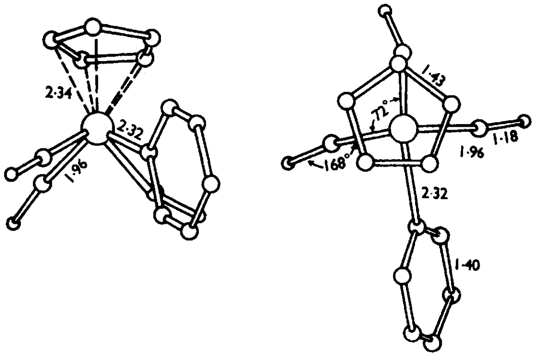
The Crystal Structure of π-Cyclopentadienyltricarbonyl-σ-phenyltungsten

By V. A. SEMION,* YU. A. CHAPOVSKII, YU. T. STRUCHKOV, and A. N. NESMEYANOV

(*Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Moscow*)

CONTINUING our structural studies of σ-aryl complexes of the transition metals,[1] we have undertaken an *X*-ray study of π-cyclopentadienyltricarbonyl-σ-phenyltungsten, $(\pi\text{-}C_5H_5)W(CO)_3(\sigma\text{-}C_6H_5)$ (I), prepared by reaction of diphenyliodonium fluoroborate with $(\pi\text{-}C_5H_5)W(CO)_3Na$, and characterised by its ^1H n.m.r. spectrum.[2] To our knowledge, (I) is the first reported σ-aryl derivative of a Group VI transition metal.



FIGURE

The yellow, prismatic crystals of (I) are monoclinic; space group $P2_1/n$, $a = 13{\cdot}303$, $b = 12{\cdot}012$, $c = 15{\cdot}809$ Å, $\beta = 89°46'$, $D_m = 2{\cdot}114$, $D_c = 2{\cdot}178$ g. cm.$^{-3}$ for $Z = 8$ (two independent molecules in the unit cell). The intensities of *ca.* 2000 non-zero independent reflections were estimated visually [from multiple-film equi-inclination Weissenberg photographs (layers 0*kl* to 4*kl* and *hk*0 to *hk*5) taken with unfiltered Cu-*K* radiation]. Absorption was neglected.

The structure was determined by Patterson and difference syntheses, and the resulting parameters were refined by isotropic full-matrix least-squares. *R* is $0{\cdot}12_9$, and the overall temperature factor, *B*, $2{\cdot}6_8$ Å^2. The bond distances and angles in the two crystallographically independent molecules coincide within the limits of experimental error, and average values are shown in the Figure.

The environment of the tungsten atom is similar to that of the molybdenum atom in the previously studied π-cyclopentadienyl complexes, $\pi\text{-}C_5H_5Mo(CO)_3Et$ (II),[3] $[\pi\text{-}C_5H_5Mo(CO)_3Mn(CO)_5]$ (III),[4] $\pi\text{-}C_5H_5Mo(CO)_3C_3F_7$ (IV),[5] and $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (V).[6]

It is convenient[6] to consider the molecule of (I) as a tungsten atom situated at the centre of a cube, with one face coincident with the plane of the cyclopentadienyl ring—their centres coinciding, too. Four W–C bonds are directed towards the four corners of the opposite face of the cube.

Within the limits of experimental error, the $W\text{–}C(C_5H_5)$ distances are equal (average $2{\cdot}3_4$ Å) in contrast to "open sandwich" π-complexes of molybdenum,[3,5,6] where the $Mo\text{–}C(C_5H_5)$ distances may vary by up to 0·1 Å. However, this W–C distance is very close to the average of previously determined $Mo\text{–}C(C_5H_5)$ distances: 2·36 (IV), 2·34 (V), and 2·33 Å in $[(C_5H_5)_2Mo_2H(PMe_2)(CO)_4]$.[7] The average W–C(Ph) bond length, *i.e.* the σ-bond length, is 2·32 Å, which is 0·06 Å shorter than the Mo–C(Et) distance in (II).

From the bond lengths we can make two approximate estimates of the covalent radius of tungsten. The $W\text{–}C(C_5H_5)$ length with the radius of cyclopentadienyl carbon taken as 0·77 Å (by analogy with ferrocene) gives 1·57 Å while the W–C(Ph) with the radius of an sp^2 hybridised carbon atom taken[8] as 0·74 Å gives 1·58 Å. These estimates are close to the half-length of a W–W single bond, 1·62 Å in $[(C_5H_5)_2W_2(CO)_6]$,[9] comparable value for molybdenum is 1·61 Å from Mo–C(Et) in (II).[3] The small difference between Mo–C and W–C bond lengths is, of course, a result of the lanthanoid contraction.[10]

The W–CO and C–O bond distances are 1·96 and 1·18 Å, respectively, *i.e.* they are *ca.* 0·1 Å shorter than the corresponding bond lengths determined for $W(CO)_6$ by electron diffraction in the vapour phase,[11] and very close to Mo–C and C–O distances in π-complexes of molybdenum. The W–C–O fragments are not quite linear; angles at the carbon atoms vary from 163° to 172° (mean value 168°). The C–W–C angles vary from 63° to 83°, the mean value (72°) being somewhat larger than the ideal angle (70°32′) between the solid diagonals of the cube.

The cyclopentadienyl and phenyl rings are essentially planar, with mean C–C bond lengths $1{\cdot}4_3$ and $1{\cdot}4_0$ Å, respectively.

(*Received, February* 26*th*, 1968; *Com.* 227.)

---

[1] R. L. Avoyan, Yu. A. Chapovskii, and Yu. T. Struchkov, *Zhur. strukt. Khim.*, 1966, **7**, 900.

[2] A. N. Nesmeyanov, Yu. A. Chapovskii, B. V. Lokshin, A. V. Kisin, and L. G. Makarova, *Doklady Akad. Nauk S.S.S.R.*, 1966, **177**, 637.

[3] M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 1963, 273.

[4] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and A. S. Beschastnov, following Communication.

[5] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1967, **6**, 1213.

[6] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **37**, 809.

[7] R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2576.

[8] O. Bastiansen and H. Tratteberg, *Tetrahedron*, 1962, **17**, 147.

[9] F. C. Wilson and D. P. Shoemaker, *Naturwiss.*, 1956, **43**, 57.

[10] L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N.Y., 3rd edn., 1960.

[11] S. P. Arnesen and H. M. Scip, *Acta Chem. Scand.*, 1966, **20**, 2711.