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Synthesis and structure of the phosphinophosphide niobocene complex $Cp_2Nb(PPh_2)(PHPh_2)$

Georgii I. Nikonov[a,*], Dmitry A. Lemenovskii[a], Konstantin Yu. Dorogov[a], Andrei V. Churakov[b]

[a] *Chemistry Department, Moscow State University, Vorob'evy Gory, 119899 Moscow, Russia*
[b] *Institute of General and Inorganic Chemistry, RAS, Leninsky prosp. 31, 117907 Moscow, Russia*

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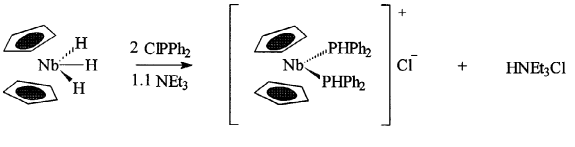
Abstract

The phosphinophosphido niobocene complex $Cp_2Nb(PHPh_2)(PPh_2)$ (**2**) was prepared by deprotonation of the cationic diphosphino complex $[Cp_2Nb(PHPh_2)_2]Cl$ (**3**). Complex **2** is thermally unstable and readily dissociates phosphine to give the *ortho*-metallated complex $Cp_2Nb(PHPhC_6H_4-)$. Crystal structure determination of **2** supported its formulation as the phosphinophosphido compound. The Nb–P(1) (phosphino) bond length is 2.524(2) Å and Nb–P(2) (phosphido) bond length is 2.610(2) Å. © 1999 Elsevier Science Ltd. All rights reserved.

Recently there has been an increased interest in the chemistry of early transition metal phosphido complexes [1–49]. Much of this interest has focused on the known ability of these compounds to form stable phosphido-bridged bimetallic complexes [19–34], although the high reactivity of the phosphido moiety in other reactions was also studied [35–47]. We were interested to prepare complexes with neighbouring hydrido and phosphido ligands that could exhibit a richer reactivity. We found that the cationic dihydridephosphino complex $[Cp_2NbH_2(PHPh_2)]^+$ can be deprotonated to give initially the dihydridephosphido complex $Cp_2NbH_2(PPh_2)$ that rapidly rearranges into $Cp_2NbH(PHPh_2)$, whereas the analogous tantalocene complex $Cp_2TaH_2(PPh_2)$ was found to be quite stable towards further transformations [48,49]. The closely related diphosphorus substituted hydride complexes could, in principle, also exist in two isomeric forms, namely, $Cp_2NbH(PPh_2)_2$ (**A**) and $Cp_2Nb(PPh_2)(HPPh_2)$ (**B**). For the methyl ring-substituted compound $Cp'_2Nb(PPh_2)(HPPh_2)$ (**1**) ($Cp'=C_5H_4Me$) only the form **B** was observed. However, the nonequivalence of the cyclopentadienyl protons in **1** and its little thermal stability complicated further studies. Therefore, we set out to prepare the unsubstituted analogue of **1**, i.e. complex $Cp_2Nb(PPh_2)(HPPh_2)$ (**2**), that has more explicit NMR features.

1. Results and discussion

The easiest route to complex **2** is via deprotonation of the cationic diphosphino complex $[Cp_2Nb(PHPh_2)_2]Cl$ (**3**). Three-step synthesis of the latter compound, using the insertion/deprotonation technique (Scheme 1), has been previously reported [48]. Now we report that complex **3** can be conveniently prepared in a one-pot synthesis shown below (1).



(1)

3

Apparently, this reaction proceeds via the same steps which are shown in Scheme 1. However, the strength of the base NEt_3 is not sufficient to effect significant deprotonation of **3** to give **2**, i.e. in this case, the equilibrium in (2) is shifted towards **3**. Complete deprotonation of **3** was achieved using aqueous NaOH. Complex **2** was isolated as oily red crystals and is highly air sensitive. The ^1H NMR spectrum of **2** obtained

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[*] Corresponding author. Fax: +7-095-932-88-46; e-mail: nikonov@org.chem.msu.su

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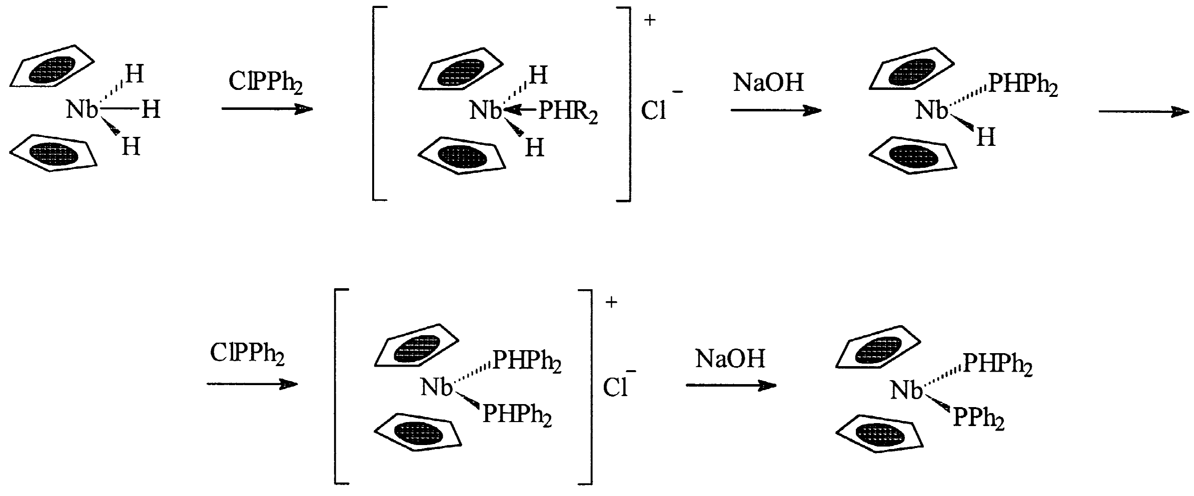
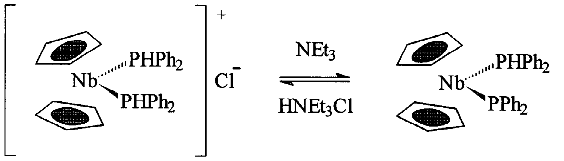


3 **2**

Scheme 1.



(2)

3 **2**

at 400 MHz shows only one signal for the cyclopentadienyl protons that appears as a triplet at 4.42 ppm ($J_{P-H} = 1.8$ Hz), consistent with the formation of the form **A**. However, a hydride signal was not observed. Also, the ^{31}P NMR spectrum of **2** shows the presence of two nonequivalent phosphorus centres with the resonances at 66.2 and 5.9 ppm, expected for the form **B**. The latter formulation was further supported by a X-ray diffraction study. Therefore, the triplet signal for the cyclopentadienyl protons is in fact composed of two overlapping doublets due to coupling to two nonequivalent phosphorus atoms with similar J_{P-H} and the structure of **2** is analogous to **1**. We expected that the phosphino and phosphido centres in **2** could be in a degenerated exchange, probably, via the diphosphidohydride form **A**. This exchange would result in a coalescence of the phosphorus resonances at higher temperatures. However, complex **2** was found to be thermally unstable, like its methyl substituted analogue **1**. Even at room temperatures it releases free $HPPh_2$ to give the previously described *ortho*-metallated product $Cp_2Nb(PHPh-C_6H_4-)$ [4a].

The formulation of **2** as the phosphidophosphine derivative **B** was confirmed by an X-ray structure determination. The molecular structure of **2** is shown in Fig. 1 and selected bond lengths and angles are given in Tables 2 and 3. Complex **2** has a disubstituted metallocene geometry, typical for d^2 niobocene complexes of the type Cp_2NbXL. The cyclopentadienyl rings are in an eclipsed conformation. The Nb–P bond distances are 2.524(2) Å for the niobium–phosphino bond and 2.610(2) Å for the niobium–phosphido bond. In the only one previously reported phosphido derivative of niobocene, complex $Cp_2Nb(CO)(PPhPr^i)$, the Nb–P bond lengths are 2.644(3) Å and 2.622(3) Å for two crystallographically independent molecules [50]. The reported niobium–phosphino bond lengths lay in the range 2.462–2.579 Å [51]. The P(1)–Nb–P(2) bond angle is 87.70(5)°, close to the value found for other d^2 niobocene derivatives and the calculated value for the d^2 complexes Cp_2MXY [52]. The P–H bond distance of 1.24(5) Å observed in **2** is somewhat shorter than the sum of covalent radii (1.40 Å) and also than the

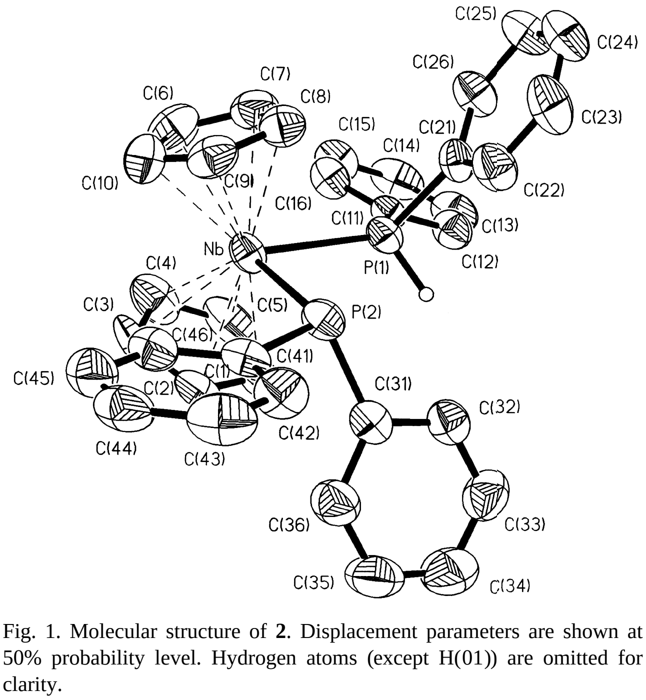


Fig. 1. Molecular structure of **2**. Displacement parameters are shown at 50% probability level. Hydrogen atoms (except H(01)) are omitted for clarity.

Table 1
Crystal data and details of data collection and structure refinement for **2**

Empirical formula	$C_{34}H_{31}NbP_2.C_7H_8.0.5C_7H_8$
Temperature	183(2)
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	$a=12.847(3)$ Å
	$b=14.134(3)$ Å
	$c=20.124(4)$ Å
	$\beta=90.72(3)$
Volume	3653.8(14) $Å^3$
Z	4
Theta range for data collection	1.76 to 20.14°
Index ranges	$-12\leq h\leq 12$, $0\leq k\leq 13$, $-19\leq l\leq 0$
Reflections collected	3221
Independent reflections	3121
refinement method	full-matrix-least-squares on F^2
R_{int}	.0404
Data/restraines/parameters	3118/17/425
Goodness -of-fit on F^2	1.065
Final R indices (all data 3121)	$R_1=0.0506$, $wR_2=0.0949$
R indices [2487 with $I>2\sigma(I)$]	$R_1=0.0337$, $wR_2=0.0891$
Largest diff. peak and hole	0.528 and −0.339 e/$Å^3$

Table 2
Selected bond lengths (Å) for **2**

Nb–P(1)	2.524(2)	Nb–P(2)	2.610(2)
P(1)–C(21)	1.833(5)	P(2)–C(31)	1.831(5)
P(1)–C(11)	1.843(5)	P(2)–C(41)	1.852(5)
Nb–C(1)	2.342(5)	Nb–C(6)	2.402(6)
Nb–C(2)	2.404(5)	Nb–C(7)	2.374(5)
Nb–C(3)	2.408(5)	Nb–C(8)	2.358(5)
Nb–C(4)	2.370(5)	Nb–C(9)	2.387(5)
Nb–C(5)	2.348(6)	Nb–C(10)	2.406(6)
P1–H(01)	1.24(5)		

Table 3
Selected bond angles for **2**

P(1)–Nb–P(2)	87.70(5)	C(21)–P(1)–C(11)	100.1(2)
C(21)–P(1)–Nb	119.2(2)	C(11)–P(1)–Nb	119.8(2)
C(31)–P(2)–C(41)	99.0(2)	C(31)–P(2)–Nb	112.3(2)
C(41)–P(2)–Nb	113.2(2)	Nb–P1–H01	118(2)

P–H bond found in the phosphinobromide complex $Cp_2NbBr(PHPr^i_2)$ (1.51 Å) [51]. This difference can be attributed to the influence of the Ph rings. In the cationic diphosphite complex $[Cp_2Nb(PH(OR)_2)_2]Cl$ the cooperative action of charge and electron-withdrawing alkoxy groups results in much shorter P–H bonds of 1.0 Å [51].

2. Experimental

All manipulations were carried out in vacuo using conventional Schlenk techniques. Solvents were dried over sodium or sodium benzophenone ketyl and distilled into the reaction vessel by high vacuum gas phase transfer. NMR spectra were recorded on a Varian VXR-400 spectrometer (^1H, 400.0 MHz; ^{31}P 161.9 MHz). ^1H NMR spectra were referenced to the residual protiosolvent (relatively to $SiMe_4$). ^{31}P NMR spectra were referenced to 85% H_3PO_4 as external standard. Cp_2NbH_3 was prepared by the modified procedure as reported earlier [48]. $ClPPh_2$ was purchased from Merck.

2.1. Preparation of $[Cp_2Nb(PHPh_2)_2]Cl$ (3)

In a typical experiment 2 equivalents of $ClPPh_2$ are added to a toluene solution containing 1 equivalent of Cp_2NbH_3 and 1.1 equivalent of NEt_3 under rapid stirring. The mixture becomes red and an orange precipitate of complex **2** deposits. The mixture is stirred overnight to ensure the completeness of the reaction. The solution is filtered and the residue is washed by toluene until the washings are almost colourless. The material thus obtained is contaminated by $ClHNEt_3$ which can be removed by washing with THF. Alternatively, it can be used as obtained to make complexes **2** and $[Cp_2Nb(PPh_2)_2]Li$ by treatment with NaOH or excess BuLi, respectively. This procedure was used to make **3** on a 1–3 g scale. Example experiment: Cp_2NbH_3 (1.07 g, 4.73 mmol)/NEt_3 (0.73 ml, 5.20 mmol)/$ClPPh_2$ (1.70 ml, 9.46 mmol)/toluene (60 ml).

2.2. Preparation of $[Cp_2Nb(PHPh_2)(PPh_2)]$ (2)

0.848 g (1.34 mmol) of $[Cp_2Nb(PHPh_2)_2]Cl$ suspended in 30 ml of toluene was treated by 25 ml of 0.2 M aqueous NaOH. The mixture is intensively stirred with intensive grinding of the oily material formed until all the oil is dissolved in organic phase. The toluene solution is then separated and dried in vacuo. Recrystallization from ether of the material formed gives red oily crystals of **2**. The yield: 0.347 g (0.584 mmol, 43%). Thermal instability of this compound prevented obtaining satisfactory combustion analysis data.

^1H NMR (toluene-d_8): 6.9–7.6 (m, 20, Ph), 6.14 (half of doublet, 0.5, P–H), 4.42 (t, J(P–H)=1.8 Hz, 10, Cp). $^{31}P\{^1H\}$ NMR (toluene-d_8): 5.9 (bs, $PHPh_2$), 66.2 (bs, PPh_2).

2.3. Crystal structure determination

Red crystals of **2** were grown from toluene-d_8 solution on keeping at −26°C for three months. The crystal was covered by oil and mounted on an Enraf–Nonius CAD-4 diffractometer at −90°C. Crystallographic data are given in Table 1. The unit cell parameters were determined using 25 accurately centered reflections, two reflections were measured every 2 h for orientation and decay control. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [53] and refined by full-matrix least squares procedures [54]. Two toluene solvate molecules were found, one of them occupies a special position and is disordered. This molecule was refined only isotropically without hydrogen atoms. In the final cycles of refinement, all other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were found from Fourier difference syntheses and were refined isotropically using a ‘‘riding’’ model. The location and magnitude of the residual electron density was of no chemical significance.

Full details of crystallographic study including the atomic coordinates and displacement coefficients, hydrogen atom parameters, and a full list of bond lengths and angles for **2** have been deposited as supplementary data with the CCDS, deposition number 102173.

Acknowledgements

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