π-Complexes of the Group V Metals with Diphenylacetylene. Crystal Structure of π-Cyclopentadienyl-π-tetraphenylcyclobutadiene-π-diphenylacetyleneniobium Carbonyl

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Summary The molecular structure of a new π-acetylenic niobium complex has been determined, the co-ordinated triple bond length being 1·26 ± 0·04 Å.

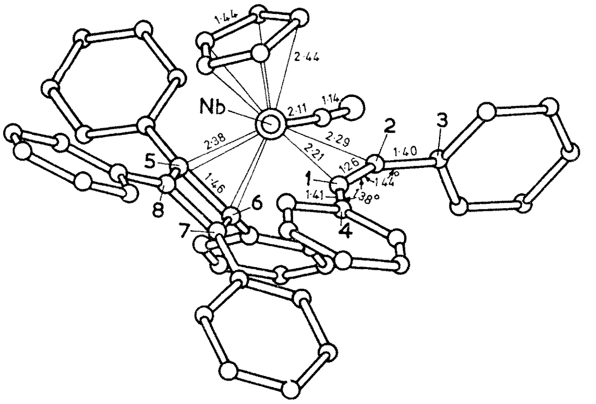
π-CYCLOPENTADIENYL-π-TETRAPHENYLCYCLOBUTADIENE-π-DIPHENYLACETYLENENIOBIUM CARBONYL, $(\pi\text{-}C_5H_5)(\pi\text{-}Ph_4C_4)Nb(\pi\text{-}Ph_2C_2)(CO)$ (I), is formed by boiling a benzene solution of $(\pi\text{-}C_5H_5)Nb(\pi\text{-}Ph_2C_2)_2(CO)$ (II) in the presence of diphenylacetylene.[1] The crystal structure of (II) has been reported previously.[2] The i.r. spectrum of (I) has a strong band due to a terminal carbonyl group at 2000 cm.$^{-1}$ and a weak band at 1780 cm.$^{-1}$ which was attributed to the $\nu(C{\equiv}C)$ of a co-ordinated triple bond. Compound (I) decomposes on heating, giving hexaphenylbenzene. According to thermographic data, this process is exothermal. Consequently, hexaphenylbenzene itself is not present in complex (I), otherwise decomposition of (I) would be endothermal. To elucidate the molecular structure of (I) we undertook its *X*-ray study.

Crystal data: (I) is monoclinic, $a = 11·52$, $b = 13·98$, $c = 24·79$ Å, $\beta = 115·5°$, $D_m = 1·32$, $D_c = 1·33$ g. cm.$^{-3}$ for $Z = 4$, space group $P2_1/c$. Intensities of *ca.* 1700 independent reflections were estimated visually, disregarding absorption correction (an equi-inclination Weissenberg goniometer, 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. At the present stage of refinement, $R = 0·14$, with standard deviations in bond lengths of 0·02—0·04 Å and in bond angles of 2—4° depending on the atomic numbers.

The molecule (Figure) contains π-cyclopentadienyl and π-tetraphenylcyclobutadiene ligand, a carbonyl group, and a tolane molecule which is co-ordinated to the niobium atom by its "triple" bond C(1)–C(2). The average distance between the Nb atom and the carbon atoms of the planar cyclopentadienyl ring (2·44 Å) agrees well with those found in other semi-sandwich π-cyclopentadienyl niobium complexes: 2·45 Å in $[(\pi\text{-}C_5H_5)Nb(CO)(\mu\text{-}Ph_2C_2)]_2$,[3] 2·46 Å in (II).[2] If one takes the average value for these three structures, the Nb single-bonded covalent radius is 2·45 − 0·77 = 1·68 Å.[4]

The cyclobutadiene ring is planar to within 0·02 Å and makes an angle of 48° with the cyclopentadienyl ring. The average Nb–C (cyclobutadiene) distance, 2·38 Å, is distinctly shorter than the Nb–C (cyclopentadienyl) distance. This shortening probably results from a greater π-acceptor ability of the π-tetraphenylcyclobutadiene ring which is due to the presence of phenyl substituents, or it is a specific feature of this ligand. The average Fe–C (cyclobutadiene) distance (2·07 Å) in $(\pi\text{-Ph}_4\text{C}_4)\text{Fe(CO)}_3$[5] is shorter than the Fe–C(cyclopentadienyl) distance in semi-sandwich complexes, *e.g.* 2·12 Å in $[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$.[6]

The geometry of the co-ordinated tolane molecule is somewhat different from that found in (II). The co-ordinated triple C–C bond (1·26 ± 0·04 Å) is shorter, the average "acetylenic" carbon bond angle (141°) and the average Nb–C (acetylenic) distance (2·25 Å) are greater than the corresponding values in the molecule (II) (1·35 ± 0·02 Å, 138°, 2·19 Å). Such regular differences show that the Nb–triple bond interaction in (I) is weaker than in (II). This weakening may be due to the fact that, according to the 18-electron rule, the tolane molecule in (I) is a two-electron donor, but in (II) it is formally a three-electron donor.[7]



FIGURE

The Nb–C(1) and Nb–C(2) distances are much shorter than the sum 2·42 Å of Nb and C(sp^2) covalent radii. The C(1)–C(2)–C(3) and C(2)–C(1)–C(4) bond angles deviate considerably from 180°. These two points testify to a strong back-donation into antibonding π^*-orbitals of a triple bond,[8] in accordance with a significant lowering of the $\nu(\text{C}{\equiv}\text{C})$ frequency to 1780 cm.$^{-1}$ compared with 2190—2260 cm.$^{-1}$ in free acetylene.[9]

The co-ordinated triple bond is roughly parallel to the C(6)–C(7) bond of the cyclobutadiene ligand [C(1) · · · C(7) 2·99, C(2) · · · C(6) 3·42 Å]. Thus formation of hexaphenylbenzene by thermal decomposition of (I) is probably effected through an intra-complex addition of the tolane molecule to the C(6)–C(7) bond of cyclobutadiene, resulting in "hexaphenyl-Dewar-benzene" as an intermediate.

This model for hexaphenylbenzene formation agrees well with the cyclobutadiene mechanism for formation of benzene derivatives by catalytic trimerization of acetylene on transition-metal complexes.

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