Journal of Organometallic Chemistry, 63 (1973) 311-319
© Elsevier Sequoia S.A., Lausanne - Printed in The Netherlands

THE STRUCTURE OF (π-h^5-CYCLOPENTADIENYL)(π-N,2,3-h^3-π-4,5,6-h^3-3,4,5,6-TETRAPHENYL-3,5-HEXADIENE-2-ONEIMINE) (PHOSPHINE)-NIOBIUM

N I KIRILLOVA, A I GUSEV, A A PASYNSKII and YU T STRUCHKOV
Institute of Organo-Element Compounds, Academy of Sciences of the U S S R, Moscow (U S.S R)

(Received April 5th, 1973)

SUMMARY

An X-ray study of a novel π-complex of niobium has shown it to be (π-C_5H_5)-(PH_3)Nb[HCPh(CPh)$_3$C(=NH)CH_3] with an unusual *hexahapto*-coordinated ligand constituting an azaallyl–allylic system, *i.e.* a 6-electron donor. The structure has been resolved through the use of a heavy atom technique and refined by an isotropic least-squares procedure to $R=0\ 104$.

INTRODUCTION

Photochemical reactions of (π-C_5H_5)Nb(CO)$_4$ with tolane, C_2Ph_2, have been studied in the Metal Carbonyl Laboratory of this Institute[1] and the structures of the complexes obtained have been elucidated by an X-ray study[2-4] In particular, the bis-tolane complex, (π-C_5H_5)Nb(CO)(π-C_2Ph_2)$_2$, has been shown to convert into (π-C_5H_5)Nb(π-C_2Ph_2) (π-C_4Ph_4) on interaction with a third tolane molecule. The latter complex contains a cyclobutadiene ligand formed by the condensation of two tolane molecules, and heating leads to further condensation with the formation of hexaphenylbenzene.

Acetylenic ligands in π-complexes are, in general, liable to condensation leading to cyclobutadiene, cyclopentadiene or benzene systems[5]. Complexes with ligands of a butadiene type formed by condensation of acetylenic molecules have also been studied, *i.e.* (PPh_3)Rh($Ph_2PC_6H_4C_4Ph_4$)[6] and (π-C_5H_5)(PPh_3)Ru[C_4-(CF_3)$_4$H][7]. Benzonitrile with a triple carbon–nitrogen bond also trimerizes giving rise to triphenyltriazene[8,9].

As a continuation of previous investigations of niobium acetylenic complexes, we have studied the photochemical reaction of the bis-tolane complex, (π-C_5H_5)Nb-(CO)(π-C_2Ph_2)$_2$, with boiling acetonitrile, $CH_3C{\equiv}N$, freshly distilled over technical P_2O_5 A complex (I) was produced by this reaction in very low yield. This complex was purified by Al_2O_3 chromatography using benzene as an eluant with subsequent crystallization from CS_2–hexane mixtures, but the quantity of material obtained in this way was insufficient for elemental analysis The infrared spectrum of (I) contains no bands attributable to the stretching vibrations of the C≡N bonds in the nitrile ligands (coordinated in the ordinary manner, *i.e.* via the unshared electron pair of the nitrogen atom). The spectrum lacks bands corresponding to coordinated triple bonds (π-tolane ligands) and metal–carbonyl groups. According to its ^{1}H NMR spectrum, complex (I) is diamagnetic and contains a π-cyclopentadienyl ligand and a methyl group (relative ratio of signals 5/3). On the basis of these data it seems reasonable to suppose that (I) is a complex containing a π-tetraphenylbutadiene ligand and a π-acetonitrile or a π-2-methyl-3,4,5,6-tetraphenylpyridine ligand (the latter being formed by cyclocondensation of two tolane and one CH_3CN molecules). However, in order to unambiguously establish the structure of (I), an X-ray study appeared to be worthwhile which led as the present communication shows to completely unexpected results

EXPERIMENTAL

Dark-orange prismatic crystals of (I) are monoclinic (space group $P2_1/n$): $a = 11\,070 \pm 0\,007$, $b = 23\,855 \pm 0\,009$, $c = 11.112 \pm 0.007$ Å, $\gamma = 102.50 \pm 0.02°$, $V = 2865$ Å^3, $d_m = 1.38$ $d_c = 1.38$ g·cm^{-3} for $Z = 4$ with mol.wt.≈ 591.

The intensities of ca. 1600 independent non-zero reflections were estimated visually from Weissenberg films taken with unfiltered copper radiation Lorentz polarization and spot-shape factors were taken into account but absorption was neglected (crystal dimensions 0.4 x 0.2 x 0.2 mm along the *a*,*b* and *c* axes, respectively).

*Structure determination and refinement**

The position of the Nb atom was located by means of a 3D Patterson function. The first Fourier series gave the positions of the Nb atom and of 14 light atoms and also revealed one peak X of an intermediate height which could be ascribed to a "half-heavy" atom (P,S,Cl). These 14 light atoms which readily conform to the known pattern of a metal-coordinated tolane ligand, were used together with the Nb atom for a sign determination of the second Fourier map which gave the positions of an additional 22 light atoms which were readily seen to correspond to a cyclopentadienyl ligand, the second tolane ligand and a three-atom group bonded to tolane via its central atom. The total number of atoms (Nb + 36 C) lead to a conventional *R* index of 0.22 with an overall *B* value of 4.3 Å^2. However, in addition to all these atoms, the peak X continued to persist in the same position although it was not taken into account in the calculation of the *F* values.

The structure was refined by the isotropic least-squares procedure using Cruickshanks's weighting scheme[10], and Waser's constraints[11] being applied in the first stages of refinement. Two versions were tried: (a) X = C, when the value of *R* immediately increased to 0.27 and (b) X = P which gave a final value of $R = 0\,104$ with $B = 3\,7$ Å^2 and a reasonable *B* value of 4 6 Å^2 for this atom. Unfortunately, it is not possible to decide whether X is really P, S or Cl solely on the basis of experimental X-ray data because the corresponding atomic numbers differ by only 1.

The final positional and thermal parameters and their standard deviations (in brackets) are given in Table 1, while the corresponding bond distances and angles are listed in Tables 2 and 3

---

* All calculations were performed by computer programmes written by B L Tarnopolskii, V I Andrianov and Z S Safina (Institute of Chemical Physics, Academy of Sciences of the U S S R , Moscow)

TABLE 1

ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS B_j (Å^2)

Atom	*x*	*y*	*z*	B_j	*Atom*	*x*	*y*	*z*	B_j
Nb	0 4127(1)	0 2266(1)	0 1240(2)	3 7(1)	C(19)	0 1889(16)	0 0814(7)	−0 0190(22)	4 2(1)
C(1)	0 6207(17)	0.2526(8)	−0 1312(23)	5 9(1)	C(20)	0 1114(16)	0 0518(7)	−0 1195(24)	5 1(1)
C(2)	0 5122(14)	0 2152(7)	−0 0688(19)	3 6(2)	C(21)	0 1652(19)	0 0377(8)	−0 2272(25)	5 8(2)
C(3)	0 5196(15)	0 1703(6)	0 0111(20)	3 2(1)	C(22)	0 2892(20)	0 0565(9)	−0 2444(24)	5 5(2)
C(4)	0 4006(14)	0 1311(6)	0 0474(21)	3 0(1)	C(23)	0 3654(17)	0 0863(8)	−0 1524(23)	4 7(2)
C(5)	0 3850(13)	0 1220(6)	0 1721(19)	2 7(1)	C(24)	0 3011(16)	0 0722(7)	0 2320(21)	3 9(1)
C(6)	0 4540(14)	0 1659(6)	0 2448(20)	3 1(1)	C(25)	0 2216(16)	0 0826(7)	0 3210(20)	4 7(1)
C(7)	0 4811(18)	0 3291(8)	0 0855(23)	5 7(2)	C(26)	0.1440(17)	0 0363(8)	0 3852(23)	6 2(1)
C(8)	0 5855(17)	0 3077(8)	0 1382(25)	5 5(2)	C(27)	0 1503(17)	−0 0189(8)	0 3512(23)	6 4(2)
C(9)	0 5568(14)	0 2895(6)	0 2577(20)	5 7(1)	C(28)	0 2288(17)	−0 0308(8)	0 2602(22)	5 4(2)
C(10)	0 4349(17)	0 2975(8)	0 2897(23)	5 4(2)	C(29)	0 3025(16)	0 0172(8)	0 2004(21)	5 2(2)
C(11)	0 3914(17)	0 3221(8)	0.1832(21)	5 0(2)	C(30)	0 4985(12)	0 1581(5)	0 3634(20)	2 7(1)
C(12)	0 6372(15)	0 1517(7)	0 0413(20)	3 5(1)	C(31)	0 5782(16)	0 1200(7)	0 3739(25)	5 4(1)
C(13)	0 7456(16)	0 1889(7)	0 0735(20)	3 1(2)	C(32)	0 6180(18)	0 1083(8)	0 4949(26)	6 3(2)
C(14)	0 8552(19)	0 1694(9)	0 0931(24)	6 3(2)	C(33)	0 5824(18)	0 1348(8)	0 5956(24)	6 2(2)
C(15)	0 8540(19)	0 1101(9)	0 0851(23)	5 8(2)	C(34)	0 5039(19)	0 1734(9)	0 5848(25)	6 4(2)
C(16)	0 7422(16)	0 0720(8)	0 0580(21)	5 2(1)	C(35)	0 4580(17)	0 1837(8)	0 4698(24)	5 2(2)
C(17)	0 6356(15)	0 0931(7)	0 0329(20)	4 2(1)	P	0 1870(4)	0 2107(5)	0 1298(5)	4 6(2)
C(18)	0 3143(15)	0 0983(7)	−0 0421(20)	3 6(1)	N	0 3852(14)	0 2216(7)	−0 0888(20)	7 6(1)

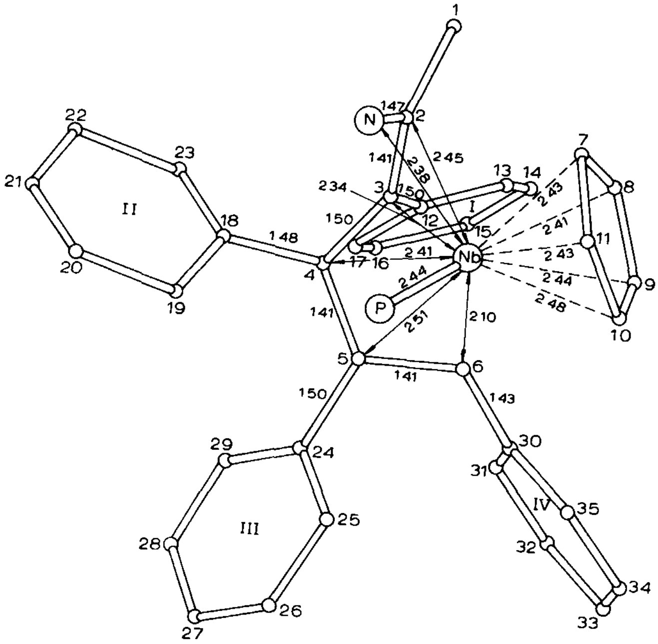


Fig 1 Main bond lengths (Å) of I, (π-C_5H_5)(PH_3)Nb[HCPh(CPh)$_3$C(=NH)CH_3]

TABLE 2

BOND LENGTHS d (Å)

Bond	*d*	*Bond*	*d*
Nb-P	2.445(5)	C(12)-C(13)	1.38(2)
Nb-N	2.38(2)	C(13)-C(14)	1.41(3)
Nb-C(2)	2.45(2)	C(14)-C(15)	1.41(3)
Nb-C(3)	2.34(2)	C(15)-C(16)	1.40(3)
Nb-C(4)	2.41(2)	C(16)-C(17)	1.41(3)
Nb-C(5)	2.51(1)	C(12)-C(17)	1.40(2)
Nb-C(6)	2.10(2)	Average value	1.40
Nb-C(7)	2.43(2)		
Nb-C(8)	2.41(2)	C(18)-C(19)	1.38(2)
Nb-C(9)	2.44(2)	C(19)-C(20)	1.49(3)
Nb-C(10)	2.48(2)	C(20)-C(21)	1.41(4)
Nb-C(11)	2.43(2)	C(21)-C(22)	1.36(3)
Average value	2.44	C(22)-C(23)	1.41(3)
		C(18)-C(23)	1.40(3)
N-C(2)	1.47(2)	Average value	1.41
C(2)-C(3)	1.41(2)		
C(3)-C(4)	1.50(2)	C(24)-C(25)	1.38(3)
C(4)-C(5)	1.41(3)	C(25)-C(26)	1.43(3)
C(5)-C(6)	1.41(2)	C(26)-C(27)	1.38(3)
		C(27)-C(28)	1.40(3)
C(1)-C(2)	1.50(3)	C(28)-C(29)	1.42(3)
C(3)-C(12)	1.50(2)	C(24)-C(29)	1.36(3)
C(4)-C(18)	1.48(2)	Average value	1.40
C(5)-C(24)	1.50(2)		
C(6)-C(30)	1.43(3)		
Average value	1.48	C(30)-C(31)	1.40(2)
		C(31)-C(32)	1.46(4)
C(7)-C(8)	1.48(3)	C(32)-C(33)	1.38(4)
C(8)-C(9)	1.41(3)	C(33)-C(34)	1.40(3)
C(9)-C(10)	1.45(3)	C(34)-C(35)	1.42(4)
C(10)-C(11)	1.45(3)	C(30)-C(35)	1.45(3)
C(7)-C(11)	1.46(3)	Average value	1.42
Average value	1.45		

Molecular structure

The molecular geometry is given in Figs. 1 and 2 which show the most important bond distances and angles. In agreement with the ^{1}H NMR spectrum, the molecule of (I) contains a cyclopentadienyl ligand which consists of a virtually planar regular pentagon C(7)-C(11) with the usual C-C bond length of 1.45±0.03 Å and an average CCC angle of 108±2° Nb-C(Cp) distances are close to each other (2.41-2.48 Å) indicating that this ligand is h^5-coordinated being a tridentate donor of 5 electrons. The average Nb-C(Cp) distance (2.44 Å) coincides with the value found previously in monocyclopentadienylniobium complexes[2-4].

The acyclic ligand. Quite unexpectedly, the molecule involves six atoms (2,3,4,5, 6 and N) arranged in a chain and separated from the niobium atom by distances of 2.1-2.5 Å, indicating the occurrence of strong interaction. The distances between these

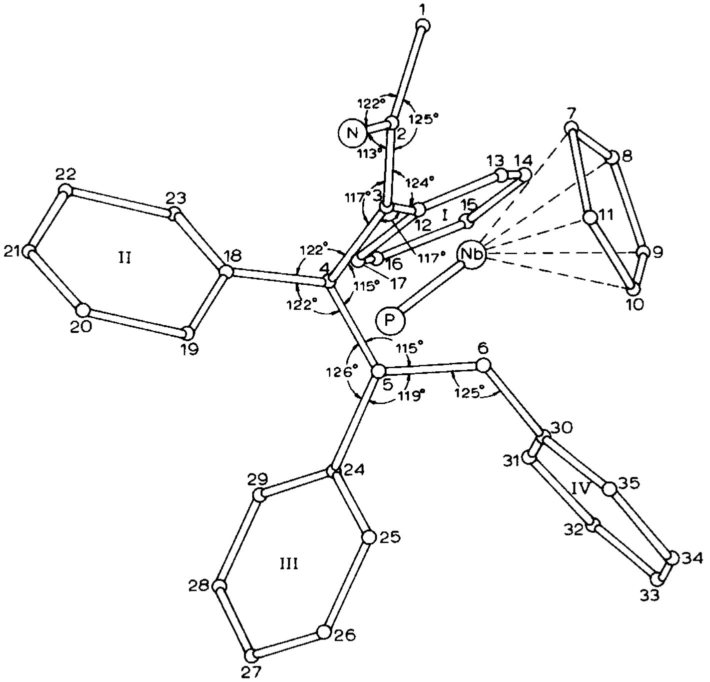


Fig 2 Main bond angles(°) of $(\pi\text{-}C_5H_5)(PH_3)Nb[HCPh(CPh)_3C(=NH)CH_3]$

light atoms are equal to 1.41–1.50 Å, *i.e.* they are close to carbon–carbon (or carbon–nitrogen) bond lengths. The atoms 3,4,5 and 6 are bonded to phenyl rings at distances of 1.43–1.50 Å, indicating that the fragment C(3)Ph–C(4)Ph–C(5)Ph–C(6)Ph is formed by condensation of two tolane molecules. In addition, there is a 3-atom unit (N,2,1) bonded to C(3) through its central atom, the 2–3 distance (1.41 Å) corresponding to a coordinated carbon–carbon double bond. The distances 1–2 (1.50 Å) and 2–N (1.47 Å) correspond to ordinary $C(sp^3)$–$C(sp^2)$ and C–N bonds, respectively. Atoms 2 and N interact with the niobium atom (at distances of 2.45 and 2.38 Å) but atom 1 does not (3.62 Å), suggesting that atom 1 is a saturated carbon atom, atom 2 is a carbon atom π-bonded to niobium and N is a nitrogen atom bonded to niobium

*The "monoatomic" X ligand.*The niobium atom is also bonded (2.44 Å) to ligand X, which according to its electron density could be a P, S, or Cl atom. However, the version X = Cl is excluded by the conditions used for the preparation of (I) and the version X = S is also improbable as (I) could be obtained in the same crystal form from hexane or ether without the addition of CS_2 However the version X = PH_3 (the hydrogen atoms being not resolved) appears to be quite reasonable as PH_3 is readily formed[12] by the interaction of water (present in moist acetonitrile) with the phosphorus suboxides present in technical grade P_2O_5.

It should be noted further that the two organic ligands donate 5 + 6 = 11 electrons and that the niobium atom needs 13 electrons in order to attain a closed noble gas electron shell*. For this reason the ligand X should be a two-electron donor,

---

* Since complex (I) is diamagnetic Sidgwick's rule probably holds

TABLE 3

BOND ANGLES ω°

Angle	ω	*Angle*	ω
N-C(2)-C(3)	113(2)	C(18)-C(19)-C(20)	116(2)
C(2)-C(3)-C(4)	117(2)	C(19)-C(20)-C(21)	121(2)
C(3)-C(4)-C(5)	115(2)	C(20-C(21)-C(22)	119(2)
C(4)-C(5)-C(6)	115(2)	C(21)-C(22)-C(23)	121(2)
		C(22)-C(23)-C(18)	121(2)
C(1)-C(2)-N	122(2)	C(23)-C(18)-C(19)	122(2)
C(1)-C(2)-C(3)	125(2)	Average value	120
C(2)-C(3)-C(12)	124(2)		
C(4)-C(3)-C(12)	117(2)		
C(3)-C(4)-C(18)	122(2)	C(24)-C(25)-C(26)	121(2)
C(5)-C(4)-C(18)	122(2)	C(25)-C(26)-C(27)	117(2)
C(4)-C(5)-C(24)	126(2)	C(26)-C(27)-C(28)	123(2)
C(6)-C(5)-C(24)	119(2)	C(27)-C(28)-C(29)	117(2)
C(5)-C(6)-C(30)	125(2)	C(28)-C(29)-C(24)	122(2)
		C(29)-C(24)-C(25)	120(2)
C(3)-C(12)-C(13)	124(2)	Average value	120
C(3)-C(12)-C(17)	117(2)		
C(4)-C(18)-C(19)	121(2)		
C(4)-C(18)-C(23)	117(2)	C(30)-C(31)-C(32)	117(2)
C(5)-C(24)-C(25)	119(2)	C(31)-C(32)-C(33)	122(2)
C(5)-C(24)-C(29)	121(2)	C(32)-C(33)-C(34)	121(2)
C(6)-C(30)-C(31)	116(2)	C(33)-C(34)-C(35)	119(2)
C(6)-C(30)-C(35)	123(2)	C(34)-C(35)-C(30)	121(2)
C(12)-C(13)-C(14)	121(2)	C(35)-C(30)-C(31)	120(2)
C(13)-C(14)-C(15)	120(2)	Average value	120
C(14)-C(15)-C(16)	119(2)		
C(15)-C(16)-C(17)	120(2)	C(7)-C(8)-C(9)	110(2)
C(16)-C(17)-C(12)	121(2)	C(8)-C(9)-C(10)	110(2)
C(17)-C(12)-C(13)	119(2)	C(9)-C(10)-C(11)	105(2)
Average value	120	C(10)-C(11)-C(7)	112(2)
		C(11)-C(7)-C(8)	103(2)
		Average value	108

i.e. $X \neq PH_2$, SH, Cl (one-electron donors). The version $X = S$ can also be discarded as the length of the Nb=S double bond is estimated as $\leqslant 2.31$ Å$^{2-4,13}$.

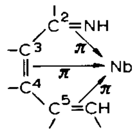
Unfortunately, the molecular structures of other phosphinic complexes of niobium are not known but despite this the Nb–P distance of $2.44 \pm 0.00_5$ Å found in complex (I) seems to be quite reasonable. Indeed, as the octahedral radius of the niobium atom is 1.43 Å^{13} and the tetrahedral radius of the phosphorus atom is 1.10 Å^{13} their sum is equal to 2.53 Å. The difference of 0.09 Å (3.6 %) between these two values which may be explained by back-donation is very similar to the corresponding difference found for the phosphinic complexes of iron and other transition metals which have been studied extensively.

Geometry and coordination of the acyclic ligand

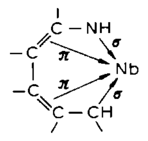
The ligand formed by the condensation of two tolane and one acetonitrile molecules with inclusion of two hydrogen atoms is a six-electron donor. The bond angles (113–126°, average 120 ± 4°) and bond lengths of the carbon atoms in the chain correspond to sp^2 hybridization (Tables 2 and 3)

In accordance with structural data mentioned above, the ligand in its uncoordinated form is 3,4,5,6-tetraphenyl-3,5-hexadiene-2-one imine, CH_3–C(=NH)–CPh=CPh–CPh=CHPh.

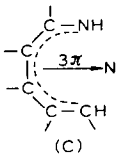
A number of resonance forms may be written which represent the structure of (I):



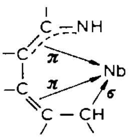
(A)



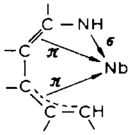
(B)



(C)



(D)



(E)

The fragment C(4)-C(5)-C(6) can be considered to be an allyl group π-bonded to the niobium atom since the C(4)–C(5) and C(5)–C(6) bonds which are 1.41 ± 0.03 Å in length have an order ~1.5 and the angle at C(5) is 115 ± 1.5°. In other π-allyl complexes which have been studied the corresponding values are 1.28–1.48 (average 1.40 Å) and 106–130° (average 119°)[14]. However, the Nb–C(6), –C(5) and –C(4) distances (2.10, 2.51 and 2.41 Å) are significantly different, suggesting that the allyl group is bonded with a marked asymmetry (resonance *D*↔*E*, or *B*↔*C*). Such asymmetric coordination of π-allyl ligands is well known[15] and has been subjected to MO treatment[16]. It should be noted that in $Fe_2(CO)_6(C_6H_5C_2H)_3$[17], where the π-allyl group is involved in a bifurcated metallocycle, the inequality of the Fe–C (allyl) distances (1.97, 2.11, 2.20 Å) has been ascribed to strain in this cyclic system despite the fact that the allyl C–C bond lengths remain equal (1.41 and 1.42 Å). In complex (I), the C–C bond lengths in the allyl group are also equal (1.41 Å) although the Nb–C (allyl) distances exhibit a significant difference (of 0.41 Å).

The 3-atom fragment NC(2)C(3) can similarly be considered to be an π-azallyl group. An analogous system has previously been found in (Ph_2C=C=NMe)-$Fe_2(CO)_6$[18] where a bridging azallene ligands forms N–Fe and C–Fe σ-bonds with one iron atom and is bonded to the other iron atom as a π-allyl group. In complex (I), the C(2)–N distance (1.47 Å) is equal to the length of an ordinary carbon–nitrogen bond, thus suggesting that the azallyl group is again bonded asymmetrically (resonance *D*↔*E* or *B*↔*C*) The value of the Nb–N distance (2.38 Å) is quite reasonable for π-interaction, this distance being less than the mean Nb–C(Cp) by 0.06 Å which is equal to the difference of the C and N covalent radii. Hence it seems unlikely that an unshared electron pair of nitrogen participates in π-interaction with the metal atom as was already noted is the case in the azabutadiene complex (PhCH = CH–CH = NPh)$Fe(CO)_3$[19]. In addition, Nb–N interaction involving a nitrogen electron pair would lead to a shorter Nb–N distance (2.28–2.33 Å) as observed in a phenanthroline complex of niobium[20].

In diallyl complexes which have been studied previously, the allyl groups are either well separated or coordinated to different metal atoms as, for example, in μ-[1-3,6-η: 1,4-6-η-1,3,6-tris(trifluoromethyl)hexa-1,3,5-triene-1,6-diyl]bis(dicarbonylcobalt) (Co–Co)[21]. Thus, as far as we are aware, complex (I) has no counterpart in the literature and represents a novel example of a π-complex containing an azallyl-allyl ligand.

It is worthwhile noting that in (I) conjugation between the allyl groups is absent and for this reason resonance form (A) may be excluded. Indeed, the C(3)–C(4) bond has the usual length (1.50 ± 0.02 Å) and the corresponding torsion angle C(4)C(5)C(6)/C(3)C(2)N is 110°, *i.e.* the ligand is distinctly non-planar (see Tables 4 and 5).

Substituents attached to the allyl carbon atoms are also deflected out of the plane of the allyl groups. In the azallyl group these deviations are small: C(1) (Me group), 0.09 Å; C(12) (Ph-group), 0.03 Å. In the allyl group C(4)C(5)C(6), however, the deviation from planarity is larger: C(18), 0.34 (towards Nb); C(30), 0.56 Å (out-

TABLE 4

EQUATIONS $Ax+By+Cz=D$ FOR PLANAR FRAGMENTS OF THE MOLECULE, AVERAGE DEVIATIONS OF CARBON ATOMS FROM THESE PLANES AND CHARACTERISTIC DEVIATIONS FROM ALLYL GROUP PLANES

Fragments	*A*	*B*	*C*	*D*	Δ_{av}(Å)
C(12)-C(13)-C(14)-C(15)-C(16)-C(17) (Ph(I))	2.46	1.38	−10.77	1.32	0.015
C(18)-C(19)-C(20)-C(21)-C(22)-C(23) (Ph(II))	−3.61	21.93	−4.13	1.20	0.015
C(24)-C(25)-C(26)-C(27)-C(28)-C(29) (Ph(III))	8.19	−3.62	7.48	3.92	0.007
C(30)-C(31)-C(32)-C(33)-C(34)-C(35) (Ph(IV))	7.06	14.48	−1.14	5.38	0.014
C(7)-C(8)-C(9)-C(10)-C(11) (Cyclopentadienyl)	2.34	20.33	3.67	8.13	0.003
N-C(2)-C(3)	−0.58	15.13	8.54	2.37	−1.88Nb 0.03 C(1) 0.09 C(12)
C(4)-C(5)-C(6)	9.77	−15.50	0.09	1.89	1.36(Nb) 0.34 C(18) 0.04 C(24) −0.56 C(30)

TABLE 5

ANGLES φ° BETWEEN PLANAR FRAGMENTS OF THE MOLECULE

Planar fragments	φ°	*Planar fragments*	φ°
N-C(2)-C(3)/Ph(I)	137	Ph(III)/Ph(IV)	66
C(4)-C(5)-C(6)/Ph(II)	136	C(1)-C(2)-C(3)/C(2)-C(3)-C(12)	3
C(4)-C(5)-C(6)/Ph(III)	41	C(3)-C(4)-C(18)/C(12)-C(3)-C(4)	110
C(4)-C(5)-C(6)/Ph(IV)	12	C(4)-C(5)-C(24)/C(18)-C(4)-C(5)	14
Ph(I)/Ph(II)	68	C(5)-C(6)-C(30)/C(24)-C(5)-C(6)	31
Ph(II)/Ph(III)	119		

wards Nb), although the Ph substituent attached to the central atom of this group is virtually in the plane (C(24), 0.04 Å)

Similar and even greater ($\leqslant$ 0.8 Å) deviations from planarity have been found previously in other π-allyl complexes[14,22] and especially where asymmetric coordination of the allyl ligand occurs. According to Canadine[23], deviation from planarity leads to a loss in resonance energy in the π-allyl system which is compensated by an increase in the metal–allyl interaction. In the present case, the biggest deviation (0.56 Å) is observed at that allyl carbon atom which is most strongly bonded to the metal atom (C(6)–Nb, 2.10 Å). Steric factors also appear to be important as the next biggest deviation of 0.34 Å at C(18) is accompanied by a significant contraction of the non-bonding C(18) N distance of 2.92 Å (the sum of the van der Waals radii being 3.4 Å).

In addition to these out-of-plane deviations, the coplanarity of the phenyl and allyl groups is also disturbed by rotation around the bonds between these groups. The corresponding dihedral (torsional) angles, *i.e* the angles between the π-orbitals, are listed in Table 5. These angles are in general consistent with C(allyl)–C(phenyl) bond lengths: the greater the angle the smaller the conjugation. It is probable that these unfavourable phenyl ring rotations are due, at least in part, to the configuration of the coordinated ligand as a whole which contains considerable steric overcrowding (*e.g.* the C(4)·C(17) and C(3) C(23) distances of 2.94 and 2.96 Å respectively are contracted by 0.6–0.7 Å).

REFERENCES

1 A N Nesmeyanov, K N Anisimov, N E Kolobova and A A Pasynskii, *Dokl Akad Nauk SSSR*, 181 (1968) 1142; 182 (1968) 112; *Izv Akad Nauk SSSR, Ser Khim.*, 100 (1969) 183
2 A I Gusev and Yu, T Struchkov, *Zh Strukt Khim*, 10 (1969) 107.
3 A I Gusev and Yu T Struchkov, *Zh Strukt Khim*, 10 (1969) 294
4 A I Gusev and Yu. T. Struchkov, *Zh Strukt Khim*, 10 (1969) 515
5 M. R. Churchill and R Mason, *Advan Organometal Chem*, 5 (1967) 93
6 I S. Ricci and J A Ibers, *J Organometal. Chem*, 27 (1971) 261
7 T Blackmore, M I Bruce, F G A Stone, R E. Davis and A Gazza, *Chem Commun*, (1971) 852
8 S F A Kettle and L E Orgel, *Proc Chem Soc*, (1959) 307.
9 W Z Heldt, *J Organometal Chem*, 6 (1966) 292
10 D W J Cruickshank, *Computing Methods and Phase Problems in X-ray Crystal Analysis*, Paper 6, Pergamon Press, Oxford, 1961
11 J Wasser, *Acta Cryst*, 16 (1963) 1091
12 G Brauer (Ed), *Handbook of Preparative Inorganic Chemistry*, New York, London, 2 nd ed , 1963, p 541
13 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N Y , 3rd ed , 1960
14 Yu T Struchkov, *D Sc Thesis Moscow*, 1973
15 R Mason and D R Russell, *Chem Commun*, (1966) 26
16 W W Folgeman, L C Cusach and H B Jonassen, *Chem Phys Lett*, 3 (1969) 52
17 L S D King, *Acta Cryst*, 15 (1962) 243
18 K Ogava, A. Torrii, H. Kobayashi-Tamura, T Watanabe, T Yoshida and S Otsuka, *Chem Commun*, (1971) 991
19 A De Cian and R Weiss, *Chem Commun*, (1968) 348
20 L. Mathern, R Weiss and R Rohmer, *Chem Commun*, (1970) 153
21 R S Dickson, P I Fraser and B M Gatehouse, *J Chem Soc (A)*, (1972) 2278
22 R Mason and A G Wheeler, *J Chem Soc (A)*, (1968) 2543
23 R M Canadine, *Allyl and Olefin Complexes of Metals, Chem Soc Symposium, Sheffield*, April, 1967