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THE CRYSTAL AND MOLECULAR STRUCTURE OF OXO-π-CYCLOPENTADIENYL-π-DIPHENYLACETYLENE-σ-PHENYLTUNGSTEN

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SUMMARY

X-Ray studies indicate that the photochemical reaction of $C_5H_5W(CO)_3C_6H_5$ with tolane results in the formation of oxo-π-cyclopentadienyl-π-diphenylacetylene-σ-phenyltungsten. The observed shortening of W–C(acetylene), W–C(σ-phenyl) and W–O bond lengths seems to be caused by an increased back donation due to the electron deficiency of the complex investigated.

INTRODUCTION

In the course of an investigation of the photochemical reaction of $C_5H_5W(CO)_3C_6H_5$ with tolane a complex has been isolated whose composition corresponds to $C_{25}H_{20}WO$ (Found: C, 57.36; H, 3.96; W, 35.37%. Calcd.: C, 57.70; H, 3.87; W, 35.34%). The complex melts with decomposition at 142°. The Raman spectrum exhibits an intense peak at 1748 cm^{-1} which is attributed to the coordinated tolane molecule. No terminal or bridging carbonyl groups are present as shown by the infrared spectrum where an intense maximum at 945 cm^{-1} was assigned to the terminal W=O bond. The ^1H NMR spectrum in $CDCl_3$ exhibits a singlet with $\delta(C_5H_5)$ 6.13 ppm and a multiplet with $\delta(C_6H_5)$ 6.92–7.89 ppm. The present X-ray study has been carried out in an attempt to provide an unequivocal determination of the molecular structure and geometry. Details of the chemical investigations will be published elsewhere.

EXPERIMENTAL

The unit cell dimensions were determined by a least-squares procedure using 12 reflections measured by means of a Hilger and Watts 4-circle autodiffractometer with Mo-K_α radiation (graphite monochromator). Reflection scanning was performed with the Peak Finder programme[1] and parameters were calculated using the programme[2] by Dobler. The crystal density was measured by a flotation method. The crystals of the complex are monoclinic with the $P2_1/c$ space group: a 13.823(6) Å, b 9.425(4) Å, c 19.595(9) Å, β 128.54(2)°, V 1996.9 Å^3, Z 4, $\rho_{calc.}$ 1.74 g/cm^3, $\rho_{obsd.}$ 1.73 g/cm^3 and $\mu R(\lambda \text{Mo-}K_\alpha) \leqslant 2.46$.

Reflection intensities with $2\theta \leq 40°$ were measured using a crystal ca. 0.1·0.4·0.2 mm in size with maximum elongation along the *b* axis, and using an ω-scan (the crystal had a small mosaic scattering) and an Ordinate Analysis routine due to Watson[3]. In all 2200 independent reflection intensities were collected. Intensities were corrected for absorption by measuring the transmission curve on the 060 reflection (χ-value close to 90°) with the crystal rotated around the φ-axis. Structure factors were calculated on a PDP-8/*I* computer using the Transmission Curve-Diffop programme of Wendell[4]. Structure factors smaller than three standard deviations were rejected from the subsequent calculations.

STRUCTURE DETERMINATION

The tungsten atom coordinates were obtained from a three-dimensional Patterson map. The first Fourier difference series with subtraction of the tungsten atom gave the positions of six carbon atoms and the rest of a molecule was localized in the second Fourier synthesis. The subsequent least-squares refinement in isotropic approximation was performed using Cruickshank's weighting scheme[5]. Obvious

TABLE 1

ATOMIC POSITIONS AND THERMAL PARAMETERS[a]

Atom	*x/a*	*y/b*	*z/c*	B_j, A^2
W	0.05512(9)	0.1726(1)	0.14055(7)	3.05(2)
C(1)	0.263(2)	0.183(2)	0.226(2)	2.4(4)
C(2)	0.325(2)	0.292(3)	0.281(2)	3.1(4)
C(3)	0.454(2)	0.297(3)	0.331(2)	3.5(5)
C(4)	0.517(2)	0.196(3)	0.318(2)	4.7(5)
C(5)	0.443(2)	0.093(3)	0.254(2)	4.3(5)
C(6)	0.322(2)	0.079(3)	0.208(2)	3.3(5)
C(7)	−0.020(2)	0.184(3)	0.205(2)	2.6(5)
C(8)	0.098(2)	0.176(3)	0.266(2)	3.2(5)
C(9)	0.192(2)	0.156(3)	0.357(2)	2.8(5)
C(10)	0.271(2)	0.046(3)	0.392(2)	3.5(5)
C(11)	0.358(2)	0.038(3)	0.484(2)	3.7(5)
C(12)	0.360(2)	0.129(3)	0.538(2)	3.8(5)
C(13)	0.274(2)	0.239(3)	0.503(2)	3.2(5)
C(14)	0.187(2)	0.256(3)	0.409(2)	3.8(5)
C(15)	−0.138(2)	0.182(3)	0.189(2)	3.6(5)
C(16)	−0.249(2)	0.140(3)	0.108(2)	3.5(5)
C(17)	−0.361(2)	0.141(3)	0.097(2)	3.3(5)
C(18)	−0.364(2)	0.178(3)	0.161(2)	3.4(5)
C(19)	−0.263(2)	0.223(3)	0.239(2)	3.9(5)
C(20)	−0.144(2)	0.224(3)	0.254(2)	3.5(5)
C(21)	−0.001(2)	0.410(3)	0.098(2)	4.2(5)
C(22)	0.081(2)	0.377(3)	0.079(2)	4.1(5)
C(23)	0.018(2)	0.269(3)	0.013(2)	4.1(5)
C(24)	−0.094(2)	0.253(2)	−0.005(2)	3.5(5)
C(25)	−0.106(2)	0.435(2)	0.046(2)	3.5(5)
O	0.023(1)	0.001(2)	0.108(1)	4.0(4)

[a] Standard deviations are given in brackets.

geometrical restrictions according to Waser[6] were used but only in the initial stages of the refinement. The final R value was 0.111 for 1607 non-zero reflections. Positional and thermal atomic parameters and their standard deviations are listed in Table 1.

MOLECULAR GEOMETRY

The present investigation shows unambiguously that the compound studied is oxo-π-cyclopentadienyl-π-diphenylacetylene-σ-phenyltungsten (Fig. 1). The values of the measured bond lengths and angles are listed in Table 2; equations of the ring planes are given in Table 3.

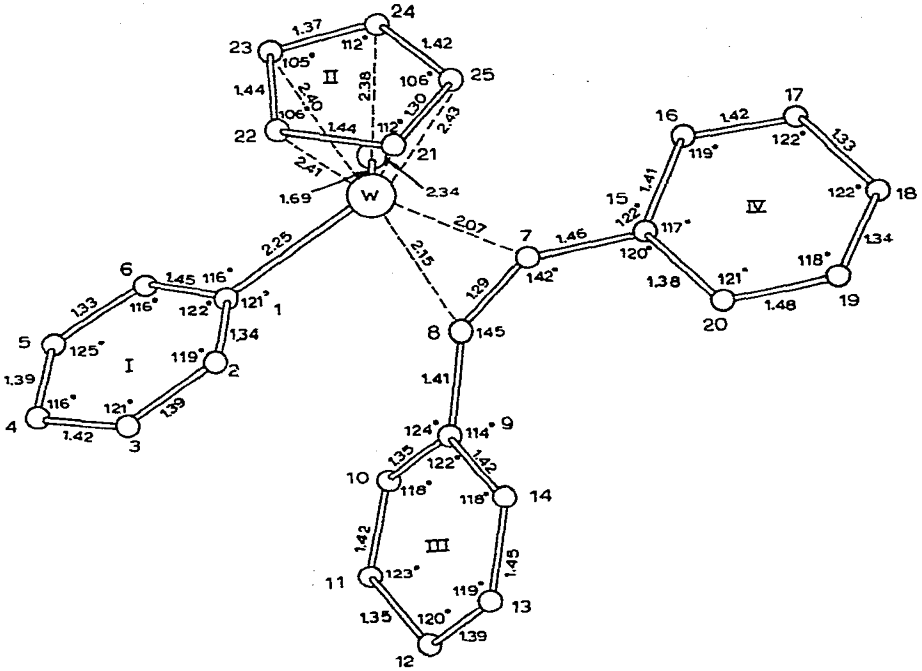

Fig. 1. A general view of the molecule, together with the corresponding bond lengths and angles.

The mean C–C bond length in the cyclopentadienyl ring is 1.39 A, the individual values being within 3σ limits of this average value. The mean W–C(C_5H_5) distance of 2.39 Å is slightly larger than that of 2.34 Å found in (π-C_5H_5)W$(CO)_3$-(σ-C_6H_5)[7] and 2.36 Å found in (π-C_5H_5)W$(CO)_3$AuP$(C_6H_5)_3$[8].

The σ-phenyl ring is planar within the accuracy of the measurements and its average C–C bond length has the normal value of 1.39 Å. The W–C(1) distance of 2.25 Å is considerably shorter than the value of 2.32 Å found in (π-C_5H_5)W$(CO)_3$-C_6H_5[7] which is equal to the sum of the tungsten and carbon covalent radii (1.59 + 0.74 = 2.33 Å)[9]. In complexes of molybdenum whose metal covalent radius 1.58 Å[9] is very close to that of tungsten; the length of the σ bond to the alkyl ligands is 2.38 Å in (π-C_5H_5)Mo$(CO)_3C_2H_5$[10] and $[C_{10}H_8Mo(CO)_3CH_3]_2$[11], and 2.36 Å in (π-$C_5H_5$)-Mo$(CO)_3(CH_2COOH)$[12]. A shortening of the σ bond has been found in the acetyl

TABLE 2

BOND LENGTHS d AND ANGLES ω

Bond	d(Å)	*Angle*	ω(°)
W–C(1)	2.25(3)	W–C(1)–C(2)	121(2)
W–C(7)	2.07(4)	W–C(1)–C(6)	116(1)
W–C(8)	2.15(4)	O–W–C(1)	103(2)
W–C(21)	2.34(2)	C(1)–C(2)–C(3)	119(3)
W–C(22)	2.41(3)	C(2)–C(3)–C(4)	121(2)
W–C(23)	2.40(3)	C(3)–C(4)–C(5)	116(2)
W–C(24)	2.38(2)	C(4)–C(5)–C(6)	125(3)
W–C(25)	2.43(5)	C(5)–C(6)–C(1)	116(2)
W–O	1.69(2)	C(6)–C(1)–C(2)	122(3)
C(1)–C(2)	1.34(3)	C(7)–C(8)–C(9)	145(4)
C(2)–C(3)	1.39(4)	C(8)–C(9)–C(10)	124(3)
C(3)–C(4)	1.42(5)	C(8)–C(9)–C(14)	114(2)
C(4)–C(5)	1.39(3)	C(9)–C(10)–C(11)	118(3)
C(5)–C(6)	1.33(4)	C(10)–C(11)–C(12)	123(2)
C(6)–C(1)	1.45(5)	C(11)–C(12)–C(13)	120(2)
C(7)–C(8)	1.29(3)	C(12)–C(13)–C(14)	119(3)
C(8)–C(9)	1.41(3)	C(13)–C(14)–C(9)	118(2)
C(9)–C(10)	1.35(3)	C(14)–C(9)–C(10)	122(2)
C(10)–C(11)	1.42(3)	C(8)–C(7)–C(15)	142(4)
C(11)–C(12)	1.35(5)	C(7)–C(15)–C(16)	122(3)
C(12)–C(13)	1.39(4)	C(7)–C(15)–C(20)	120(2)
C(13)–C(14)	1.45(3)	C(15)–C(16)–C(17)	119(3)
C(14)–C(9)	1.42(5)	C(16)–C(17)–C(18)	122(2)
C(7)–C(15)	1.46(5)	C(17)–C(18)–C(19)	122(3)
C(15)–C(16)	1.41(3)	C(18)–C(19)–C(20)	118(3)
C(16)–C(17)	1.42(5)	C(19)–C(20)–C(15)	121(2)
C(17)–C(18)	1.33(5)	C(20)–C(15)–C(16)	117(3)
C(18)–C(19)	1.34(3)	C(21)–C(22)–C(23)	106(2)
C(19)–C(20)	1.48(5)	C(22)–C(23)–C(24)	105(3)
C(20)–C(15)	1.38(5)	C(23)–C(24)–C(35)	112(2)
C(21)–C(22)	1.44(5)	C(24)–C(25)–C(21)	106(3)
C(22)–C(23)	1.44(3)	C(25)–C(21)–C(22)	112(3)
C(23)–C(24)	1.37(5)		
C(24)–C(25)	1.42(5)		
C(25)–C(21)	1.30(3)		

complex $(\pi\text{-}C_5H_5)MoPPh_3(CO)_2(\sigma\text{-}COCH_3)$ (2.26 Å[13]) and in complexes with fluorocarbon radicals $(\pi\text{-}C_5H_5)Mo(CO)_3(C_3F_7)$ (2.28 Å[14]) and $(\pi\text{-}C_5H_5)Mo(CO)_3(C_6F_5)$ (2.24 Å[15]), where it was explained as being due to back donation to the antibonding ligand orbitals. The complex studied in this investigation is electron deficient as a C_5H_5 ligand donates five electrons, an oxo-oxygen two, C_6H_5 one and tolane two, *i.e.* 10 electrons in all instead of the 12 required for completion of the noble gas shell of the tungsten atom. It is reasonable therefore to suppose that the observed shortening of the σ W–C bond is due to extra donation from filled p_π orbitals of the aryl ligand to the empty metal orbitals[16]. A similar shortening to 2.014 Å relative to the sum of the covalent radii (2.22 Å) has been found in the electron-deficient complex $(p\text{-}CH_3C_6H_4)CrCl_2(OC_4H_8)_3$[17].

TABLE 3

COEFFICIENTS IN EQUATIONS OF THE TYPE $Ax+By+Cz+D=0$ FOR AROMATIC RINGS PLANES AND DEVIATIONS OF ATOMS FROM THESE PLANES

Plane	*Atoms and their deviations from planes (Å)*	*A*	*B*	*C*	*D*
I	C(1) C(2) C(3) C(4) C(5) C(6) −0.03 0.04 −0.01 −0.02 0.02 0.00	15.73	−5.45	−5.47	−1.09
II	C(21) C(22) C(23) C(24) C(25) 0.03 −0.03 0.02 0.00 −0.02	−11.34	0.85	6.78	−1.70
III	C(9) C(10) C(11) C(12) C(13) C(14) 0.02 −0.03 0.01 0.01 −0.01 −0.00	9.68	−11.28	−5.44	−0.46
IV	C(15) C(16) C(17) C(18) C(19) C(20) 0.01 0.00 −0.01 0.02 −0.01 −0.01	−5.56	0,57	8.89	−0.50

The geometry of the coordinated tolane molecule is normal for acetylene complexes[18]: the C≡C bond length is increased to 1.29 Å relative to the value of 1.205 Å for that in acetylene itself and the bond angles at the acetylenic carbon atoms are decreased to 143.5° so that the tolane molecule acquires a *cis*-stilbene configuration. The torsional angle around a C≡C bond is very small (2°) however, the phenyl rings (which are planar) are rotated by 57° (C(9)–C(14) ring) and 27° (C(15)–C(20) ring) respectively relative to the C(7), C(8), C(9), C(15) plane. The W–C distances to the acetylenic carbons (average 2.11 Å) are considerably shorter than those to the cyclopentadienyl carbons (average 2.39 Å). In the niobium complex $(\pi\text{-}C_5H_5)Nb(CO)(Ph_2C_2)(\pi\text{-}Ph_4C_4)$ which also possesses tolane and cyclopentadienyl ligands, the corresponding distances are 2.22 Å and 2.42 Å[19] respectively. Thus the difference between the W–C(tolane) and W–C(C_5H_5) distances is equal to 0.28 Å, *i.e.* it is greater than the corresponding value of 0.20 Å in the electron-complete niobium complex. This may be explained in terms of a second filled acetylene p_π orbital being involved in bonding with a metal atom as was initially suggested by King[20]. In comparison, it should be noted that the Nb–C(tolane) and Nb–C(C_5H_5) distances in the electron-deficient complex $(\pi\text{-}C_5H_5)Nb(CO)(Ph_2C_2)_2$ are 2.19 and 2.44 Å respectively, *i.e.* a difference equal to 0.25 Å, and it was supposed[21] that in this complex both tolane molecules are three-electron donors.

Only one acetylenic complex of tungsten $(Ph_2C_2)_3WCO$[22] has been studied previously, its bond distances and angles having been found to be very similar to those discussed in this paper: W–C(tolane), 2.06 Å; acetylenic C≡C 1.30 Å; C(acetylenic)–C(phenyl) 1.46 Å; the average angle of the acetylenic carbons being 139.6°.

The W–O bond length of 1.69 Å is considerably shorter than that of 1.89 Å in $WOCl_4(CH_3)_2As(C_6H_4)As(CH_3)_2$[23] but virtually the same as that of 1.68 Å in $[(C_5H_5)MoO]_2S_2$[24] where this bond was ascribed an order of 2.4–2.5. Thus in the present complex the W–O bond as well as the bonds with tolane and phenyl ligands exhibit an increased bond order.

The tungsten atom is six coordinated. The projection of the molecule on to the cyclopentadienyl ring plane together with the shortest interligand distances is shown in Fig. 2. Relative to the sums of the corresponding van der Waals radii, these distances are shorter by 0.6–0.7 Å indicating considerable steric overcrowding.

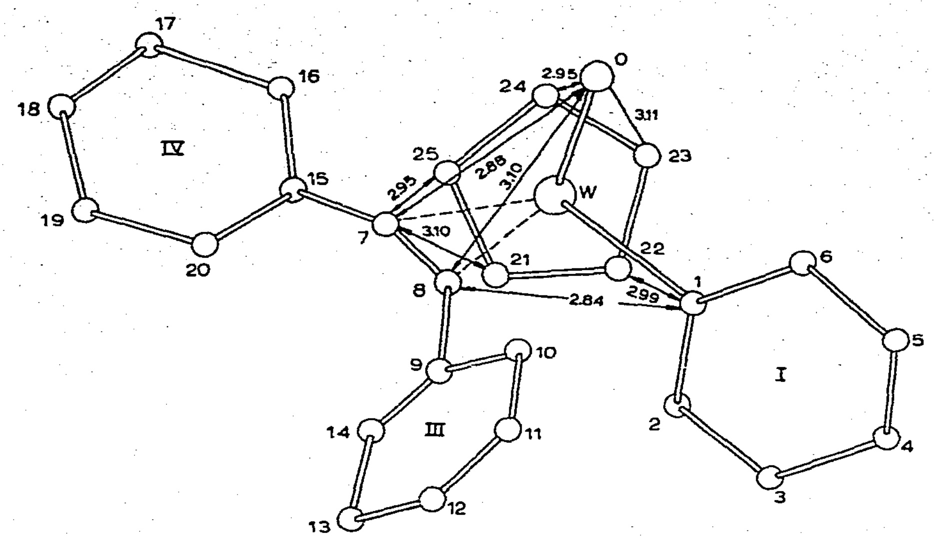

Fig. 2. A projection of the molecule on to the C_5H_5-ligand plane together with the shortest non-bonded distances.

TABLE 4

INTERMOLECULAR DISTANCES d (Å)

I corresponds to the reference molecule at x, y, z, II at $\bar{x}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$, III at $1-x, \bar{y}, 1-z$, IV at $\bar{x}, 1-y, \bar{z}$ and V at $x, \frac{1}{2}-y, z+\frac{1}{2}$.

Atoms		*d*	*Atoms*		*d*
C(2)...C(18)	II	3.75	C(24)...O	IV	3.63
C(4)...C(12)	III	3.78	C(19)...C(6)	II	3.74
C(10)...C(15)	II	3.74	C(20)...C(10)	II	3.76
C(10)...C(25)	II	3.69	C(20)...C(21)	II	3.73
C(11)...C(11)	III	3.65	C(20)...O	II	3.36
C(11)...C(25)	II	3.62	C(21)...C(22)	IV	3.54
C(12)...C(18)	II	3.49	C(21)...C(23)	IV	3.65
C(13)...C(23)	V	3.65	C(22)...C(22)	IV	3.36
C(14)...C(16)	II	3.78	C(22)...C(23)	IV	3.63
C(14)...O	II	3.57	C(22)...C(25)	IV	3.76

The crystal is built up of discrete molecules, the shortest intermolecular contacts being listed in Table 4 and are close to the sums of the corresponding van der Waals radii.

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