7)	2123(11)	3107(35)	1194(24)	15(10)	36(12)	39(12)	−14(9)	7(9)	−13(9)
C(8)	1814(12)	2707(54)	−237(21)	20(10)	110(22)	17(9)	−14(15)	9(8)	−5(13)
C(9)	1527(12)	4348(40)	−977(22)	25(12)	48(13)	22(10)	−10(10)	7(9)	3(9)
C(10)	1470(12)	6167(43)	−507(25)	19(12)	57(15)	38(13)	0(11)	8(10)	21(11)
C(11)	1734(12)	6657(40)	805(26)	19(11)	52(14)	48(14)	0(10)	12(10)	12(11)
C(12)	31(10)	1268(34)	2184(19)	11(10)	35(10)	22(9)	4(8)	7(8)	7(8)
C(13)	518(11)	1315(36)	1267(20)	15(11)	45(11)	12(8)	−11(9)	−4(7)	−4(5)
C(14)	614(11)	3519(38)	1069(23)	9(10)	47(12)	32(11)	14(9)	−19(8)	12(9)
C(15)	529(13)	4624(52)	2260(27)	18(13)	105(21)	37(14)	9(13)	2(10)	2(14)
C(16)	124(10)	3037(20)	2729(14)	85(12)	10(6)	21(6)	−7(7)	16(8)	−2(5)
C(17)	−240(13)	3553(40)	3545(24)	25(12)	54(14)	28(11)	−9(11)	−1(9)	5(10)
C(18)	−603(13)	1913(58)	3849(23)	22(12)	125(26)	22(10)	28(15)	1(9)	23(14)
C(19)	−610(12)	120(36)	3250(26)	18(11)	32(11)	44(13)	−8(9)	0(10)	−2(10)
C(20)	−254(12)	−269(39)	2432(23)	20(11)	52(13)	30(11)	−27(10)	−3(9)	−2(10)

5.94, $\delta_X = 5.64$ ppm, $J(AX) = 2.8$ Hz (five-membered ring); $AA'BB'$ spectrum at 7.3—7.5 ppm (six-membered ring). Analysis found: C, 34.62; H, 2.04; Cl, 8.37; W, 43.58. $C_{12}H_7ClO_3W$ calcd.: C, 34.43; H, 1.68; Cl, 8.47; W, 43.94%.

Synthesis of η^5-$C_9H_7(CO)_3WBr$ (VII)

CBr_4 (0.34 g) was added to a stirred solution of η^5-$C_9H_7(CO)_3W^-K^+$ at 0°C. After treatment as for VI, VII was obtained as dark red crystals (0.21 g, 44%). $\nu(C{\equiv}O)$ (THF): 1945, 1965, 2047 cm^{-1}. Proton NMR ($CDCl_3$): A_2X spectrum, $\delta_A = 5.97$, $\delta_X = 5.61$ ppm, $J(AX) = 2.8$ Hz (five-membered ring); $AA'BB'$ spectrum in the region 7.3—7.5 ppm (six-membered ring).

Synthesis of η^5-$C_9H_7(CO)_3WI$ (VI)

Acetic acid (0.06 g) was added to a solution of η^5-$C_9H_7(CO)_3W^-K^+$. After stirring at 25°C for 10 min, the mixture showed the IR spectrum containing bands of η^5-$C_9H_7(CO)_3WH$ [14]. Iodine (0.18 g) was added to the solution cooled to 0°C, the mixture was stirred for 0.5 h, the solvent was distilled off under vacuum, and the residue was dissolved in benzene. The extract was filtered through alumina (2 × 5 cm). After the removal of benzene under vacuum and recrystallization from CH_2Cl_2 with heptane, VI was obtained in the form of dark red crystals (0.28 g, 53%). $\nu(C{\equiv}O)$ (THF): 1943, 1963, 2042 cm^{-1}. Proton NMR ($CDCl_3$): A_2X spectrum, $\delta_A = 5.99$, $\delta_X = 5.55$ ppm, $J(AX) = 2.8$ Hz (five-membered ring); $AA'BB'$ spectrum in the region 7.3—7.5 ppm (six-membered ring). Analysis found: C, 28.16; 28,37; H, 1.26, 1.22; I, 24.39; 24.60; W, 35.93; 35.74. $C_{12}H_7IO_3W$ calcd.: C, 28.25; H, 1.37; I, 24.90; W, 36.07%.

Synthesis of I from η^5-$C_9H_7(CO)_3WX$

A solution of η^5-$C_9H_7(CO)_3WCl$ (0.16 g, 0.38 mmol) in 10 ml benzene in the presence of $AlCl_3$ (0.061 g, 0.46 mmol) and indene (0.058 g, 0.5 mmol) was heated at 80°C with stirring for 1 h. After that, the mixture showed no IR bands of initial V. The solution was then cooled to 25°C and treated with potassium t-butoxide (0.12 g). The mixture was stirred for 20 min and decomposed with water. The benzene layer was isolated and dried over $CaCl_2$. After filtration and removal of benzene, the residue was chromatographed on silica gel plate (L 40/100 μ, Chemapol, ČSSR) using petroleum ether/benzene (1 : 1) as eluent. A yellow-orange band (I) was extracted with methylene chloride to give I (0.013 g, 7%).

Using a similar procedure I was obtained from VI and VII in yields of 4 and 6%, respectively.

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