Unprecedented formation of ethylene during the synthesis of a Nb–Rh bimetallic complex: molecular structure of $Cp'_2Nb(\mu\text{-}PPh_2)_2RhC_2H_4$

Georgii I. Nikonov [a,*], Dmitry A. Lemenovskii [a,*], Ludmila G. Kuzmina [b]

[a] Chemistry Department, Moscow State University, 119889 Moscow, Russia
[b] Institute of General and Inorganic Chemistry, Russian Academy of Science, Leninsky prosp. 31, 117907 Moscow, Russia

Abstract

Reaction between $Cp'_2Nb(PPh_2)_2Li$ and $(ClRhCOD)_2$ (COD = cyclooctadiene) in tetrahydrofuran followed by the treatment of the reaction product with Et_2O leads to the unprecedented formation of coordinated ethylene to give the new heterobimetallic complexes $Cp'_2Nb(PPh_2)_2RhC_2H_4$ (Cp = C_5H_5 (1a); Cp' = $C_5H_4CH_3$ (1b)) and LiCl. The structure of 1 was established spectroscopically (for 1a), and by X-ray diffraction (for 1b). 1b: P-1 (Z = 2) with $a = 10.363(2)$ Å, $b = 10.605(2)$ Å, $c = 17.629(4)$ Å, $\alpha = 77.11(3)°$, $\beta = 74.66(3)°$, $\gamma = 61.51(3)°$ and $V = 1631.37$ Å^3, $R = 6.07$, $R_W = 6.38$ and $G = 3.734$. The geometry at rhodium is pseudotriangular, the $Nb(\mu\text{-}P_2)RhC_2$ fragment being almost planar; the Nb–Rh bond distance is 2.869(2) Å.

Keywords: Niobium; Rhodium

1. Introduction

Bimetallic complexes containing both early and late transition metals have attracted sustained attention [1,2]. Interest in the early–late heterobimetallics (ELHB) is substantiated by their potential ability to serve as catalysts for important industrial and fine chemical processes [1,3]. The chemistry of ELHBs, containing Group 5 metals, is comparatively undeveloped [4]. However, one can expect these species to exhibit an interesting reactivity, owing to the easy accessibility of various oxidation states on the Group 5 metals, and the flexibility of their coordination sphere for rearrangements. In a previous paper [5], we described the synthesis of a novel potential organometallic bisphosphido anionic ligand $Cp_2Nb(\mu\text{-}PPh_2)_2^-$; here we report its use in the preparation of a new niobium–rhodium mixed-metal complex.

2. Results and discussion

2.1. $Cp_2Nb(\mu\text{-}PPh_2)RhC_2H_4$

$Cp_2Nb(PPh_2)_2Li$ reacts readily with 0.5 equivalents of $(ClRhCOD)_2$ (COD = cyclooctadiene) in tetrahydro-

furan (THF) to form a red oily substance. Dissolving this material in Et_2O, followed by slow removal of the solvent in vacuo, resulted in the formation of 1a, as a microcrystalline substance; according to the ^1H NMR spectrum of the initial crude product, the yield was about 80%. Recrystallization from THF afforded large red crystals of 1a with a yield of about 40%:

$$Cp_2Nb(PPh_2)_2Li$$
$$+ \tfrac{1}{2}(CODRhCl)_2$$
$$\xrightarrow[\text{(2) }Et_2O]{\text{(1) THF}} Cp_2Nb(\mu - PPh_2)_2RhC_2H_4 \qquad (1)$$
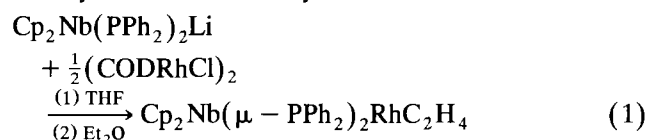
The ^1H NMR spectrum of 1a (THF-d_8) showed the presence of coordinated ethylene (doublet at $\delta = 3.00$ ppm, $J_{Rh-H} = 2.1$ Hz); Cp protons appear as a slightly broadened singlet at $\delta = 4.61$ ppm. A ^{13}C NMR spectrum (dioxane-d_8) supports the presence of C_2H_4 ($\delta = 67.90$ ppm), and no signals attributable to COD were observed.

In order to obtain good crystals, we also prepared a methyl-substituted cyclopentadienyl compound (1b), analogous to 1a, by the reaction of $Cp'_2Nb(PPh_2)_2Na$ [5] with $(ClRhCOD)_2$. Crystals of 1b, suitable for an X-ray diffraction study, were grown directly from ether solution, kept at room temperature overnight. An X-ray analysis of 1b confirmed the presence of coordinated ethylene, but not that of the expected COD ligand.

* Corresponding authors.
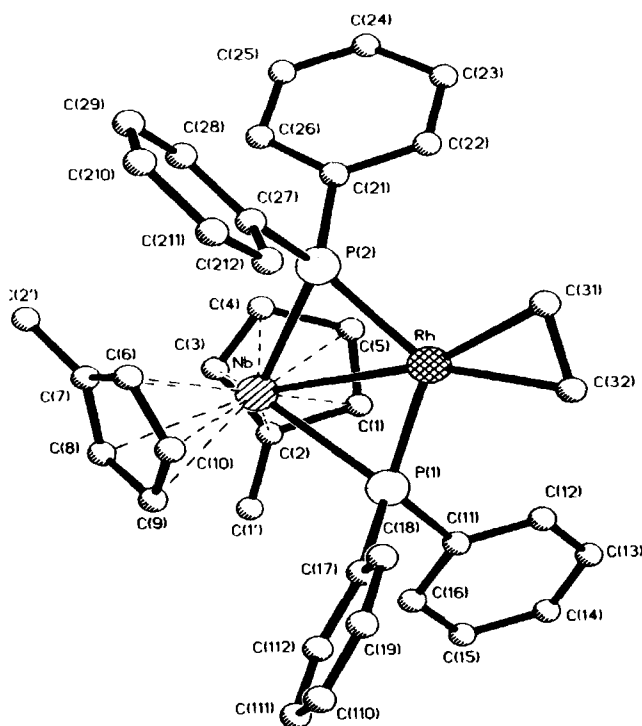
Fig. 1. Molecular structure of **1b**.

Compound **1a** turned out to be markedly reactive; it decomposes in toluene solution to give a mixture of products, probably owing to reactions with the solvent. Prolonged storage of **1a** in Et_2O also results in a decomposition reaction, while THF solutions, on the other hand, seem to be more stable. Nevertheless, heating a THF-d_8 solution of **1a** at 45°C for 1.5 h in an NMR tube results in partial elimination of ethylene (a singlet at $\delta = 5.36$ ppm), and the appearance of a broad singlet at 4.40 ppm; the latter is assigned to the Cp protons of $Cp_2Nb(\mu\text{-}PPh_2)_2Rh \cdot THF$. A thorough exploration of the reactivity of **1a** will be the subject of further investigations.

2.2. Structure of $Cp'_2Nb(\mu\text{-}PPh_2)_2RhC_2H_4$

The molecular structure of **1b** was determined by a single-crystal X-ray diffraction study (Fig. 1 and Table 1). Selected bond lengths and angles are listed in Tables 2 and 3. Neglecting the RhC_2H_4 moiety for a moment, the geometry at niobium is pseudotetrahedral, typical for bent metallocene complexes. The cyclopentadienyl rings are eclipsed; the methyl substituents are in a *trans* orientation. The Nb–X (X = centroid of the Cp ring) distances of 2.087–2.11 Å are almost identical with those in Cp_2NbCl_2 (2.09 Å) [6] and in some Nb(V) metallocenes (2.10–2.13 Å) [7,8]. The X(1)–Nb–X(2) angle (132.5°) falls within the range found for Nb(IV) and Nb(V) biscyclopentadienyls [8].

The Nb–P(1) and Nb–P(2) bond lengths (2.555(6)

and 2.602(5) Å respectively) are shorter than the Nb–P (P–phosphido) distances in $Cp_2Nb(CO)PPh(^iPr)$ (2.633 and 2.644 Å) [9]. This may be attributed to the diminished repulsion between the non-bonding orbital $1a_1$ [10] at niobium and the phosphorous lone pair, upon complexation with rhodium. The P(1)–Nb–P(2) angle (94.7(2)°) falls within the range calculated for the d^0 and d^1 Cp_2MY_2 complexes [10]. The $Nb(\mu\text{-}P)_2RhC_2$ fragment is almost planar, the mean deviation from a best plane being 0.066 Å. The NbP_2Rh ring is slightly puckered; the dihedral angle between the Nb(P1)Rh and Nb(P2)Rh planes is 10.3°. There is a minor deviation from symmetry in the $Nb(\mu\text{-}P)_2Rh$ core, since the P(1)–Nb and P(1)–Rh bonds are shorter than those for

Table 1
Positional parameters and their estimated standard deviations for $Cp'_2Nb(\mu\text{-}PPh_2)_2RhC_2H_4$

Atom	x	y	z	U_{iso} / U_{eq}
Nb(1)	1.2273(2)	−0.0985(2)	0.2434(1)	0.0232(9)
Rh	1.2024(1)	−0.3512(1)	0.2315(1)	0.0242(8)
P(1)	1.0030(5)	−0.1518(5)	0.2675(3)	0.027(2)
P(2)	1.4250(5)	−0.3635(5)	0.2243(3)	0.033(2)
C(1)	1.135(1)	0.009(1)	0.118(1)	0.00(6) [a]
C(2)	1.126(2)	0.126(2)	0.154(1)	0.04(1)
C(3)	1.281(2)	0.083(2)	0.152(1)	0.05(1)
C(4)	1.372(2)	−0.044(2)	0.123(1)	0.03(1)
C(5)	1.285(2)	−0.091(2)	0.101(1)	0.07(1)
C(6)	1.331(3)	−0.179(2)	0.363(1)	0.10(2)
C(7)	1.345(2)	−0.049(2)	0.328(1)	0.03(1)
C(8)	1.199(2)	0.066(2)	0.329(1)	0.022(9)
C(9)	1.100(2)	0.002(2)	0.365(1)	0.04(1)
C(10)	1.188(3)	−0.148(2)	0.384(1)	0.08(2)
C(21)	1.574(2)	−0.391(2)	0.136(1)	0.04(1)
C(22)	1.581(2)	−0.467(2)	0.080(1)	0.04(1)
C(23)	1.696(2)	−0.498(2)	0.011(1)	0.07(2)
C(24)	1.797(2)	−0.438(2)	−0.000(1)	0.03(1)
C(25)	1.791(2)	−0.369(2)	0.054(1)	0.04(1)
C(26)	1.681(2)	−0.340(2)	0.123(1)	0.017(9)
C(27)	1.533(2)	−0.481(2)	0.302(1)	0.03(1)
C(28)	1.673(2)	−0.505(2)	0.304(1)	0.03(1)
C(29)	1.744(3)	−0.597(3)	0.366(1)	0.04(1)
C(210)	1.671(3)	−0.655(2)	0.428(1)	0.08(2)
C(211)	1.532(3)	−0.629(2)	0.426(1)	0.06(2)
C(212)	1.463(3)	−0.545(2)	0.364(1)	0.10(2)
C(11)	0.852(2)	−0.042(2)	0.211(1)	0.027(9)
C(12)	0.845(2)	−0.092(2)	0.148(1)	0.05(1)
C(13)	0.737(2)	0.189(2)	0.100(1)	0.05(1)
C(14)	0.641(2)	0.132(2)	0.114(1)	0.03(1)
C(15)	0.650(2)	0.189(2)	0.173(1)	0.05(1)
C(16)	0.758(2)	0.105(2)	0.222(1)	0.03(1)
C(17)	0.891(2)	−0.159(2)	0.368(1)	0.05(1)
C(18)	0.928(3)	−0.296(2)	0.412(1)	0.08(2)
C(19)	0.850(3)	−0.311(3)	0.488(1)	0.10(2)
C(110)	0.746(3)	−0.200(3)	0.522(1)	0.11(2)
C(111)	0.700(2)	−0.054(2)	0.483(1)	0.04(1)
C(112)	0.780(2)	−0.043(2)	0.406(1)	0.04(1)
C(31)	1.258(2)	−0.565(2)	0.216(1)	0.017(8)
C(32)	1.100(2)	−0.483(2)	0.230(1)	0.06(1)
C(1')	0.990(2)	0.262(2)	0.174(1)	0.06(1)
C(2')	1.480(2)	−0.022(3)	0.301(1)	0.04(1)

[a] The C(1) atom is non-positive defined.

P(2). The short Nb–Rh distance (2.869(2) Å), although somewhat more than the sum of metal radii (2.80 Å) [11], unequivocally indicates the presence of a metal-metal bond, compared with other bimetallic niobocene complexes [12].

The geometry at rhodium is unprecedented, in that the rhodium lies in the distorted triangle formed by two phosphorus atoms and the center of the ethylene ligand. Some related isoelectronic complexes of the formula $Cp_2M(\mu\text{-}PR_2)_2M'L$ have been recently reported for $M = Hf$ or Zr and $M' = Pd$ or Pt by Baker et al. [2] The Rh–P(1) and Rh–P(2) bonds are the shortest reported to date for rhodium-containing bimetallics with phosphido bridges [12]. We failed to find any structurally characterized terminal phosphido rhodium complexes. The Rh–P (P–phosphine) bond length lies in the range from 2.200 Å in $((Ph_3P)_2RhCl)_2$ [13] to 2.320 Å in $Cp_2Zr(\mu\text{-}PPh_2)_2Rh(CO)(H)(PPh_3)$ [12b].

The origin of the coordinated ethylene in **1** is the most intriguing aspect of this study; it is evident that it could be derived either from the COD ligand or from the solvents. However, treatment with Et_2O seems to be necessary for the formation of **1**, since it is not possible to isolate **1** directly from the reaction mixture by evaporating THF and, moreover, there are no signals for ethylene in the ^1H NMR spectrum (THF-d_8) of the reaction mixture. Therefore we suppose that ethylene is more likely to originate from Et_2O. However, as a whole the mechanism is not yet clear and we hope that the planned labeling experiment will elucidate this problem.

3. Experimental section

All manipulations were carried out in vacuo using conventional Schlenk techniques. Solvents were dried

Table 2
Selected bond distances (Å) for $Cp'_2Nb(\mu\text{-}PPh_2)_2RhC_2H_4$

Nb(1)–Rh	2.869(2)	Nb(1)–P(1)	2.555(6)
Nb(1)–P(2)	2.602(5)	Nb(1)–C(1)	2.46(2)
Nb(1)–C(2)	2.47(2)	Nb(1)–C(3)	2.40(2)
Nb(1)–C(4)	2.38(2)	Nb(1)–C(5)	2.42(2)
Nb(1)–C(6)	2.42(2)	Nb(1)–C(7)	2.43(2)
Nb(1)–C(8)	2.41(2)	Nb(1)–C(9)	2.38(2)
Nb(1)–C(10)	2.38(2)	Rh–P(1)	2.209(5)
Rh–P(2)	2.218(6)	Rh–C(31)	2.12(2)
Rh–C(32)	2.13(2)	P(1)–C(11)	1.84(2)
P(1)–C(17)	1.86(2)	P(2)–C(21)	1.84(2)
P(2)–C(27)	1.84(2)	C(1)–C(2)	1.47(2)
C(1)–C(5)	1.40(3)	C(2)–C(3)	1.44(4)
C(2)–C(1')	1.49(3)	C(3)–C(4)	1.35(3)
C(4)–C(5)	1.38(3)	C(6)–C(7)	1.44(3)
C(6)–C(10)	1.32(4)	C(7)–C(8)	1.42(3)
C(7)–C(2')	1.50(4)	C(8)–C(9)	1.43(3)
C(9)–C(10)	1.42(3)	C(31)–C(32)	1.42(3)
Nb–X(1) [a]	2.111	Nb–X(2) [a]	2.087

[a] X(1) and X(2) are the gravity centers of the cyclopentadienyl rings.

Table 3
Selected bond angles (°) for $Cp'_2Nb(\mu\text{-}PPh_2)_2RhC_2H_4$

Rh–Nb(1)–P(1)	47.6(1)	Rh–Nb(1)–P(2)	47.5(1)
P(1)–Nb(1)–P(2)	94.7(2)	Nb(1)–Rh–P(1)	58.7(1)
Nb(1)–Rh–P(2)	59.9(1)	Nb(1)–Rh–C(31)	161.9(5)
Nb(1)–Rh–C(32)	158.9(6)	P(1)–Rh–P(2)	117.9(2)
P(1)–Rh–C(31)	139.3(5)	P(1)–Rh–C(32)	100.4(6)
P(2)–Rh–C(31)	102.0(5)	P(2)–Rh–C(32)	141.1(6)
C(31)–Rh–C(32)	39.2(8)	Nb(1)–P(1)–Rh	73.7(2)
Nb(1)–P(1)–C(11)	120.3(6)	Nb(1)–P(1)–C(17)	121.2(7)
Rh–P(1)–C(11)	124.6(6)	Rh–P(1)–C(17)	118.1(7)
C(11)–P(1)–C(17)	99.9(9)	Nb(1)–P(2)–Rh	72.5(2)
Nb(1)–P(2)–C(21)	116.8(6)	Nb(1)–P(2)–C(27)	121.4(6)
Rh–P(2)–C(21)	126.8(6)	Rh–P(2)–C(27)	117.8(6)
C(21)–P(2)–C(27)	101.4(9)	C(2)–C(1)–C(5)	108(1)
C(1)–C(2)–C(3)	102(2)	C(1)–C(2)–C(1')	127(2)
C(3)–C(2)–C(1')	131(2)	C(2)–C(3)–C(4)	113(2)
C(3)–C(4)–C(5)	108(2)	C(1)–C(5)–C(4)	109(2)
C(7)–C(6)–C(10)	109(2)	C(6)–C(7)–C(8)	108(2)
C(6)–C(7)–C(2')	131(2)	C(8)–C(7)–C(2')	121(2)
C(7)–C(8)–C(9)	105(2)	C(8)–C(9)–C(10)	108(2)
C(6)–C(10)–C(9)	110(2)	P(2)–C(21)–C(22)	118(1)
P(2)–C(21)–C(26)	124(1)	P(2)–C(27)–C(28)	125(2)
P(2)–C(27)–C(212)	117(2)	P(1)–C(11)–C(12)	121(1)
P(1)–C(11)–C(16)	120(1)	P(1)–C(17)–C(18)	117(2)
P(1)–C(17)–C(112)	127(2)	Rh–C(31)–C(32)	71(1)
Rh–C(32)–C(31)	70(1)	X(1)–Nb–X(2) [a]	132.5
Cp(1)–Cp(2) [b]	132.1		

[a] X(1) and X(2) are the gravity centers of the cyclopentadienyl rings.
[b] Cp(1)–Cp(2) denotes the angle between the normals to the cyclopentadienyl rings.

over sodium benzophenone ketyle and distilled into the reaction vessel by high vacuum gas phase transfer. $(ClRhCOD)_2$ was prepared according to the literature [14]. NMR spectra were recorded on a Varian VXR-400 spectrometer (^1H, 400 MHz; ^{13}C, 100.4 MHz). Elemental analysis was conducted in the analytical laboratory of the Chemistry Department of Moscow University.

3.1. Preparation of $Cp_2Nb(\mu\text{-}PPh_2)_2RhC_2H_4$ (**1a**)

0.423 g (0.705 mmol) of $Cp_2Nb(PPh_2)_2Li$, dissolved in 5 ml of THF, was added to a suspension of 0.173 g (0.351 mmol) of $(ClRhCOD)_2$ in 5 ml of THF. The resulting red–brown solution was decanted, and all volatiles were removed in vacuo. 20 ml of Et_2O was added to the red–brown residue. The solution was kept for 3 days at room temperature; then the solvent was removed in vacuo. The residue was dissolved in 5 ml of THF, and the solution slowly concentrated in vacuo overnight. Large red crystals covered with oil were obtained. The crystals were washed with cold THF and dried in vacuo (yield, 0.110 g, 0.152 mmol (43,3%)).

^1H NMR (THF-d_8): δ 7.78, 7.26 and 7.17 (m, 20, Ph), 4.61 (s, 10, Cp), 3.00 (d, $J_{Rh-H} = 2.0$ Hz, C_2H_4) ppm. ^{13}C NMR (THF-d_8): δ 95.95 (Cp) ppm. ^1H NMR (dioxane-d_8): δ 7.80, 7.26–7.12 (m, 20, Ph), 4.44 (s, 10, Cp), 2.99 (d, $J_{Rh-H} = 2.0$ Hz, C_2H_4) ppm. ^{13}C

Table 4
Crystal data and parameters of the crystallographic data collection

Empirical formula	$C_{38}H_{38}P_2NbRh$
Colour	Red
Crystal size (mm)	$0.24 \times 0.25 \times 0.43$
Crystal system	Triclinic
Space group	$P-1$
Unit-cell parameters:	
a (Å)	10.364(2)
b (Å)	10.605(2)
c (Å)	17.628(4)
α (°)	77.11(3)
β (°)	74.66(3)
γ (°)	61.51(3)
Z	2
Wavelength	0.71073
Density (calculated) (g cm^{-3})	1.537
Absorption coefficient (mm^{-1})	0.96
$F(000)$	818
Temperature (K)	293
2θ range (°)	3–50
Scan mode	ω
Number of reflections collected	5340
Number of absorbed reflections ($F > 4.0\sigma(F)$)	2690
Absorption correction	DIFABS
Weighting scheme	Unit
Final R indices (observed data)	
R	0.0607
R_w	0.0638
R indices (all data)	
R	0.0889
R_w	0.0889
Goodness of fit	$S = 3.74$

NMR: δ 95.28 (Cp), 67.90 (s, C_2H_4) ppm. Anal. Found: C, 59.99; H, 4.87. $C_{36}H_{34}NbRhP_2$ calc.: C, 59.68; H, 4.73%.

3.2. Preparation of Cp′₂Nb(μ-PPh₂)₂RhC₂H₄ (1b)

Compound **1b** was prepared in an analogous way from Cp′₂Nb(μ-PPh₂)₂Na. Crystals suitable for X-ray diffraction study were grown in a small amount from an etheral solution of **1b** at room temperature.

^{1}H NMR (THF-d_8): δ 7.78, 7.25–7.10 (m, 20, Ph), 4.63 and 4.53 (bs, 10, C₅H₄Me), 3.03 (d, $J_{Rh-H} = 2.0$ Hz, C₂H₄), 1.85 (s, 6, Me) ppm.

3.3. X-ray diffraction study of 1b

Relevant crystallographic data are given in Table 4. Unit-cell parameters were determined from least-squares refinement of a set of 25 centered reflections. Two reflections were measured every 2 h as orientation and intensity check; significant decay of intensity was not observed. Heavy atoms were located from Patterson synthesis, and the remaining non-hydrogen atoms were found in the Fourier map. Full-matrix least-squares refinement of the structure was made with SHELX-76

[15]. After isotropic refinement, absorption correction was carried out with anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were kept at calculated positions, and were refined groupwise together with the positions of the corresponding carbon atom by a riding model with fixed isotropic thermal parameters ($U = 0.08$). Owing to the poor quality of the crystal, the final discrepancy factor and error of atomic coordinates are rather high, but the overall structure is reliable and allows discussion of its general features.

Acknowledgments

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