π-Complexes of the Group V Metals with Diphenylacetylene. Crystal Structure of Dicarbonylbiscyclopentadienylbis-μ-diphenylacetylenediniobium

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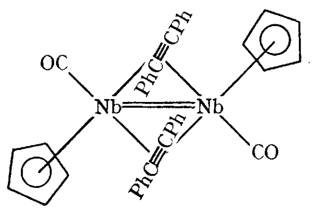
WE have reported[1] that when $C_5H_5Nb(CO)_4$ is irradiated with ultraviolet light in the presence of diphenylacetylene (tolan), $C_5H_5Nb(CO)_2Ph_2C_2$ is formed. Further photochemical reactions of $C_5H_5M(CO)_4$ (M=V,Nb, or Ta) with tolan gave $C_5H_5V(CO)_2Ph_2C_2$, $C_5H_5V(CO)(Ph_2C_2)_2$,[2] $C_5H_5Nb(CO)(Ph_2C_2)_2$, and $C_5H_5Ta(CO)(Ph_2C_2)_2$.[3] From these complexes, $C_5H_5V(CO)_2(\pi\text{-}Ph_4C_4)$, $[C_5H_5Nb(CO)Ph_2C_2]_2$, $[C_5H_5Ta(CO)Ph_2C_2]_2$,[2] and $C_5H_5Nb(CO)(Ph_2C_2)_3$,[3] were synthesised in the absence of u.v.-irradiation. For certain of these complexes, a preliminary *X*-ray study has been published.[4]

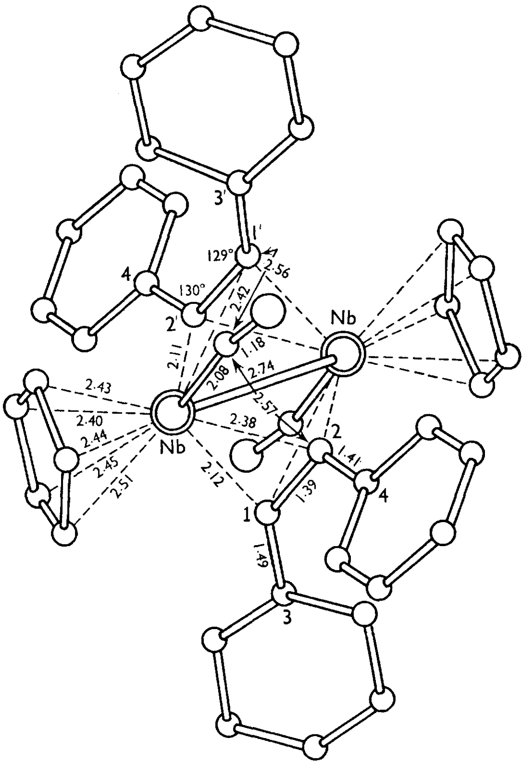
Now we report the results of an *X*-ray study of $[C_5H_5Nb(CO)Ph_2C_2]_2$ (I) (m.p. 248—250° decomp.), which is formed, as air-stable, dark violet prisms, by heating (80°) a concentrated solution of $C_5H_5Nb(CO)_2Ph_2C_2$ in toluene. According to cryoscopic data, the complex (I) is dimeric, *M* 670, calc. 728, whilst ^1H n.m.r. and i.r. spectra ($CDCl_3$), show that each Nb atom is bonded to the cyclopentadienyl ring, one terminal carbonyl group, and two bridging tolan molecules (a sharp singlet of C_5H_5-ring protons at τ 4·17 p.p.m.; one band at ν ($C{\equiv}O$) 1970 cm.$^{-1}$; there is no band of a non-bridging co-ordinated triple bond in the region[5] 1600—1900 cm.$^{-1}$). According to the mass spectrum there is a Nb–Nb bond (a peak of $[C_5H_5Nb]_2^+$ with $m/e = 316$, but no peak for $[C_5H_5Nb]^+$). The diamagnetism of (I) suggests a double character for the Nb–Nb bond. On this basis the following molecular structure was proposed, which is confirmed by the present *X*-ray



analysis. Compound (I) is the first organometallic complex studied with a Nb–Nb bond and the first π-complex with two bridging acetylenic ligands between two metal atoms.

Crystal data: (I) is triclinic, $a = 10{\cdot}43$, $b = 9{\cdot}60$, $c = 9{\cdot}12$ Å, $\alpha = 110{\cdot}3°$, $\beta = 71{\cdot}1°$, $\gamma = 114{\cdot}1°$, $D_m = 1{\cdot}54$, $D_c = 1{\cdot}58$ g.cm.$^{-3}$ for $Z = 1$, $M = 728$, space group $P\bar{1}$. Intensities of *ca.* 1400 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, $R = 0{\cdot}13$, with standard deviations in bond lengths of 0·005—0·03 Å and in bond angles of 0·3—2·0° depending on the atomic numbers.

The dimeric molecule (Figure) is situated in the inversion centre. The tolan ligand geometry is defined by the torsion angle C(3)C(1)C(2)/C(1)C(2)-C(4) which is equal to 28° and by the angle of 49° between phenyl ring planes. The co-ordinated triple bond length ($1\cdot39 \pm 0\cdot02$ Å) is greater than that for two known complexes, each with one bridging tolan group, $Ni_2(C_5H_5)_2Ph_2C_2$ (II)[6] and $Co_2(CO)_6Ph_2C_2$ (III),[7] where this bond length is $1\cdot35 \pm 0\cdot03$ and 1·369 Å.[8] But the bond angles at acetylenic carbon atoms in (II) are 138 and 142° and in (III) 137 and 139°, *i.e.*, distinctly larger than the C(3)C(1)C(2) and C(4)C(2)C(1) angles in (I). This difference cannot be accounted for by steric hindrances but is probably caused by the lesser *s*-character of the co-ordinated triple bond in (I) than in (II) and (III). It is of interest that, because of a steric repulsion between the carbonyl group carbon atom and the C(2) atom (see the Figure), the acetylenic group is not symmetrical with respect to the Nb–Nb bond, *e.g.* the angle between the C(1)–C(2) and Nb–Nb vectors is equal to 80° instead of 90°.



FIGURE

The average distance between the Nb-atom and the carbon atoms of the planar cyclopentadienyl ring is 2·45 Å, but the deviations of the individual values from this average are quite significant. Probably this "inclination" of the C_5H_5-ring is be caused by the very short intermolecular contacts C · · · C (3·27 and 3·29 Å) in which just those C_5H_5-ring atoms having the minimum distances (2·40 and 2·43 Å) from the Nb-atom participate.

The Nb–Nb bond distance (2·74 Å) is much shorter than the analogous distance (3·31 Å) in α-NbI_4[9] and somewhat less than the interatomic distance in Nb metal (2·86 Å). If one takes the half of the Nb–Nb distance (1·66 Å) in α-NbI_4 as an Nb single bond covalent radius then the distance Nb–C(cyclopentadienyl) may be estimated as $1\cdot66 + 0\cdot77 = 2\cdot43$ Å (0·77 Å is the sp^3-hybridized carbon atom radius) which is reasonably close to the average experimental value in (I). Insofar as the Nb–Nb bond in (I) is much shorter than the doubled Nb radius and the complex is diamagnetic, this metal-to-metal bond probably has double-bond characteristics, which is consistent with the 18-electron rule.

Just as in $C_5H_5Nb(CO)_4$,[10] the Nb atom in (I) is 7-co-ordinated; however, its co-ordination polyhedron is severely distorted because of the metal-to-metal bond formation.

Now we are completing the *X*-ray studies of $C_5H_5Nb(CO)(Ph_2C_2)_2$, $C_5H_5Nb(CO)(Ph_2C_2)_3$, and $C_5H_5V(CO)_2(\pi\text{-}Ph_4C_4)$ and have found that the first compound is monomeric, with two tolan molecules co-ordinated independently.

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