π-Complexes of the Group V Metals with Diphenylacetylene. Crystal Structure of Carbonylbisdiphenylacetylene-π-cyclopentadienylniobium

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Summary The crystal structure of carbonylbisdiphenylacetylene-π-cyclopentadienylniobium has been determined.

CARBONYLBISDIPHENYLACETYLENE-π-CYCLOPENTADIENYLNIOBIUM (I) is formed[1] by u.v. irradiation of $(\pi\text{-}C_5H_5)Nb(CO)_4$ and diphenylacetylene (tolan) in 1:2 molar proportions in solution in pentane, hexane, benzene, or tetrahydrofuran, and also by the photochemical reaction of $(\pi\text{-}C_5H_5)Nb(CO)_2(Ph_2C_2)$ with tolan. It crystallises as yellow prisms (m.p. 135—136°) and is monomeric in benzene solution according to ebulliscopic and cryoscopic measurements. ^1H N.m.r. spectral data indicate that it is diamagnetic.

It decomposes exothermally at 180°; the pyrolysis products include 1,2,3,4-tetraphenylbutadiene, evidently formed by dimerisation of tolan. When heated under reflux in toluene, (I) is converted into the dimeric complex $[(\pi\text{-}C_5H_5)Nb(CO)(Ph_2C_2)]_2$ (II), which contains an Nb–Nb bond and two bridging tolan groups.[2]

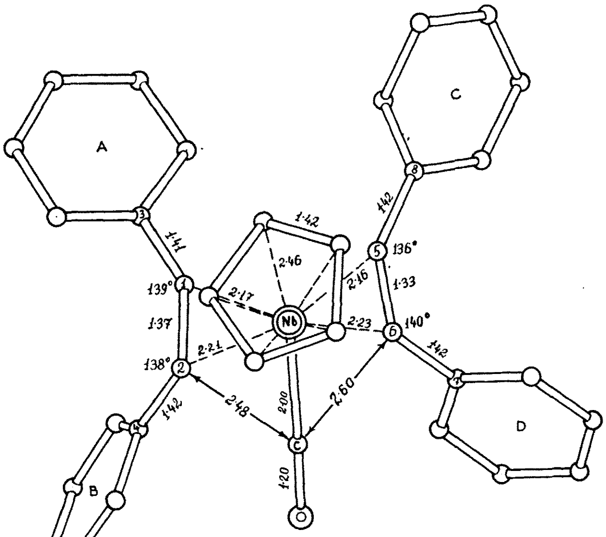
We report the results of an *X*-ray study of (I). The crystals are triclinic, $a = 11{\cdot}72$, $b = 11{\cdot}80$, $c = 10{\cdot}06$ Å, $\alpha = 100{\cdot}5°$, $\beta = 103{\cdot}4°$, $\gamma = 78{\cdot}6°$, $D_m = 1{\cdot}37$, $D_c = 1{\cdot}38$ g. cm.$^{-3}$ for $Z = 1$, space group $P\bar{1}$. The intensities of *ca.* 1600 independent reflections were estimated visually, without regard to absorption correction. An equi-inclination Weissenberg goniometer was used, with unfiltered copper radiation. The structure was solved by the heavy-atom technique, and refined by the full-matrix least-squares method with isotropic temperature factors; $R = 0{\cdot}15$, with standard deviations in bond lengths 0·02—0·03 Å and in bond angles 2—3° depending upon the atomic numbers.

The crystal consists of discrete molecules of (I) with two tolan ligands independently co-ordinated to each niobium atom (Figure). Only two other complexes with two independently co-ordinated alkyne molecules are known: $ReCl(PhC_2H)_2$[3] and $(Ph_4C_4)Mo(CO)(Ph_2C_2)_2$;[4] such complexes are difficult to isolate, since the alkyne molecules readily cyclise to give cyclobutadiene or cyclopentadienone ligands.

In (I) the $Nb\text{–}C(C_5H_5)$ distance is 2·44—2·48 Å—the average (2·46 Å) agreeing well with that (2·45 Å) found[2] for (II). The Nb single-bonded covalent radius[5] is 2·46 − 0·77 = 1·69 Å, reasonably close to that of 1·66 Å found[2] from the Nb–Nb distance in $\alpha\text{-}NbI_4$,[6] the latter probably being contracted as a result of iodine bridging.

The two tolan ligands are equivalent. Their co-ordination is similar to that found[7] in $(PPh_3)_2Pt(Ph_2C_2)$ where the C≡C bond length is 1·32 Å. If one assumes that in (I) only one π-orbital of the triple bond interacts with niobium and each tolane molecule donates two electrons, then (I) is an electron-deficient complex (*i.e.*, the niobium atom acquires a 16-electron shell). It was supposed that the co-ordinated triple-bond length would be less than the standard double-bond length (1·337 Å) just as in π-ethylenic complexes the usual value of a co-ordinated double-bond length (1·40—1·47 Å) is always shorter than the single-bond length (1·541 Å). However, in (I) the average length of the co-ordinated triple bonds is 1·35 ± 0·02 Å. This may be taken to indicate that there is partial overlapping of the second π-orbitals of the triple bonds with the vacant orbital of the niobium atom.

The average distance between niobium and C(1), C(2), C(5), and C(6), 2·19 Å, is shorter by 0·24 Å than the sum of



FIGURE

the single-bonded covalent radii of Nb (1·69 Å) and sp^2-hybridised carbon (0·74 Å). This indicates some double-bond character, and can again be explained by the interaction of a second π-orbital from the triple bond with the niobium atom. It does not rule out a contribution from back-donation to antibonding triple-bond orbitals by filled niobium orbitals.

As a result of steric repulsion by the carbonyl group C(2) and C(6) are further away from Nb than C(1) and C(5).

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