

NIOBIUM ORGANOMETALLIC CHEMISTRY

XI *. DIELS–ALDER REACTION OF A η^1 -CYCLOPENTADIENYL GROUP. CRYSTAL STRUCTURE OF A NIOBIUM DERIVATIVE CONTAINING A η^1 -SUBSTITUTED NORBORNADIENYL UNIT

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(Received October 25th, 1982)

Summary

Hexafluorobutyne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$, HFB) reacts with tetracyclopentadienylniobium [$\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$] to give a diamagnetic niobium derivative, the structure of which has been determined by single-crystal X-ray diffraction. Crystal data are space group $P2_1/n$, a 7.983(2) Å, b 27.600(7) Å, c 8.689(2) Å, β 113.22(2)°, Z = 4. A terminal oxygen atom (Nb–O 1.63(3) Å) and a η^1 -substituted norbornadienyl unit (arising from a Diels–Alder addition of HFB on a $\eta^1\text{-C}_5\text{H}_5$ group) are bonded to a bent [$\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2$] system.

Introduction

In previous papers on niobium organometallic complexes we examined some new aspects of the reactivity of some di- η^5 -cyclopentadienylniobium derivatives such as [$\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$] [1–4], [$\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2$] [5–7] and [$\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_3$] [8–10]. We now report the results of reactions with tetracyclopentadienylniobium, which contains two *pentahapto* and two *monohapto* cyclopentadienyl groups. The presence of the $\eta^1\text{-C}_5\text{H}_5$ ligands prompted us to investigate the reactions of this paramagnetic complex with dienophilic acetylenes, since it is well established that ($2\pi + 4\pi$) additions between $\eta^1\text{-C}_5\text{H}_5$ metal species and acetylenes can be efficient

* For X see ref. 25.

routes for the synthesis of various bicyclo[2.2.1]hepta-2,5-diene metallo derivatives [11–15]. This paper describes the synthesis and structural characterization of a niobium derivative containing a η^1 -substituted norbornadienyl unit, the oxodi- η^5 -cyclopentadienyl[2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-dien-7-yl]niobium(V).

Results and discussion

$[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2]$ reacts at room temperature with hexafluorobut-2-yne (HFB) to give complex I. Although $[\text{Nb}(\text{C}_5\text{H}_5)_4]$ also reacts with other acetylenes $\text{RC}\equiv\text{CR}'$ ($\text{R} = \text{CF}_3$, $\text{R}' = \text{H}$; $\text{R} = \text{R}' = \text{CN}$; $\text{R} = \text{CN}$, $\text{R}' = \text{H}$), we were unable to isolate characterisable products from these reactions.

The diamagnetism of I, which contrasts with the paramagnetic properties of the niobium starting material, is clearly indicated by the sharpness of the peaks in the ^{13}C NMR spectrum. The ^1H NMR spectrum exhibits a singlet at δ 5.96 ppm, which is clearly due to the $\eta^5\text{-C}_5\text{H}_5$ group, and three unresolved multiplets which appear as broad singlets at 6.83, 4.30 and 3.68 ppm (relative intensities 2/2/1). This spectrum is consistent with the presence of a substituted norbornadienyl unit bonded to a bent $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2]$ sandwich system. Following previous assignments [14–16], we assume that in I the peak at highest field is due to the proton attached to the C atom bonded to the metal, that at 4.30 ppm to the two H atoms attached to sp^3 -hybridised C atoms, and that the low field signal is from the protons of an uncomplexed olefinic group.

Since the mass spectrum showed the presence of an oxygen atom, the formula $[\text{NbO}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_7\text{H}_5(\text{CF}_3)_2)]$ was tentatively assigned to I. An X-ray study was undertaken and confirmed this formulation. The overall molecular configuration, with the atom numbering system, is given in Fig. 1, while Tables 1, 2 and 3 summarise the crystallographic results.

The crystal structure is built up of discrete molecular units of $[\text{NbO}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_7\text{H}_5(\text{CF}_3)_2)]$ showing that major modifications occur upon formation of I: one $\eta^1\text{-C}_5\text{H}_5$ group undergoes a Diels–Alder reaction with HFB to give a substituted

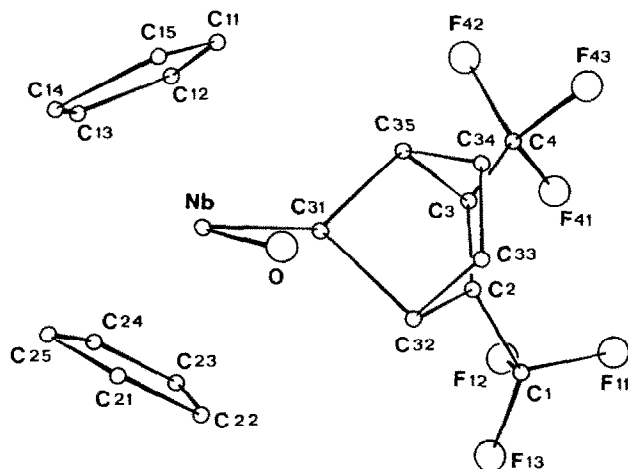


Fig. 1. View of the molecular shape of complex I (projection down [010]).

TABLE 1

ATOMIC FRACTIONAL CELL COORDINATES ($\times 10^3$) AND ISOTROPIC THERMAL PARAMETERS (\AA^2) FOR COMPLEX I (Least-squares estimated standard deviations are given in parentheses. The atoms are numbered as shown in Fig. 1.)

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Nb	211(5)	176(1)	214(4)	2.4(0.3)
O(1)	102(4)	223(1)	103(3)	5.7(0.7)
C(11)	411(5)	166(1)	057(4)	3.4(0.8)
C(12)	431(5)	127(1)	151(4)	3.7(0.8)
C(13)	526(6)	141(2)	323(5)	5.7(1.1)
C(14)	529(6)	192(2)	341(6)	6.8(1.2)
C(15)	471(6)	210(2)	156(6)	5.9(1.1)
C(21)	145(6)	208(2)	444(6)	6.1(1.1)
C(22)	-008(5)	187(1)	349(5)	5.4(1.0)
C(23)	055(5)	136(1)	369(4)	3.7(0.8)
C(24)	231(5)	137(2)	477(5)	5.1(0.9)
C(25)	292(6)	177(2)	517(6)	7.0(1.1)
C(31)	052(5)	116(1)	041(4)	3.7(0.8)
C(32)	-171(5)	119(2)	-036(5)	5.0(1.0)
C(33)	-190(6)	160(1)	-177(5)	5.1(1.0)
C(34)	-079(6)	155(2)	-245(5)	5.6(1.0)
C(35)	040(5)	108(2)	-138(5)	4.9(0.9)
C(1)	-378(7)	048(2)	-153(7)	9.8(1.5)
C(2)	-220(5)	079(1)	-151(5)	5.0(0.9)
C(3)	-109(5)	066(1)	-203(5)	4.3(0.9)
C(4)	-098(8)	017(2)	-311(8)	10.7(1.7)
F(11)	-479(6)	041(2)	-308(6)	15
F(12)	-341(5)	-009(2)	-147(5)	15
F(13)	-443(6)	047(2)	-052(5)	15
F(41)	-210(5)	-007(1)	-335(5)	15
F(42)	066(6)	015(2)	-296(6)	15
F(43)	-125(5)	044(1)	-457(5)	15

norbornadienyl moiety acting as a one electron ligand; the second $\eta^1\text{-C}_5\text{H}_5$ group is displaced; a terminal oxygen atom coordinates to the niobium to give the metal an eighteen electron configuration.

The molecular structure does not show an approximate C_s symmetry since the (Nb, O, C(31)) plane, which approximately bissects the $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2]$ system, is not a mirror for the norbornadiene unit.

The niobium–oxygen bond (1.63(3) Å), which appears slightly shorter than the corresponding distance in $[\text{NbOCl}_2(\text{OEt})(\text{bipy})]$ ($\text{bipy} = \text{C}_{10}\text{H}_8\text{N}_2$; 1.71 Å) [17], $[\text{Ph}_4\text{As}]_2[\text{NbO}(\text{NCS})_5]$ (1.70 Å) [17] and $[\text{NbO}(\text{C}_2\text{O}_4)_3]^{3-}$ (1.71 Å) [18], is consistent with a Nb–O multiple bond. The overall geometry of the norbornadiene skeleton resembles that in the free ligand in the gas phase [19]. As expected, the C–C distances fall into two sets, the C(2)–C(3) and C(33)–C(34) bonds (respectively 1.20(6) and 1.25(7) Å) being shorter than the other C–C bonds (mean 1.58 Å). The Nb–C(31) distance 2.27(4) Å is similar to that of the Nb–C σ bond found in $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{CH}=\text{CH}_2)(\text{S}_2)]$ (2.309 Å) [20] and $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)]$ (2.316 Å) [21].

The geometry of the $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2]$ moiety is that commonly found in bent

TABLE 2
INTERATOMIC DISTANCES (Å) AND ANGLES (deg) IN COMPLEX I

a. Interatomic distances

Nb–O(1)	1.63(3)	Nb–C(31)	2.27(4)
Nb–C(11)	2.48(4)	Nb–C(21)	2.43(5)
Nb–C(12)	2.44(4)	Nb–C(22)	2.48(4)
Nb–C(13)	2.51(5)	Nb–C(23)	2.44(4)
Nb–C(14)	2.37(5)	Nb–C(24)	2.49(4)
Nb–C(15)	2.50(5)	Nb–C(25)	2.46(5)
C(11)–C(12)	1.31(6)	C(21)–C(22)	1.30(6)
C(12)–C(13)	1.43(6)	C(22)–C(23)	1.49(6)
C(13)–C(14)	1.41(7)	C(23)–C(24)	1.34(6)
C(14)–C(15)	1.57(7)	C(24)–C(25)	1.22(6)
C(15)–C(11)	1.46(6)	C(25)–C(21)	1.38(7)
C(31)–C(32)	1.64(6)	C(1)–C(2)	1.52(7)
C(32)–C(33)	1.62(6)	C(2)–C(3)	1.20(6)
C(33)–C(34)	1.25(7)	C(3)–C(4)	1.68(7)
C(34)–C(35)	1.66(6)	C(2)–C(32)	1.45(6)
C(35)–C(31)	1.53(6)	C(3)–C(35)	1.59(6)
C(1)–F(11)	1.28(7)	C(4)–F(41)	1.06(7)
C(1)–F(12)	1.38(7)	C(4)–F(42)	1.26(7)
C(1)–F(13)	1.18(7)	C(4)–F(43)	1.41(7)

b. Angles

C(11)–C(12)–C(13)	109(5)	C(21)–C(22)–C(23)	99(5)
C(12)–C(13)–C(14)	111(5)	C(22)–C(23)–C(24)	106(5)
C(13)–C(14)–C(15)	103(5)	C(23)–C(24)–C(25)	114(5)
C(14)–C(15)–C(11)	103(5)	C(24)–C(25)–C(21)	105(5)
C(15)–C(11)–C(12)	112(5)	C(25)–C(21)–C(22)	116(5)
C(31)–C(32)–C(33)	96(5)	O–Nb–C(31)	99(5)
C(32)–C(33)–C(34)	114(5)	C(31)–C(32)–C(2)	101(5)
C(33)–C(34)–C(35)	100(5)	C(33)–C(32)–C(2)	95(5)
C(34)–C(35)–C(31)	104(5)	C(31)–C(35)–C(3)	102(5)
C(35)–C(31)–C(32)	88(5)	C(34)–C(35)–C(3)	101(5)
C(32)–C(2)–C(1)	116(5)	C(35)–C(3)–C(2)	102(5)
C(32)–C(2)–C(3)	117(5)	C(35)–C(3)–C(4)	126(5)
C(1)–C(2)–C(3)	125(5)	C(2)–C(3)–C(4)	132(5)
C(2)–C(1)–F(11)	106(6)	C(3)–C(4)–F(41)	113(6)
C(2)–C(1)–F(12)	112(6)	C(3)–C(4)–F(42)	106(6)
C(2)–C(1)–F(13)	128(6)	C(3)–C(4)–F(43)	93(6)
F(11)–C(1)–F(12)	86(7)	F(41)–C(4)–F(42)	138(7)
F(11)–C(1)–F(13)	120(7)	F(41)–C(4)–F(43)	109(7)
F(12)–C(1)–F(13)	96(7)	F(42)–C(4)–F(43)	85(7)

di- η^5 -cyclopentadienylniobium systems [22]. The two C_5H_5 rings are almost planar, and the dihedral angle between these two planes is 53(1). The Nb–C distances are in the range 2.37–2.51 Å (mean 2.46 Å) and the C–C distances within the rings are in the range 1.22–1.57 Å (mean 1.40 Å) and do not vary in any systematic manner.

Finally, synthesis of complex I, which is a further example of Diels–Alder addition of σ -coordinated cyclopentadienyl groups, confirms the strong tendency of the $[Nb(\eta^5-C_5H_5)_2X_2]$ 17 electron complexes to adopt an 18 electron configuration. The origin of the oxygen atom has not been elucidated; it may come from the THF used in the chromatography or from traces of air or water during the experiment.

TABLE 3

EQUATIONS OF SELECTED LEAST-SQUARES BEST PLANES AND INTERPLANAR ANGLES IN COMPLEX I

1. Equations of least-squares planes

The equations are of the form $Ax + By + Cz + D = 0$ where x, y, z (in Å) refer to the orthogonal system a, b, c^* .

Plane	Atoms in plane	A	B	C	D	Planeity (Å)
P(1)	five atoms C(11) to C(15)	-0.9963	+0.0864	-0.0025	+2.6701	0.045
P(2)	five atoms C(21) to C(25)	-0.6115	-0.0798	+0.7872	-2.5457	0.029
P(3)	Nb, O, C(31)	-0.8862	-0.0238	+0.4628	+0.1733	0
P(4)	C(31), C(32), C(35)	-0.1103	-0.9866	+0.1198	+3.1518	0
P(5)	C(32), C(33), C(34), C(35)	-0.3906	-0.6082	-0.6910	+1.3404	0.016
P(6)	C(32), C(2), C(3), C(35)	+0.1800	-0.5825	+0.7926	+2.4146	0.046
P(7)	^a	-0.8984	+0.0037	+0.4391	+0.0695	-

2. Interplanar angles (deg)

P(1)-P(2): 53(1)	P(3)-P(4): 80(2)
P(1)-P(3): 28(1)	P(4)-P(5): 56(1)
P(2)-P(3): 25(1)	P(4)-P(6): 49(1)
P(3)-P(5): 88(2)	P(5)-P(6): 105(2)
P(3)-P(6): 77(2)	P(3)-P(7): 2(1)

^a P(7) = plane which bissects P(1) and P(2).

Experimental

1. Preparative studies

All operations were performed under pure dinitrogen. Solvents were purified by standard methods and degassed just before use. The IR spectrum was measured on a Perkin-Elmer 557 spectrometer. ¹H, ¹³C and ¹⁹F spectra were recorded on a JEOL FX 100 spectrometer operating in the FT model. The mass spectrum was obtained with a Varian MAT 311 spectrophotometer. All chemical analyses were performed by Centre de Microanalyse du CNRS, France.

Tetracyclopentadienylniobium was prepared as previously described [23].

Synthesis. A mixture of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2]$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ (HFB/Nb ca. 2) in toluene was stirred at room temperature for ca. 4 days. After concentration under reduced pressure, the solution was chromatographed on a Florisil column. Elution with a 1/1 $\text{CH}_2\text{Cl}_2/\text{THF}$ mixture and concentration gave grayish microcrystals (yield ca. 10%).

Analysis. Found: C, 48.3; H, 3.5; F, 23.4. $\text{C}_{19}\text{H}_{15}\text{F}_6\text{NbO}$ calcd.: C, 48.9; H, 3.2; F, 25.3%.

Mass spectrum. The parent peak P^+ was found at m/e 466.0059 (calcd. for $\text{C}_{19}\text{F}_6\text{H}_{15}\text{NbO}$ 466.0090).

NMR spectra (solvent: CDCl_3). ¹H (TMS): δ 3.68,s, H(31); 4.30,s, H(32) and

H(35); 5.96, s, $\eta^5\text{-C}_5\text{H}_5$; 6.83, s, H(33) and H(34) ppm (for the atom-numbering system see Fig. 1). ^{13}C (TMS): δ 62.5, s, C(32) and C(35); 110.6, s, $\eta^5\text{-C}_5\text{H}_5$; 140.8, s, C(33) and C(34) ppm. ^{19}F ($\text{CF}_3\text{CO}_2\text{D}$): δ 16.1, s, CF_3 ppm.

IR spectrum: 980, m, $\nu(\text{Nb}=\text{O})$; 1100–1200, vs, $\nu(\text{C}-\text{F})$; 1680, m, $\nu(\text{C}=\text{C})$ cm^{-1} .

2. Crystallographic studies

X-ray data collection. Grayish crystals, slightly unstable in the air were obtained by recrystallisation from dichloromethane.

Crystal data. $\text{C}_{19}\text{F}_6\text{H}_{15}\text{NbO}$. $M = 466.00$, monoclinic; a 7.983(2), b 27.600(7), c 8.689(2) Å, β 113.22(2)°, V 1759 Å³, D_m 1.73(3) g cm⁻³, $Z = 4$, $D_c = 1.76$ g cm⁻³, Mo- K_α radiation, λ 0.7107 Å, $\mu(\text{Mo-}K_\alpha)$ 6.5 mm⁻¹, space group: $P2_1/n$.

Preliminary cell dimensions and the space group were determined from Weissenberg and precession photographs. The crystal selected for X-ray analysis, of approximate dimensions 0.05 × 0.22 × 0.35 mm, was sealed in a Lindemann tube. Data were collected on an ENRAF–NONIUS CAD-4 automatic four circle diffractometer (Centre de diffractométrie automatique de LYON-FRANCE). Unit cell dimensions given above were determined from a least-squares treatment of 25 independent reflections by using Mo- K_α radiation with a graphite monochromator. Intensity data for reflections with $\theta < 26^\circ$ were collected using the ω - 2θ scan method. Two standard reflections, scanned every 100 reflections, were used to place the intensity data on a common scale; systematic variations in these standards were not observed. Of 3125 reflections originally scanned, 877 unique ones with $I > 2.5 \sigma(I)$ were used in subsequent calculations. The intensities and $\sigma(I)$ values were corrected for Lorentz and polarization effects but no absorption corrections were applied. The scattering factors were taken from International Tables for X-ray Crystallography [24].

Structure solution and refinement. The structure was solved using the heavy atom method which employed a three-dimensional Patterson synthesis to locate the position of the niobium atoms. The remaining non-hydrogen atoms were located in subsequent electron-density maps. The function minimized in the refinement was $[\sum w^{1/2}(F_0 - |F_c|)/w^{1/2}F_0]$ with $w^{1/2} = 1$ if $F_0 < P_1$ and $w^{1/2} = P_1/F_0$ if $F_0 > P_1$ with $P_1 = (F_{0\text{max}}^2/10)^{1/2}$.

Final refinement with anisotropic temperature factors for all the non-hydrogen atoms excepted F gave $R_w = 0.112$. During the final stage of refinement, no parameter shifted by more than 0.25σ . Refinement to a higher accuracy proved impossible. This is probably due to: (i) important thermal motion of the fluorine atoms, (ii) absorption effects due to the shape of the crystal (although μ is low). Although the R factor reached in this structure is not very good, it is clear that we obtained an adequate description of the molecular structure of the complex.

Final positional and thermal parameters are listed in Table 1. Interatomic distances and angles with estimated standard deviations are given in Table 2. Relevant least squares plane data for selected atomic groups are listed in Table 3. The atom-numbering system and the configuration of the molecule are illustrated in Fig. 1. Tables of observed and calculated structure factors are available on request from the authors.

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