

The carbenoid nature of halophosphines. Carbene-like insertion mechanism in the reaction of chlorophosphines with Cp_2NbH_3

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Abstract

We have studied the reactivity of Cp_2NbH_3 (**1**) with different chlorophosphines and showed that all the reactions occur at the niobium-hydride bond and proceed by two competitive routes, via the direct insertion of a chlorophosphine into the Nb–H bond and electron or/and hydride transfer mechanism. Reaction of **1** with the unhindered dialkyl- and diaryl-chlorophosphines CIPR_2 ($\text{R} = \text{Et}, \text{Bu}, \text{Pr}^i, \text{Ph}$) gave the insertion product — the ionic complexes $[\text{Cp}_2\text{NbH}_2(\text{PHR}_2)]\text{Cl}$ (**2**) — in high yields. In contrast, reaction of **1** with the bulkier CIPBu_2 proceeded much slower and resulted in the steady formation of Cp_2NbCl_2 and HPBu_2 . Cp_2NbCl_2 was also the product of the reactions of **1** with excess of ClP(OEt)_2 and catecholechlorophosphine **7**. The reaction of **1** with one equivalent of cyclic chlorodiaminophosphine $\text{CIP}(\text{N}(\text{CH}_3)_2\text{CH}_2)_2$ (**5**) resulted in two competitive routes that led to the ionic complex $[\text{Cp}_2\text{NbH}_2(\text{HP}(\text{NR}_2)_2)]\text{Cl}$ (**2f**) and molecular complex $\text{Cp}_2\text{NbCl}(\text{HP}(\text{NR}_2)_2)$ (**6f**). The reaction of **1** with two equivalents of cyclic 1-chloro-5,5-dimethyl-1-phospha-2,6-dioxahexane gave cationic diposphite complex $[\text{Cp}_2\text{Nb}(\text{PHR}_2)_2]\text{Cl}$ (**8**) in high yield. This reactivity was explained in terms of the carbenoid nature of halophosphines due to the proposed relationship in the electronic structures of halophosphines and singlet methylene. Thus, reaction of **1** with the unhindered dialkyl- and diaryl-chlorophosphines proceeded by the direct insertion of a chlorophosphine ClPR_2 into the Nb–H bond whereas with the more electron withdrawing substituents R a phosphorus the electron or/and hydride transfer mechanisms, leading to **6** and eventually to Cp_2NbCl_2 , could be operative. This concept also allowed us to explain the reactivity of chlorophosphines toward different unsaturated organic products. The facile syntheses of complexes $\text{Cp}_2\text{Nb}(\text{PHR}_2)\text{Cl}$ (**6**) and $\text{Cp}_2\text{Nb}(\text{PHR}_2)_2\text{H}$ (**11**) by the thermolysis and deposition of **2**, respectively, was performed and the comparison with other methods was undertaken. Crystallographic studies of complexes **8** and $\text{Cp}_2\text{Nb}(\text{P}(\text{HPh})_2)_2\text{Br}$ are reported. © 1997 Elsevier Science S.A.

Keywords: Niobium; Hydrides; Chlorophosphine; Carbenoid; Insertion reactions

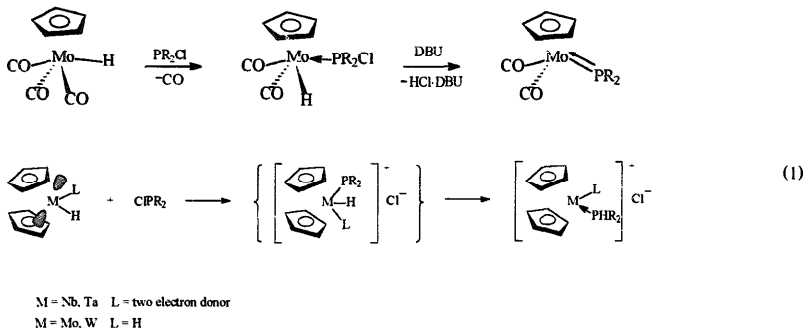
1. Introduction

The chemistry of phosphorus substituted early transition metal complexes has recently received a great deal of attention [1–6], mainly in the groups of Stephan [1], Baker [2] and Hey–Hawkins [3]. Metathetical and oxidative addition reactions are the common routes to these complexes. However, these methods sometimes give complex reaction mixtures requiring difficult work-up, or result in unexpected products [5]. Moise et al. have suggested an alternative approach based on the nucleophilic substitution of a halide in a halophosphine for a basic organometallic fragment, but until recently these reactions have been restricted only to the d^2 metallocenes [6].

During our search for alternative routes to phosphorus substituted complexes, we found that ClPPh_2 can insert directly into the M–H bond of Cp_2MH_3 ($\text{M} = \text{Nb}, \text{Ta}$) giving phosphino complexes $[\text{Cp}_2\text{MH}_2(\text{P}(\text{HPh})_2)]\text{Cl}$ [7]. Complexes of this type serve as very convenient starting materials to a variety of other phosphorus substituted

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metallocenes, including new precursors to early-late heterobimetallics [8]. Application of this insertion method to other group 15 monohalides led to the first arsenido [9] and bismuthido [10] complexes of the group 5 metallocenes. These findings raise general questions about the reactivity of transition metal–hydrogen bonds toward halophosphines. Such reactivity has not been studied before this work. The reactions of transition metal hydrides with halophosphines are believed to occur only at the metal center [6a, 11]. These reactions include the coordination of ClPR_2 via the phosphorus lone pair to a coordinatively unsaturated species, such as $\text{Cp}(\text{CO})_2\text{MoH}$ [11] (Eq. (1)), or substitution of a halide in HalPR_2 (Hal = halide) for a d^2 complex [6a] (Eq. (2)), followed by subsequent reactions with the M–H bond. The d^0 complex Cp_2NbH_3 (**1**) lacks both a metal centered lone pair and an available coordination site, thus presenting itself as a unique substrate to test the reactivity of halophosphines directly with a transition metal–hydrogen bond.

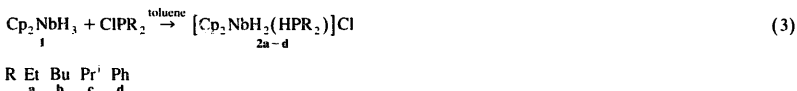


Here we report the first focused study of such reactivity, using the reaction between **1** and chlorophosphines ClPR_2 as an example. We have found that the reaction pathway depends on the substituent R. The unhindered dialkyl- and diaryl-chlorophosphines ClPR_2 exhibit an insertion reaction whereas the bulky and electron withdrawing group R favours another mechanism. The general concept of the carbenoid nature of halophosphines is proposed to explain this reactivity. Convenient methods for the preparation of a variety of new phosphorus substituted niobocenes are also presented.

2. Results and discussion

2.1. Reaction of Cp_2NbH_3 with unhindered chlorophosphines ClPR_2 (R = alkyl, aryl)

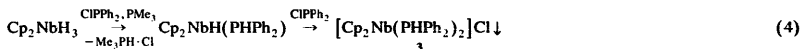
The interaction of Cp_2NbH_3 (**1**) with the unhindered dialkyl- and diaryl-chlorophosphines ClPR_2 (R = Et, Bu, Pr^i , Ph) occurs readily in aromatic and ethereal solvents, giving the ionic complexes $[\text{Cp}_2\text{NbH}_2(\text{PHR}_2)]\text{Cl}$ (**2**) [12] in high yields. For R = Et, Bu, Ph the complexes **2a**, **b**, **d** immediately precipitate as white voluminous flakes after mixing the reactants (Eq. (3)). For somewhat more hindered ClIPr_2 a small induction period of 6 s was observed.



The low solubility of the complexes **2** in hydrocarbon, ethereal and aromatic solvents provides for very easy isolation

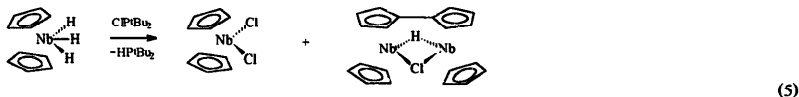
of the products in analytically pure form. However, the compounds **2** are sufficiently soluble in acetone, methanol and water to allow their NMR spectra to be recorded. The structures of **2a–d** were established on the basis of ^1H , ^{13}C and ^{31}P NMR and IR spectra. The complexes **2** are stable for a short time in air, but prolonged exposure **2** to air results in formation of yellow insoluble materials, probably polymeric oxo-complexes.

Reaction 3 is very fast even at low temperatures (-20°C). Under these conditions complex **1** does not decompose for a long time. Therefore we can state that reaction 3 proceeds via the direct interaction of CIPR_2 with **1** rather than with a product of its decomposition such as Cp_2NbH . The absence of a direct Nb–Cl bond in the product **2** also suggest that other unsaturated complexes, such as $[\text{Cp}_2\text{NbH}_2]^+$, cannot be the intermediates in reaction 3. The noninvolvement of coordinatively unsaturated intermediates in reaction 3 was supported by the following observation. Addition of 1 equivalent of CIPPh_2 to a toluene solution of Cp_2NbH_3 in the presence of a tenfold excess of the highly nucleophilic PMe_3 resulted in the formation of a coloured solution and a white precipitate of **2d**. However, addition of two more equivalents of CIPR_2 caused further precipitation of an orange powder that was collected and shown by NMR to be a mixture of $\text{Me}_3\text{PH} \cdot \text{Cl}$ and the previously described complex $[\text{Cp}_2\text{Nb}(\text{PPhPh}_2)_2]\text{Cl}$ (**3**) [**7a**]. Formation of these products is in accord with the reaction sequence shown in Eq. (4). This reaction is analogous to the reaction of CIPPh_2 with $(\text{C}_5\text{H}_4\text{Me})_2\text{NbH}_3$ in the presence of NEt_4 [**7a**]. Thus PMe_3 plays only the role of an external base. It is essential that no PMe_3 incorporation into the coordination sphere of niobium was observed. Therefore, we conclude that the unhindered chlorophosphines CIPR_2 can directly insert into the Nb–H bond of **1**. Apparently, the insertion process maintains the coordinative saturation of the metal center thus preventing formation of the stable M–Cl bond.



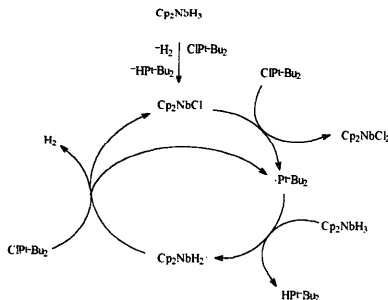
2.2. Reaction of Cp_2NbH_3 with CIPBu^t_2

Reaction of **1** with the bulky chlorophosphine CIPBu^t_2 in ether occurs with an induction period of about 30 min. After spontaneous initiation, a fast reaction was observed that was accompanied by developing a dark-brown colour, vigorous gas evolution and formation of a dark precipitate. The gas evolved cannot be condensed in vacuum by cooling with liquid nitrogen and is apparently H_2 . The precipitate was found to consist of Cp_2NbCl_2 (confirmed by ESR) and a binuclear complex $[\text{Cp}_2\text{Nb}_2]_2(\eta^{10}, \mu\text{-C}_{10}\text{H}_{10})(\mu\text{-Cl})(\mu\text{-H})$ [**13**] (confirmed by NMR). The formation of these products was established by comparison with authentic samples. The formation of expected white complex $[\text{Cp}_2\text{NbH}_2(\text{P}^t\text{Bu}_2)]\text{Cl}$ (**2e**) was not observed.



The ESR spectrum of the mother liquor showed the presence of a signal due to Cp_2NbCl_2 along with a weak signal of another paramagnetic substance (decet of doublets, $\langle a_{\text{Nb}} \rangle = 85$, $\langle a_{\text{P}} \rangle = 5$ G) attributable to the chlorophosphido complex $\text{Cp}_2\text{Nb}(\text{P}^t\text{Bu}_2)\text{Cl}$ (**4**). Given the very high sensitivity of ESR, the concentration of **4** should be very low. Indeed, the ^{31}P NMR spectrum of the product isolated from the mother liquor contained only a signal for HPBu^t_2 .

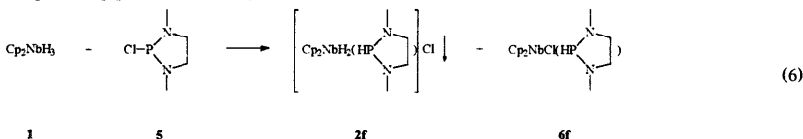
We attempted an independent synthesis of complex **2e** by the action of HCl on $\text{Cp}_2\text{Nb}(\text{HPBu}^t_2)\text{H}$ (vide infra). Complex **2e** was obtained in the form of a light-grey powder, insoluble in nonpolar solvents. It exhibits bands at 2286 cm^{-1} and 1664 cm^{-1} in the IR spectrum attributable to the P–H and Nb–H stretching modes, respectively. Unfortunately, **2e** decomposes in the polar solutions (methanol, acetone and D_2O) preventing recording of the NMR spectra. Complex **2e** is stable at room temperature at least for some hours and therefore cannot be the unstable insertion product in the reaction 5. Therefore, we conclude that the insertion mechanism is not operative for reaction 5 because of the bulkiness of CIPBu^t_2 and another mechanism must be considered. The cause of reaction 5 suggests that the induction period results in the formation of a reactive intermediate that is further involved in a chain reaction. The possible mechanism of this reaction is shown in Scheme 1. Complex $[\text{Cp}_2\text{Nb}_2]_2(\eta^{10}, \mu\text{-C}_{10}\text{H}_{10})(\mu\text{-Cl})(\mu\text{-H})$ is probably formed via an interaction of intermediate complex Cp_2NbCl with niobocene hydrides [**13**]. Reaction of Cp_2NbCl with the radical P^tBu_2 accounts for the formation of **4**.



Scheme 1.

2.3. Reaction of Cp_2NbH_3 with chlorodiaminophosphine

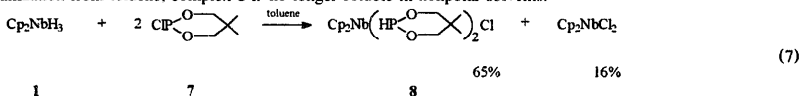
The reaction of chlorodiaminophosphine $CIP(NR_2)_2$ (**5**) with **1** results in the precipitation of beige $[Cp_2NbH_3(HP(NR_2)_2)Cl]$ (**2f**) and a highly coloured brown solution (Eq. (6)).



Like its alkyl- and aryl-analogous complex **2f** is insoluble in non-polar solvents. Unfortunately, it apparently decomposes in alcohol and acetone solutions, as shown by a rapid colour change, most likely due to solvolysis of the labile P–N bond. Thus, the NMR spectra from the freshly prepared sample of **2f** in these solvents always contain a variable number of signals for decomposition products along with the signals assigned to **2f**. The removal of solvent from the mother liquor results in a green–brown oily material that according to the 1H NMR spectrum was a 95% pure (by integration of the Cp-region) $Cp_2NbCl(HP(NR_2)_2)$ (**6f**). The structure of **6f** was established by NMR and IR data. The 1H NMR spectrum of **6f** contains a doublet Cp signal at 4.82 ($J(P-H) = 2.2$ Hz) and a doublet P–H signal at 6.44 ppm ($^1J(P-H) = 274$ Hz), while the IR spectrum exhibits a band at 2167 cm^{-1} , attributable to a P–H bond stretching mode. Since the complex **2f** is stable at room temperature for hours, complex **6f** cannot be formed as a result of its thermal decomposition (thermolysis of complexes **2** to give **6** is discussed in detail below). Therefore, the simultaneous formation of **2f** and **6f** indicates two competitive routes in the reaction of **1** with **5**. The first route, providing **2f**, is an insertion reaction analogous to the insertion of the chlorophosphines to give **2**, the second one, affording **6f**, will be discussed in more detail below (Section 2.7.).

2.4. Reaction of Cp_2NbH_3 with chlorophosphites

A different route was found in the reaction of **1** with the cyclic chlorophosphite **7** (Eq. (7)). Addition of 2 equivalents of **7** to a toluene solution of **1** gives a small amount of Cp_2NbCl_2 (16%) and a steady crystallisation of a new cationic d^2 complex of $[Cp_2Nb(PH(OR)_2)_2]Cl$ (**8**) (65% yield) as a toluene solvate. Reaction of **1** with only one equivalent of chlorophosphine **7** gives **8** in only 13% yield with a mixture of unidentified products. After crystallization from toluene, complex **8** is no longer soluble in nonpolar solvents.



However, as with other cationic niobocene complexes described in this study, it is soluble in acetone and methanol, enabling its NMR to be recorded. The structure of **8** was unequivocally established on the basis of the spectroscopic data. The ^1H NMR spectrum of **8** exhibits a Cp resonance as a triplet at 5.38 ppm ($J(\text{P-H}) = 2.8$ Hz), supporting the presence of two equivalent phosphorus centers; the P-H protons give rise to a doublet at 7.99 ppm ($J(\text{P-H}) = 366$ Hz). The presence of a P-H bond also follows from a band at 2250 cm^{-1} in the IR spectrum. Recrystallization from acetone afforded yellow crystals of **8** in the solvate-free form, suitable for X-ray diffraction.

The most likely mechanism for the formation of complex **8** in reaction 7 is that one analogous to reaction 4. It proceeds via an intermediate insertion product **2g** which further reacts with 7 to give **8** [14]. Cp_2NbCl_2 could emerge as a result of the consumption of released HCl by the basic Cp_2NbH_3 (**1**) [15]. Alternatively, we cannot exclude the possibility of a competitive mechanism, probably of a radical nature, leading to Cp_2NbCl_2 . Supporting the latter possibility is the fact that when the reaction between 7 and the 'partially oxidised' complex **1** [16] was carried out, the yield of compound **8** was highly diminished but a substantial amount of chlorophosphine complex $\text{Cp}_2\text{Nb}(\text{HPR}_2)\text{Cl}$ (**6g**) (29%) was obtained. We think that traces of oxygen may serve as the initiator of a radical process which produces **6g**.

Cationic group 5 metallocene complexes have rarely been structurally characterized [17] and only one structure for a niobocene complex with a terminal phosphine ligand has been reported [17b]. Therefore, the X-ray analysis of **8** was undertaken to obtain more structural information about these two types of compounds and to support the result of Eq. (8). The molecular structure of **8** is shown in Fig. 1 and important bond distances and angles are given in Table 1. In the solid state, compound **8** consists of a positively charged niobocene diphosphine complex and chloride counterion. No unusual contacts were found between the metallocene moieties and the chloride anion. The metallocene part of compound **8** exhibits a pseudotetrahedral geometry, typical for disubstituted metallocene complexes. The $\text{P}(1)\text{--Nb--P}(2)$ angle of $82.96(4)^\circ$ is in a good agreement with the value calculated for d^2 metallocenes [18]. The Nb–P distances of 2.462(1) Å and 2.479(1) Å are considerably shorter than the corresponding distances found for d^2 $\text{Cp}_2\text{Nb}(\text{P}(\text{HPr})_2)\text{Br}$ (2.567(2) Å, *vide infra*) and $\text{Cp}_2\text{Nb}(\text{P}(\text{HPh})_2)\text{PPh}_2$ [14] (2.529(2) Å for the metal–phosphine bond). The positive charge could account in principle for this shortening. However, comparison with another ionic niobocene phosphine complex $[\text{Cp}_2\text{Nb}(\text{CO})\text{P}(\text{Ph})_2\text{SCH}_3]^+\text{I}^-$ (Nb–P bond of 2.579(1) Å) [17b] and a related ionic tantalum compound $[\text{Cp}_2\text{Ta}(\text{PPh}_2\text{CH}_2)_2]^+\text{Cl}^-$ [19] (metal–phosphine bond lengths of 2.534(1) Å and 2.536(1) Å) shows that consideration of the charge alone is not decisive. Thus, the more important factor seems to be a rehybridization effect caused by the presence of electronegative oxygen substituents at phosphorus. This provides more phosphorus p-orbital character for the P–O bonds, thus leaving more s-character for the P–Nb and P–H bonds and so causing their contraction [20]. Another possible factor contributing to this contraction could be the donation of a metallocene lone pair (orbital a_1 in Ref. [18]), located in the NbP₂ bisecting plane of the niobocene moiety, to a P–O bond antibonding orbital located in the O–P–O plane — so-called 'negative hyperconjugation' [21]. However, in our case this possibility can be ruled out since the angles between two O–P–O planes and the NbP₂ bisecting plane (56.5 and 55.8°) deviate too much from 0° to allow any significant orbital overlap.

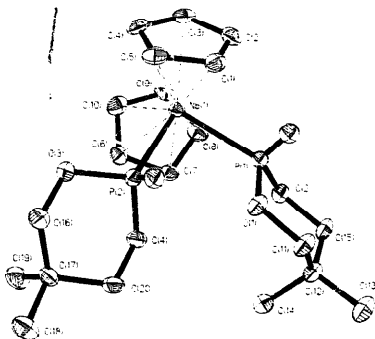


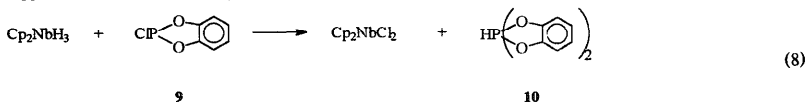
Fig. 1. Molecular structure of the metallocene part of **8**.

Table 1
Selected bond distances [Å] and angles [deg] for **8**

Bond distances			
Nb(1)–P(1)	2.4616(12)	Nb(1)–P(2)	2.4794(12)
P(1)–O(1)	1.613(3)	P(2)–O(4)	1.610(3)
P(1)–O(2)	1.612(3)	P(2)–O(3)	1.612(3)
P(1)–H	1.000	P(2)–H	1.000
Bond angles			
P(1)–Nb(1)–P(2)	82.96(4)	C(4)–P(2)–O(3)	102.2(2)
O(1)–P(1)–O(2)	103.8(2)	Cp1–Cp2 ^a	141.0

^aCp1–Cp2 denotes the plane between cyclopentadienyl rings.

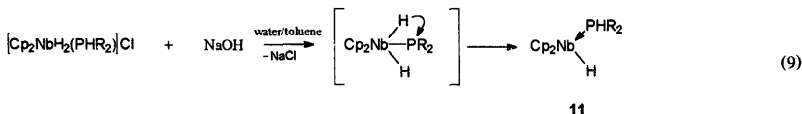
Reactions of **1** with an excess of ClP(OEt)₂ and with the cyclic chlorophosphite **9** lead to the formation of Cp₂NbCl₂ as the main organometallic product. In the case of chlorophosphite **9** two phosphorus by-products were observed by the ³¹P NMR spectroscopy. One of them exhibits a singlet at 127.2 ppm and has no phosphorus bound proton. The nature of this product remains unknown. The second product was identified as phosphorane **10** (doublet at –22.9 ppm, *J*(P–H) = 909 Hz) (Eq. (8)) [22].



At present the nature of these reactions is not quite clear. Our working hypothesis is that an electron or hydride transfer mechanism is valid for the reactions of **1** with these chlorophosphites. An analogous route may be operative for reactions 5 and 6.

2.5. Preparation of hydridophosphines Cp₂NbH(PHR₂)

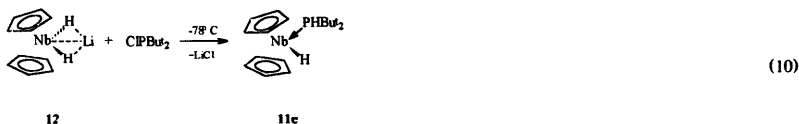
The cationic complexes [Cp₂NbH₂(PHR₂)₂]⁺Cl[–] (**2**) are useful precursors to a number of other phosphorus substituted niobocenes. For example, deprotonation of the complexes **2** can be achieved easily with aqueous NaOH to give phosphinohydrides Cp₂NbH(PHR₂) (**11**) in high yields (Eq. (9)). This reaction is carried out in two-phase system water/toluene enabling easy extraction and isolation of the product. In our earlier study we showed that proton abstraction from [Cp₂NbH₂(PPh₂)₂]⁺ occurs at the P–H bond. Therefore, deprotonation of **2d** must initially produce the dihydridephosphido species [Cp₂NbH₂(PPh₂)₂] which is then transformed eventually into Cp₂NbH(PPh₂) (**11d**) by intramolecular insertion of PPh₂ into an Nb–H bond [7a]. This mechanism is consistent with the lower stability of the P–H bond as compared with the Nb–H bond and is apparently applicable to deprotonation reactions of other complexes of the type [Cp₂NbH₂(PHR₂)₂]⁺.



Further support for this mechanism is the observation that deprotonation of an analogous tantalum complex [Cp₂TaH₂(PPh₂)₂]⁺Cl[–] gives the dihydridephosphido Cp₂TaH₂(PPh₂) which is a thermodynamically stable product in this system [7b]. In this context it is interesting to note that proton abstraction from the molybdenum complex Cp(CO)₂Mo(PHPh₂)H gives the phosphine complex [Cp(CO)₂Mo(PHPh₂)][–] [23] while deprotonation of [Cp₂Mo(PHPh₂)H]⁺ results in the phosphidohydride Cp₂Mo(PPh₂)H [6d]. Thus, we conclude that the formation of the phosphino versus phosphido-hydride form is a function of the stability of the metal–hydride bond that in turn depends on the nature of the metal and its supporting ligands.

The complexes **11** contain two useful functionalities, namely the P–H and Nb–H bonds. They are, therefore, valuable precursors to a number of other phosphorus substituted complexes [14]. However, in the case of R = Bu⁺ and

OR' the corresponding precursors **2e, g** for the preparation of **11e, g** are not accessible by the insertion reaction (Eq. (3)) and the development of alternative routes was required. The interaction between the available anionic complex $[\text{Cp}_2\text{NbH}_2]\text{Li}$ (**12**) and ClPR_2 serves as this alternative. In the case of unhindered phosphines this method is laborious and produces lower yields (30% for $\text{R} = \text{Ph}$ [**7a**]) than the insertion/deprotonation technique. This is caused by the possibility of a subsequent reaction between the emerging $\text{Cp}_2\text{NbH}(\text{PHR}_2)$ and starting chlorophosphine to give $[\text{Cp}_2\text{Nb}(\text{PHR}_2)_2]\text{Cl}$ [**7a**] and eventually a mixture of compounds. In the case of bulkier $\text{R} = \text{Bu}^t$ insertion of ClPBu_2 into the Nb–H bond of $\text{Cp}_2\text{NbH}(\text{PHBu}_2)$ (**11e**) is suppressed and the complex **11e** can be obtained according to Eq. (10) in high yield (98%). It is noteworthy that when reaction between **12** and ClPBu_2 is carried above -40°C a substantial amount of bis(niobocene) [**25**] is produced. This probably forms due to the oxidation of **12** by ClPBu_2 to give HBPu_2 and $[\text{Cp}_2\text{NbH}]$, the latter dimerizing to give bis(niobocene) [**25**].



Reaction between **12** and chlorophosphite **7** gave a mixture of Cp_2NbH_3 and the target complex $\text{Cp}_2\text{NbH}(\text{PH}(\text{OCH}_2)_2\text{CMe}_2)$ (**11g**) in the ratio 1:3 from which complex **11g** was isolated in 22% yield after recrystallization from ether.

Complex **11d** eliminates dihydrogen at room temperature selectively transforming into the ortho-metallated complex $\text{Cp}_2\text{NbH}(\text{P}(\text{HPh})(\text{C}_6\text{H}_5\text{-o}))$ [**7a**]. In contrast, the complexes **11a, b, c** (with more basic alkylphosphines) and complex **11g** are stable even when heated up to 70°C . The strained complex **11e** decomposes at 50°C to give unidentified products.

2.6. Preparation of halophosphines $\text{Cp}_2\text{NbX}(\text{PHR}_2)$ ($\text{X} = \text{Cl, Br}$)

Complexes **2a, b, d** easily eliminate dihydrogen to give chlorophosphine adducts $\text{Cp}_2\text{NbCl}(\text{PHR}_2)$ (**6a, b, d**) (Eq. (11)). Similarly, thermolysis of **2c** gives **6c**, although a small amount of **11c** is also formed in this case. For $\text{R} = \text{Ph}$ thermolysis occurs readily at room temperature while for $\text{R} = \text{alkyl}$ heating at $50\text{--}60^\circ\text{C}$ in THF is required. Since the starting complexes **2a–d** are insoluble in nonpolar solvents, the products **6** can be isolated easily from the reaction mixture by filtration and removal of the solvent. Thus, the insertion/thermolysis technique provides an efficient access to **6** from **1**. This method is restricted to such chlorophosphines that give the initial insertion product **2**. Nevertheless, as stated above, complexes $\text{Cp}_2\text{NbCl}(\text{PH}(\text{N}(\text{Me})\text{CH}_2)_2)$ (**6f**) and $\text{Cp}_2\text{NbCl}(\text{PH}(\text{OCH}_2)_2\text{CMe}_2)$ (**6g**) were obtained among the products from the reaction of the corresponding chlorophosphines with **1**.



R: Et Bu Ph
a b c d

Alternative approaches to the halophosphine derivatives of niobocene are by reaction of PR_3 with $[\text{Cp}_2\text{NbCl}]_2$ [**26**] and by hydride for halogen exchange in $\text{Cp}_2\text{NbH}(\text{PR}_3)$ [**27**]. The former method is sometimes inconvenient due to difficulties in isolating the reaction product in pure form [**26d**]. To compare the latter method with our insertion/thermolysis approach, we allowed $\text{Cp}_2\text{NbH}(\text{P}(\text{HPh})_2)$ to react with one equivalent of EtBr. This reaction occurs immediately, affording a substantial amount of Cp_2NbBr_2 (**13**) together with the target $\text{Cp}_2\text{NbBr}(\text{P}(\text{HPh})_2)$ (**14**) and starting **11e**. Complex **13** apparently forms as a result of oxidation of **14** by EtBr [**19a**] and this competing redox reaction is a limitation of this procedure. Formation of **13** means that the reaction of **11e** and **14** with EtBr occurs at comparable rates. Given the difference in the electronegativity of the hydride and bromide ligands, this result seemed to be surprising and we decided that X-ray structure determination of **14** could shed more light on it.

The molecular structure of **14** is shown in Fig. 2 and important bond distances and angles are given in Table 2. Complex **14** exhibits a pseudotetrahedral geometry typical for d^2 Cp_2NbXL ($\text{X} = \text{one-electron ligand}$, $\text{L} = \text{two-electron ligand}$) complexes. An unusual feature of **14** is the increased P(1)–Nb–Br bond angle of $92.0(1)^\circ$ [**18**], consistent with a strong mutual repulsion between two bulky $\text{P}(\text{HPh})_2$ and Br ligands. Supporting this view are the long Nb–P bond distance ($2.567(2)$ Å) as compared with $\text{Cp}_2\text{Nb}(\text{P}(\text{HPh})_2)\text{PPh}_2$ [**14**] ($2.529(2)$ Å for the metal–phosphine bond), and the very long Nb–Br bond distance of $2.753(1)$ Å, as compared with $2.673(5)$ Å found in $\text{Cp}_2\text{NbBr}(\text{N}_2\text{CPh}(\text{BrC}_6\text{H}_4))$.

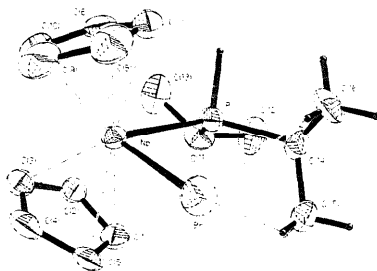


Fig. 2. Molecular structure of **15**. Hydrogen atoms on carbons, except those on C(15) and C(16), are omitted.

[28]. Furthermore, the shortest contact between the Br and $\text{P}(\text{H})\text{R}_2$ groups is the Br–H(16) contact of 2.652 Å that is 0.47 Å smaller than the sum of van der Waals radii. Therefore we conclude that complex **14** is highly strained. Possibly it is the strained nature of **14** that facilitates its reaction with EtBr compared to the reaction of **11e** with EtBr, in spite of the presence of the electron-withdrawing bromine substituent.

2.7. The concept of carbene-like nature of chlorophosphines

Cp_2NbH_3 is an electronically and coordinatively saturated complex. This means that the reaction shown in Eq. (3) inevitably occurs at the Nb–H bond. Two features of this reaction are noteworthy. First of all, the speed of this transformation is very high even at low temperatures (–40 to –20°C), implying a small activation barrier. Secondly, the observation of an induction period for the precipitation of **2c** in the case of ClPR_2 and quenching of the reaction **3** in the case of the bulky ClP^tBu_2 imply a close proximity of the reactants in the transition state. Both these features are characteristic for the concerted reactions, suggesting that a direct insertion of chlorophosphine into the Nb–H bond occurs. What is the nature of this process? We notice that there is a certain similarity in the electronic structure of chlorophosphines ClPR_2 and the singlet methylene CH_2 [29]. Thus, the phosphorus lone pair (ψ_p in Fig. 3) corresponds to the a_1 orbital of CH_2 and the antibonding P–Cl orbital ($\psi_{p-\text{Cl}}$ in Fig. 3, note that $\psi_{p-\text{Cl}}^*$ is the LUMO for ClPR_2) corresponds to the vacant b_2 orbital of CH_2 . Moreover, in respect to the insertion reaction with the symmetry C_∞ both these fragments, ClPR_2 and CH_2 , are isolobal [30]. Therefore, the insertion of ClPR_2 must be quite analogous to the insertion of methylene into a transition metal–hydride bond. It is reasonable to assume that the reaction starts with pre-coordination of the chlorophosphine along the polarized M–H bond [15] (structure **A** in Scheme 2). The resultant lengthening of the M–H bond is accompanied by pivoting the chlorophosphine around the M–H vector (**B**). The symmetry of this reaction coordinate is C_∞ and the corresponding orbitals of ClPR_2 and CH_2 are of the same symmetry. Near the transition state the orbital interactions probably involve the interaction of the P–Cl antibonding orbital with the M–H bonding orbital and the interaction of the M–H antibonding orbital with the phosphorus lone pair (Fig. 4). Presumably, the metal atom preserves its 18 electron configuration and the coordination saturation along the reaction coordinate thus preventing the formation of a stable M–Cl bond.

Table 2
Selected bond distances (Å) and bond angles (in deg) for **15**

Bond distances			
Nb–Br	2.753(1)	Nb–P	2.567(2)
P–C(11)	1.882(9)	P–C(14)	1.870(8)
P–H	1.513		
Bond angles			
Br–Nb–P	92.0(1)	Nb–P–C(11)	118.4(3)
Nb–P–C(14)	124.0(3)	C(11)–P–C(14)	105.5(4)
Cp1–Cp2 ^a	133.5		

^aCp1–Cp2 denotes the plane between cyclopentadienyl rings.

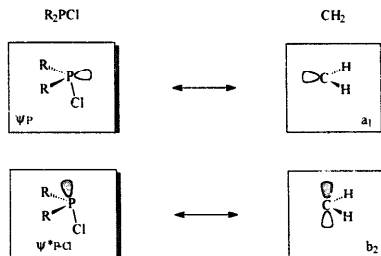
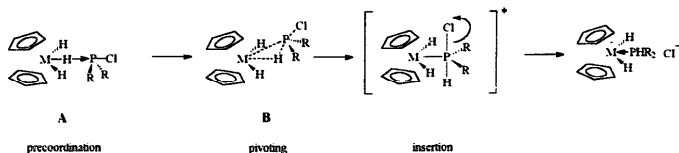


Fig. 3.

It is interesting that the chloride anion abstraction from CIPR_2 results in the phosphonium cation PR_2^+ that is an isolobal analog of carbene [31]. In this process the $\psi_{\text{P-Cl}}$ orbital of CIPR_2 becomes the vacant orbital of PR_2^+ . The similarity between carbenes and phosphinidenes has long been accepted [31] whereas a relationship between the electronic structure of carbenes and halophosphines has not previously been proposed. However, this relationship has a chemical consequences. Thus, in 1966 Nefedov and Monakov pointed out that the cyclization of $\text{Cl}_x\text{PR}_{3-x}$ with 1,3-dienes (Eq. (12)) is analogous to the cyclization of methylene with dienes to form cyclopentenes [32]. However, these authors did not recognise the similarity of the electronic structures of chlorophosphines and methylene, and even after their work the usual way to explain the reactivity of halophosphines was in terms of their electrophilic or biphilic behaviour [33]. The latter is often only referred to as the 'dienophilic properties of phosphines' [34]. Nevertheless, additions of halophosphines to other unsaturated organic compounds, such as olefins and acetylenes etc are also known [33,35]. These reactions can be described now in terms of the carbene-like nature of halophosphines. Our proposed concept therefore allows us to explain a wealth of reactivity of halophosphines from one point of view, based on the nature of the electronic structure of halophosphines.



Let us now look at what happens as the electronegativity of substituents R at phosphorus increases. The theoretical and experimental data on the insertion reactions of carbenoids show that increasing electronegativity of substituents R at a carbenoid center results in high activation barriers and a late transition state of insertion [36]. For CIPR_2 , the increase in electronegativity of R pulls the P–Cl antibonding orbital down in energy, increasing its electron affinity [37], and also diminishes the electron-donating ability of the lone pair of chlorophosphine CIPR_2 . Therefore, increasing electronegativity of substituents R should result in the stabilization of the structure A in Scheme 2 in respect to insertion. Increasing electron affinity of the P–Cl antibonding orbital also facilitates another reaction pathway. Namely, it makes a direct electron or hydride transfer onto CIPR_2 possible. It was shown that electron transfer onto chlorophosphites results in phosphorus radicals and chloride anion [38]. This transfer should generate electronically and coordinatively unsaturated species like $[\text{Cp}_2\text{NbH}_2]^+$, amenable to the formation of the Nb–Cl bond, HPR_2 [39] and chloride ion. Probably, this proposed electron or hydride transfer mechanism is possible for the dialkylchlorophosphines too but occurs much slower than the insertion. This explains the slow reaction between 1 and

Scheme 2. Mechanism of insertion of halophosphine into the M–H bond of Cp_2MH_2 ($\text{M} = \text{Nb}, \text{Ta}$).

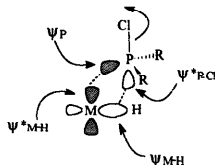


Fig. 4.

CIPBu_2^1 for which insertion is not possible for steric reasons. The observation of $\text{Cp}_2\text{NbCIPBu}_2^1$ in reaction 5 is also in accord with the radical route. The smooth increase in electronegativity of R from alkyls to amido and eventually to alkoxy substituents provides the fine tuning of the mechanism. The only exception from this series is the reaction of **1** with the cyclic chlorophosphite **7**. We think that in this case the position of the LUMO in **7**, crucial for the type of mechanism, is determined by the small bond angles at phosphorus. It is known that small angles cause an increase in the energy of the LUMO [37]. In **7** the small bond angles at phosphorus are caused by the conformation of the six-membered ring [40].

3. Conclusions

This report presents the first systematic study on the reactivity of a transition metal–hydrogen bond toward halophosphines. We have shown that, depending on the nature of the substituent R in CIPR_2 , two reaction routes exist. The first one, insertion of a halophosphine into a transition metal–hydride bond, is realized in the case of unhindered alkyl and aryl R groups and gives the ionic complexes $[\text{Cp}_2\text{NbH}_2(\text{PHR}_2)]\text{Cl}$ (**2**). The second route, leading to the intermediate complex $\text{Cp}_2\text{NbCl}(\text{PHR}_2)$ and eventually to Cp_2NbCl_2 , may occur either by an electron or hydride transfer step and operates for electronegative (OR^*) or bulky (Bu^1) substituents R. In the case of R being an amido group, both routes compete, while for the cyclic chlorophosphite **11** one more reaction path was found leading to the cationic diphosphine complex **8**. The insertion reaction together with a wide range of other reactions of halophosphines with organic molecules can be explained from one point of view, namely the proposed concept of the carbenoid nature of halophosphines.

The rich chemistry of the insertion products **2** is exemplified here by two principal reactions. These are (i) thermolysis to produce $\text{Cp}_2\text{NbCl}(\text{PHR}_2)$ and (ii) deprotonation to give $\text{Cp}_2\text{NbH}(\text{PHR}_2)$. The insertion/thermolysis and insertion/deprotonation methods are probably the most convenient routes to these reactive molecules, which contain reactive P–H and M–H or M–Cl functionalities. The application of these functionalities to the synthesis of other phosphorus substituted group 5 metallocenes is now in progress.

4. Experimental section

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; ^{13}C , 100.4 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. IR spectra were obtained in Nujol with a Perkin-Elmer series spectrometer. Mass-spectra (EI) were obtained with a CH7 Varian MAT spectrometer. CIPeEt_2 , CIPPr_2^1 and CIP(OEt)_2 were purchased from Merck. CIPBu_2 , CIPBu_2^1 , **5** and other chlorophosphites were prepared according to standard methods. Cp_2NbH_3 was prepared by the modified procedure as reported earlier [7a]. $[\text{Cp}_2\text{NbH}_3]\text{Li}$ was synthesised according to literature method [26]. Elemental analysis was performed in the analytical laboratory of the Chemistry Department of the Moscow State University. Compounds $[\text{Cp}_2\text{NbH}_2(\text{PPh}_2)]\text{Cl}$ (**2d**) and $\text{Cp}_2\text{Nb}(\text{PPh}_2)_2\text{H}$ (**11d**) were previously reported [7a].

4.1. Preparation of $[\text{Cp}_2\text{NbH}_2(\text{PHEt}_2)]\text{Cl}$ (**2a**)

1.57 g (6.95 mmol) of Cp_2NbH_3 in 100 mL of THF was treated by 0.84 mL of CIPeEt_2 (6.95 mmol). White voluminous precipitate was immediately formed. The resulted mixture was vigorously stirred and the solution

decanted. The resulted precipitate was washed twice with 35 mL of ether and dried in vacuo. Yield: 1.950 g (5.56 mmol, 80%). IR (KBr): $\nu_{\text{P-H}} = 2304 \text{ cm}^{-1}$, $\nu_{\text{Nb-H}} = 1717 \text{ cm}^{-1}$. ^1H NMR (methanol- d_4): δ 5.65 (d, $J(\text{P-H}) = 1.1$ Hz, 10, Cp), 4.60 (dt, $J(\text{P-H}) = 354.9$ Hz and $^3J(\text{H-H}) = 5.9$ Hz, 1, P-H), 2.0–1.60 (m, 4, CH_2), 1.19 (dt, $^3J(\text{P-H}) = 18$ Hz and $^3J(\text{H-H}) = 7.5$ Hz, 6, CH_3), -2.70 (dd, $^2J(\text{P-H}) = 73.8$ Hz and $^3J(\text{H-H}) = 5.1$ Hz, Nb-H). ^{13}C NMR (methanol- d_4): δ 93.7 (s, Cp), 21.2 (d, $J(\text{P-C}) = 26.6$ Hz), 10.5 (d, $J(\text{P-C}) = 5.3$ Hz). MS (EI): 312 ($\text{Cp}_2\text{NbPEt}_2$)⁺ 314.0 ($\text{Cp}_2\text{NbH}(\text{PHEt}_2)$)⁺, 349 and 351 ($\text{Cp}_2\text{NbH}_2(\text{PHEt}_2)\text{Cl}$)⁺. Anal. Calc. for $\text{C}_{14}\text{H}_{23}\text{ClPNb}$: C, 47.95; H, 6.61. Found: C, 47.50; H, 6.28.

4.2. Preparation of [$\text{Cp}_2\text{NbH}_2(\text{PHBu}_2)$] Cl (**2b**)

1 mL of ClPBu_2 (7.78 mmol) was added to a suspension of 0.879 g (3.89 mmol) of Cp_2NbH_3 in 40 mL of Et_2O . The resulted mixture was vigorously stirred for 5 min, after that the solution was decanted from the white voluminous precipitate. The precipitate was washed twice with 20 mL of ether and dried in vacuo. Yield: 0.956 g (2.35 mmol, 60.4%). IR (nujol): $\nu_{\text{P-H}} = 2300 \text{ cm}^{-1}$, $\nu_{\text{Nb-H}} = 1740 \text{ cm}^{-1}$. ^1H NMR (methanol- d_4): δ 5.72 (d, $J(\text{P-H}) = 0.5$ Hz, 10, Cp), 4.77 (dt, $J(\text{P-H}) = 373.8$ Hz and $^3J(\text{H-H}) = 3.6$ Hz, 1, P-H), 2.03–1.41 (m, 12, CH_2), 1.00 (t, $J(\text{H-H}) = 7.1$ Hz, 6, CH_3), -2.10 (dd, $J(\text{P-H}) = 74.2$ Hz and $^3J(\text{H-H}) = 3.6$ Hz, Nb-H). ^{13}C NMR (methanol- d_4): δ 93.8 (s, Cp), 28.3 (d, $J(\text{P-C}) = 9.5$ Hz), 27.9 (d, $J(\text{P-C}) = 9.8$ Hz), 24.2 (d, $J(\text{P-C}) = 11.8$ Hz), 13.41 (s, CH_3). ^{31}P NMR (methanol- d_4): δ -6.9 ppm. MS: 370.0 ($\text{Cp}_2\text{NbH}(\text{PHBu}_2)$). HRMS: Calc. for $\text{C}_{17}\text{H}_{27}\text{PNb}$ 370.11105. Found: 370.11045. Anal. Calc. for $\text{C}_{18}\text{H}_{31}\text{ClPNb}$: C, 53.15; H, 7.68, Cl, 8.72. Found: C, 52.67; H, 7.30, Cl, 8.45.

4.3. Preparation of [$\text{Cp}_2\text{NbH}_2(\text{P}^i\text{Pr}_2)$] Cl (**2c**)

Solution of 0.65 mL (4.10 mmol) of ClP^iPr_2 in 5 mL of THF was added to a solution of 0.928 g (4.10 mmol) of Cp_2NbH_3 in 25 mL of THF. In 5–6 s the initially transparent solution became opaque, and white flakes of **2c** were formed. Sedimentation was completed within 10–15 min. Light blue solution was decanted, and the precipitate was washed with 20 mL of THF and dried in vacuo. Yield: 1.09 g (2.87 mmol, 70%). ^1H NMR (methanol- d_4): δ 5.71 (c, 10, Cp), 4.47 (d, $J(\text{P-H}) = 346$ Hz, 1, P-H), 2.36 (m, 2, CH), 1.25 (dd, $J(\text{H-H}) = 6.8$ Hz and $J(\text{P-H}) = 16.8$ Hz, 6, CH_3), 1.21 (dd, $J(\text{H-H}) = 7.2$ Hz and $J(\text{P-H}) = 17.6$ Hz, 6, CH_3), -2.34 (d, $J(\text{P-H}) = 68.8$ Hz, Nb-H). ^{13}C NMR (methanol- d_4): δ 94.2 (s, Cp), 25.6 (d, $J(\text{P-C}) = 24.2$ Hz, CH), 21.0 (s, CH_3), 19.7 (s, CH_3). ^{31}P NMR (methanol- d_4): δ 35.5 ppm. Anal. Calc. for $\text{C}_{16}\text{H}_{27}\text{ClPNb}$: C, 50.74; H, 7.19. Found: C, 50.28; H, 6.80.

4.4. Reaction of Cp_2NbH_3 with ClPBu_2

Solution of 0.325 g (1.44 mmol) of Cp_2NbH_3 in 40 mL of ether was treated by 0.255 g (1.41 mmol) of ClPBu_2 in 3 mL of THF. In approximately 30 min the solution turned an intense blue and the formation of a dark precipitate appeared. The solution was decanted from the precipitate. Solvent was removed in vacuo, and the NMR spectra of the residue showed the presence of HPBu_2 . The precipitate was washed by toluene and dried in vacuo to give 0.132 g (32%) of Cp_2NbCl_2 . The substance obtained from the toluene solution mainly consist of $[\text{Cp}_2\text{Nb}_2]_2(\eta^{10}-\mu-\text{C}_{10}\text{H}_{10})(\mu-\text{Cl})(\mu-\text{H})$. The presence of an oily impurity hampered the yield determination.

4.5. Reaction of Cp_2NbH_3 with $\text{ClP}(\text{N}(\text{Me})\text{CH}_2)_2$ (**5**) to give **2f** and **6f**

Solution of 0.704 g (3.11 mmol) of Cp_2NbH_3 in 50 mL Et_2O was treated by 0.43 mL of **5**. Grey-bedge precipitate and green-brown solution were formed. The solution was filtered off and the precipitate dried in vacuo. Yield of **2f**: 0.248 g. Dissolving this compound in MeOD or acetone results initially in a greenish solution that then turns brown apparently due to the solvolysis of the P-N bonds. The signals assigned to **2f**: IR (KBr): $\nu_{\text{P-H}} = 2451 \text{ cm}^{-1}$, $\nu_{\text{Nb-H}} = 1765 \text{ cm}^{-1}$. ^1H NMR (methanol- d_4): δ 7.26 (d, $J(\text{P-H}) = 299.3$ Hz, 1, P-H), 5.22 (d, $J(\text{P-H}) = 2.6$ Hz, 10, Cp), 2.84 (d, $J(\text{P-H}) = 13.8$ Hz, 4, CH_2), 2.66 (d, $J(\text{P-H}) = 12.8$ Hz, 6, CH_2), -2.68 (d, $J(\text{P-H}) = 79.7$ Hz, Nb-H). ^{13}C NMR (methanol- d_4): δ 93.2 (Cp), 53.4 (CH_2), 34.0 (CH_3). ^{31}P NMR (methanol- d_4): δ 166.0 ppm.

The solution obtained after filtration was dried in vacuo to give 0.494 g of a green-brown compound **6f**. Spectroscopic data for **6f**. IR (nujol): $\nu_{\text{P-H}} = 2167 \text{ cm}^{-1}$. ^1H NMR (benzene- d_6): δ 6.44 (d, $J(\text{P-H}) = 274.0$ Hz, 1, P-H), 4.82 (d, $J(\text{P-H}) = 2.2$ Hz, 10, Cp), 3.02–2.40 (m, 10, CH_2 and CH_3). ^{13}C NMR (benzene- d_6): δ 95.6 (s, Cp), 53.9 (d, $J(\text{P-C}) = 7.3$ Hz), 36.1 (d, $J(\text{P-C}) = 6.2$ Hz). ^{31}P NMR (benzene- d_6): δ 174.3 ppm.

4.6. Reaction of Cp_2NbH_3 with $\text{ClP}(\text{OEt})_2$

Solution of 0.292 g (1.305 mmol) of Cp_2NbH_3 in 30 mL Et_2O was treated by a solution of 0.19 mL of $\text{ClP}(\text{OEt})_2$ in 5 mL of Et_2O . No immediate changes were observed. A black precipitate of Cp_2NbCl_2 is formed during some

days that was confirmed by the ESR spectrum. Solution was decanted and the precipitate dried in vacuo. Yield of Cp_2NbCl_2 : 0.217 g (57.2%).

4.7. Reaction Cp_2NbH_3 with $\text{CIP}(\text{O}_2\text{C}_6\text{H}_4)$

Solution of 0.722 g (3.19 mmol) Cp_2NbH_3 in 15 mL THF was treated by 0.70 mL (6.4 mmol) of $\text{CIP}(\text{O}_2\text{C}_6\text{H}_4)$. An immediate reaction occurred, accompanied by the release of dihydrogen, formation of a dark solution and precipitation of Cp_2NbCl_2 (tested by ESR). The solution was decanted from precipitate and the solvent was removed in vacuo. The resultant residue was washed with ether: The ether solution had burgundy colour and did not contain any cyclopentadienyl compounds. The NMR spectrum showed the presence of two phosphorus compounds, one of them being $\text{HP}(\text{O}_2\text{C}_6\text{H}_4)_2$. Yield of Cp_2NbCl_2 : 0.753 g (80.2%).

4.8. Preparation of $[\text{Cp}_2\text{Nb}(\text{HP}(\text{OCH}_2)_2\text{CMe}_2)_2]\text{Cl}$ (**8**)

Solution of 0.461 g (2.04 mmol) of Cp_2NbH_3 in 30 mL of toluene was treated by 0.55 mL (4.04 mmol) of $\text{CIP}(\text{OCH}_2)_2\text{CMe}_2$. In some minutes the formation of a small amount of brown precipitate (Cp_2NbCl_2 by ESR) was observed. Solution was decanted from precipitate and left at room temperature. Within a week a yellow crystalline precipitate was formed, shown by NMR to be the toluene solvate of **8**: $\text{Cp}_2\text{Nb}(\text{HP}(\text{OCH}_2)_2\text{CMe}_2)_2\text{Cl} \cdot 0.5\text{C}_7\text{H}_8$. Solution was decanted and the precipitate dried in vacuo. Yield 0.502 g (0.867 mmol, 43%). The second crop of **8** was obtained from the solution with the total yield of 65%. The solvate free form of **8** can be obtained by recrystallization from acetone. Yield of Cp_2NbCl_2 : 0.097 g. IR (nujol): $\nu_{\text{P-H}} = 2250 \text{ cm}^{-1}$. ^1H NMR (methanol- d_4): δ 7.99 (d, $J(\text{P-H}) = 366.4 \text{ Hz}$, 2, P-H), 5.38 (t, $J(\text{P-H}) = 2.8 \text{ Hz}$, 10, Cp), 3.99 (m, 8, CH_2), 1.33 (s, 6, CH_3), 0.85 (s, 12, CH_3). ^{13}C NMR (methanol- d_4): δ 91.4 (d, Cp), $J(\text{P-C}) = 10.6 \text{ Hz}$, 82.0 (OCH_2), 33.0 ($\text{C}(\text{CH}_3)_2$), 22.1 (CH_3), 21.2 (CH_3). ^{31}P NMR (methanol- d_4): δ 214.8 ppm. Anal. Calc. for $\text{C}_{23.5}\text{H}_{34}\text{ClO}_2\text{P}_2\text{Nb}$: C, 49.27; H, 6.16. Found: C, 49.19; H, 5.97.

4.9. Preparation of $\text{Cp}_2\text{Nb}(\text{HPBu}_2)_2\text{H}$ (**11b**)

0.467 g (1.14 mmol) of $\text{Cp}_2\text{Nb}(\text{HPBu}_2)_2\text{H}_2\text{Cl}$ in 30 mL of toluene was treated by 10 mL of 0.5 M aqueous solution of NaOH. The mixture was vigorously stirred. Within some minutes the precipitate dissolved and the organic phase turned dark red. The toluene solution was decanted and dried in vacuo. The red residue was recrystallized from Et_2O . Yield: 60%. ^1H NMR (toluene- d_8): δ 4.42 (d, $J(\text{P-H}) = 2.4 \text{ Hz}$, 10, Cp), 4.17 (d, $J(\text{P-H}) = 297.1 \text{ Hz}$, 1, P-H), 1.66–1.02 (m, 12, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.81 (t, $J(\text{P-H}) = 7.2 \text{ Hz}$, 6, CH_3), -7.99 (d, $J(\text{P-H}) = 26.6 \text{ Hz}$, Nb-H). ^{13}C NMR (toluene- d_8): δ 81.88 (s, Cp), 24.2 (d, $J(\text{P-C}) = 7.2 \text{ Hz}$, P-CH_2), 24.2 (s), 21.4 (s), 14.0 (s), 1.3 (s). ^{31}P NMR (toluene- d_8): δ 73.0 ppm. Anal. Calc. for $\text{C}_{18}\text{H}_{30}\text{PNb}$: C, 58.38; H, 8.17. Found: C, 57.85; H, 8.01.

4.10. Preparation of $\text{Cp}_2\text{Nb}(\text{H})\text{P}(\text{H})\text{Pr}_2\text{Cl}$ (**11c**)

Method A. 0.18 mL (1.22 mmol) of DBU was added to 0.463 g (1.22 mmol) of $\text{Cp}_2\text{NbH}_2\text{P}(\text{H})\text{Pr}_2\text{Cl}$ in 8 mL of toluene. The mixture was stirred for 5 h and left overnight. The resulted solution was decanted from precipitate and dried in vacuo. The product was recrystallized from pentane. Yield: 0.377 g (1.10 mmol, 90%), red crystals.

Method B. 2.33 g (6.14 mmol) of $\text{Cp}_2\text{NbH}_2\text{P}(\text{H})\text{Pr}_2\text{Cl}$ in 50 mL of toluene was treated by 70 mL of 0.25 M solution of NaOH. The mixture was stirred for 2 h, after that the solution was decanted and dried in vacuo. The resulted red substance was recrystallized from hexane. Yield 1.99 g (5.81 mmol, 95%).

^1H NMR (toluene- d_8): δ 4.40 (d, $J(\text{P-H}) = 2.0 \text{ Hz}$, 10, Cp), 3.56 (d, $J(\text{P-H}) = 296.0 \text{ Hz}$, 1, P-H), 1.65 (m, 2, CH), 0.98 and 0.94 (dd, $J(\text{P-H}) = 12.6 \text{ Hz}$ and $J(\text{H-H}) = 6.8 \text{ Hz}$, CH_3), -8.15 (d, $J(\text{P-H}) = 24.8 \text{ Hz}$, Nb-H). ^{13}C NMR (toluene- d_8): δ 81.6 (s, Cp), 24.0 (d, $J(\text{P-C}) = 17.5 \text{ Hz}$, CH), 21.2 and 20.6 (s, CH_3). ^{31}P NMR (toluene- d_8): δ 76.1 ppm. The performance of an elemental analysis was precluded by the extreme sensitivity of the substance to air (pyrophoric in microcrystalline form!).

4.11. Preparation of $\text{Cp}_2\text{Nb}(\text{HPBu}_2)_2\text{H}$ (**11e**)

1.3 mL of $\text{Bu}_2\text{P}_2\text{Cl}$ in 10 mL of THF was added to 1.59 g (6.85 mmol) of $\text{Cp}_2\text{NbH}_2\text{Li}$ in 50 mL of THF at -78°C . Solution turned red-brown. The mixture was stirred for 15 min and then allowed to warm to room temperature. The solution was decanted and dried in vacuo to give red-brown substance. This material was extracted by 70 mL of ether, filtration and solvent removal gave 2.48 g (98%) of red crystalline substance. IR (nujol): $\nu_{\text{P-H}} = 2335 \text{ cm}^{-1}$.

$\nu_{\text{Nb-H}} = 1692 \text{ cm}^{-1}$. ^1H NMR (benzene- d_6): δ 4.45 (d, $J(\text{P-H}) = 1.5 \text{ Hz}$, 5, Cp), 4.35 (d, $J(\text{P-H}) = 2.2 \text{ Hz}$, 5, Cp), 3.61 (d, $J(\text{P-H}) = 296.3 \text{ Hz}$, 1, P-H), 1.16 (d, $J(\text{P-H}) = 12.3 \text{ Hz}$, 9, CH_3), 1.02 (d, $J(\text{P-H}) = 11.8 \text{ Hz}$, 9, CH_3), –8.60 (d, $J(\text{P-H}) = 21.1 \text{ Hz}$, Nb-H). ^{13}C NMR (benzene- d_6): δ 83.0 and 82.1 (s, Cp), 33.2 (d, $J(\text{P-C}) = 9.3 \text{ Hz}$, CH_3) and 31.8 (d, $J(\text{P-C}) = 13.2 \text{ Hz}$, CH_3). ^{31}P NMR (benzene- d_6): δ 94.0 ppm. Anal. Calc. for $\text{C}_{18}\text{H}_{30}\text{PNb}$: C, 58.38; H, 8.17. Found: C, 57.89; H, 7.95.

4.12. Preparation of $\text{Cp}_2\text{NbH}(\text{HP}(\text{-OCH}_2)_2\text{CMe}_2)$ (**11g**)

0.3 mL of $\text{ClP}(\text{-OCH}_2)_2\text{CMe}_2$ was added at -78°C to a solution of 0.519 g (2.24 mmol) of $\text{Cp}_2\text{NbH}_3\text{Li}$ in 10 mL of THF under intensive stirring. The solution rapidly turned brown. The mixture was gently warmed to room temperature and stirred for 30 min. THF was removed in vacuo to give a brown oily material a mixture of Cp_2NbH_3 and **11j** in the ratio 1:3. This material was extracted by ether. Ether solution was filtered, concentrated to 50 mL and put into freezer (-26°C). Dark brown substance precipitated. The solution was decanted and the precipitate dried in vacuo. Yield 0.178 g (22%). IR (nujol): $\nu_{\text{P-H}} = 2429 \text{ cm}^{-1}$, $\nu_{\text{Nb-H}} = 1708 \text{ cm}^{-1}$. ^1H NMR (benzene- d_6): δ 4.71 (d, $J(\text{P-H}) = 3.0 \text{ Hz}$, 10, Cp), 7.56 (d, $J(\text{P-H}) = 322.5 \text{ Hz}$, 1, P-H), 3.51 and 3.36 (m, 4, CH_2), 1.04 (s, 3, CH_3), 0.1; (s, 3, CH_3), –7.14 (d, $J(\text{P-H}) = 20.0 \text{ Hz}$, Nb-H). ^{13}C NMR (benzene- d_6): δ 82.8 (s, Cp), 29.6 (d, $J(\text{P-C}) = 12.6 \text{ Hz}$, CH_2), 22.5 (s, CH_3) and 21.5 (s, CH_3). ^{31}P NMR (benzene- d_6): δ 230.0 ppm. Anal. Calc. for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{PNb}$: C, 50.29; H, 6.19. Found: C, 49.93; H, 6.05.

4.13. Generation of $[\text{Cp}_2\text{NbH}_2(\text{HPBu}_2^+)]\text{Cl}$ (**2e**)

Solution of **11e** in toluene was treated by excess of HCl. White flakes along with a dark precipitate were formed. This material was filtered, washed with ether and dried. The IR spectrum showed bands assigned to the P-H and Nb-H stretching vibrations. Attempted preparation of the NMR sample in methanol resulted in decomposition. IR (nujol): $\nu_{\text{P-H}} = 2286 \text{ cm}^{-1}$, $\nu_{\text{Nb-H}} = 1700 \text{ cm}^{-1}$.

4.14. Preparation of $\text{Cp}_2\text{Nb}(\text{HPEt}_2)\text{Cl}$ (**6a**)

1.887 g (5.38 mmol) of $\text{Cp}_2\text{Nb}(\text{HPEt}_2)_2\text{H}_2\text{Cl}$ was refluxed in THF for 5.5 h. On heating the initial white precipitate is dissolved, accompanied by the release of gas and formation of a green solution. The solution was decanted and dried in vacuo. Yield: 1.231 g (3.53 mmol, 65.9%) of greenish crystalline compound. IR (nujol): $\nu_{\text{P-H}} = 2315 \text{ cm}^{-1}$. ^1H NMR (benzene- d_6): δ 4.74 (d, $J(\text{P-H}) = 2.0 \text{ Hz}$, 10, Cp), 3.86 (dt, $^1J(\text{P-H}) = 311.4 \text{ Hz}$, $^3J(\text{H-H}) = 5.0 \text{ Hz}$, 1, P-H), 1.39 (dm, $J(\text{P-H}) = 79.4 \text{ Hz}$ and $J(\text{H-H}) = 7.0 \text{ Hz}$, 8, CH_2), 0.80 (dt, $J(\text{P-H}) = 4.1 \text{ Hz}$ and $J(\text{H-H}) = 7.0 \text{ Hz}$, 6, CH_3). ^{13}C NMR (benzene- d_6): δ 93.6 (Cp), 15.9 (d, $^1J(\text{P-C}) = 21.5 \text{ Hz}$), 12.1 (d, $^2J(\text{P-C}) = 5.3 \text{ Hz}$). ^{31}P NMR (benzene- d_6): δ 34.4 ppm. Anal. Calc. for $\text{C}_{14}\text{H}_{21}\text{ClPNb}$: C, 48.23; H, 6.07. Found: C, 47.89; H, 5.79.

4.15. Preparation of $\text{Cp}_2\text{Nb}(\text{HPBu}_2)\text{Cl}$ (**6b**)

1.373 g (3.38 mmol) $\text{Cp}_2\text{Nb}(\text{HPBu}_2)_2\text{H}_2\text{Cl}$ was heated in THF at 50°C for 4.5 h. On heating the initial white precipitate is dissolved, accompanied by the release of gas and formation of a dark green solution. The solution was decanted and dried in vacuo. Yield: 1.33 g (3.30 mmol, 97.6%). ^1H NMR (toluene- d_8): δ 4.68 (d, $J_{\text{P-H}} = 2.1 \text{ Hz}$, 10, Cp), 3.92 (dt, $J(\text{P-H}) = 328 \text{ Hz}$, $J(\text{H-H}) = 4.2 \text{ Hz}$, 1, P-H), 1.6–1.1 (m, 8, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.75 (t, $J(\text{H-H}) = 7.3 \text{ Hz}$, 6, CH_3). ^{13}C NMR (toluene- d_8): δ 93.6 (Cp), 30.1 (d, $J(\text{P-C}) = 5.0 \text{ Hz}$), 24.4 (d, $J(\text{P-C}) = 9.6 \text{ Hz}$), 23.1 (d, $J(\text{P-C}) = 20.3 \text{ Hz}$), 13.98 (s, CH_3). ^{31}P NMR (toluene- d_8): δ 21.5 ppm. Anal. Calc. for $\text{C}_{18}\text{H}_{29}\text{ClPNb}$: C, 53.41; H, 7.22. Found: C, 52.99; H, 6.91.

4.16. Modified preparation of $\text{Cp}_2\text{Nb}(\text{HPPh}_2)\text{Cl}$ (**6d**)

Was prepared analogously to **6b**. Yield of brown compound: 95%. Characterization data were reported earlier [7a].

4.17. Thermolysis of **2c** to give $\text{Cp}_2\text{Nb}(\text{HPPr}_2)\text{Cl}$ (**6c**)

2.33 g (6.16 mmol) $\text{Cp}_2\text{NbH}_3\text{PPr}_2\text{Cl}$ was refluxed 1 h in 100 mL of THF. White precipitate dissolved to form brown solution and small amount of black precipitate — Cp_2NbCl_2 . The solution was decanted from precipitate and dried in vacuo. ^1H NMR spectrum showed the presence of $\text{Cp}_2\text{Nb}(\text{HPPr}_2)\text{Cl}$ and $\text{Cp}_2\text{Nb}(\text{HPPr}_2)\text{H}$ in the ratio 5:1. Yield: 1.575 g. ^1H NMR (toluene- d_8): δ 4.75 (d, $J(\text{P-H}) = 2.4 \text{ Hz}$, 10, Cp), 3.46 (dt, $J(\text{P-H}) = 307 \text{ Hz}$ and

$J(\text{H}-\text{H}) = 4.2 \text{ Hz}$, $1, \text{P}-\text{H}$, 1.94 (m, 2, CH), 0.97 (dd, $J(\text{P}-\text{H}) = 13.6 \text{ Hz}$ and $J(\text{H}-\text{H}) = 7.0 \text{ Hz}$, 6, CH_3), 0.84 (dd, $J(\text{P}-\text{H}) = 14.2 \text{ Hz}$ and $J(\text{H}-\text{H}) = 6.9 \text{ Hz}$, 6, CH_3). ^{13}C NMR (toluene- d_8): δ 94.1 (Cp), 24.7 (d, $J(\text{P}-\text{C}) = 17.4 \text{ Hz}$), 21.4 and 21.1 (with, CH_3). ^{31}P NMR (toluene- d_8): δ 58.6 ppm.

4.18. Preparation of $\text{Cp}_2\text{NbCl}(\text{HP}(-\text{OCH}_2)_2\text{CMe}_2)$ (**6g**)

1.24 mL of $\text{CIP}(-\text{OCH}_2)_2\text{CMe}_2$ was added to a solution of 1.05 g (4.6 mmol) of blue Cp_2NbH_3 [28] in 40 mL of toluene under intensive stirring. The solution turned red–brown and dark substance precipitated. This precipitate was shown to be a mixture of **8** and unidentified products. The solution was decanted and put into freezer to give in a 1.5 month a dark red–brown crystalline **6g**. Yield 0.521 g (28.6%). IR (nujol): $\nu_{\text{P}-\text{H}} = 2300 \text{ cm}^{-1}$. ^1H NMR (benzene- d_6): δ 4.97 (d, $J(\text{P}-\text{H}) = 2.7 \text{ Hz}$, 10, Cp), 7.61 (d, $J(\text{P}-\text{H}) = 334.0 \text{ Hz}$, 1, P–H), 3.43 and 3.21 (m, 4, CH_2), 1.00 (s, 3, CH_3), 0.11 (s, 3, CH_3). ^{13}C NMR (benzene- d_6): δ 94.3 (s, Cp), 81.0 (d, $J(\text{P}-\text{C}) = 12.6 \text{ Hz}$, CH_2), 32.5 (c, C), 22.5 (s, CH_3) and 21.0 (s, CH_3). Anal. Calc. for $\text{C}_{15}\text{H}_{21}\text{ClPbO}_2\text{Nb}$: C, 45.88; H, 5.39. Found: C, 45.49; H, 5.18.

4.19. Crystal structure determinations

8. The yellow crystals of **8** were grown from acetone solution. The crystals were covered by oil and mounted at -120°C on the Siemens three-circle diffractometer with area CCD detector (SMART system). The crystallographic data are given in Table 3. The structure amplitudes for 5144 independent reflections were obtained after the usual Lorentz and polarization corrections. A semi-empirical absorption correction based on ψ -scans was applied. The structure was solved by direct methods [41] and refined by full-matrix least squares procedures [42], using $\omega(|F_o|^2 - |F_c|^2)^2$ as the refined function. Only the reflections with $F_o^2 > 2\sigma F_o^2$ were used in the refinements. Hydrogen atoms on phosphorus were found from the difference map and other hydrogen atoms were imposed at calculated positions and refined isotropically. In the final cycles of refinement, all the non-hydrogen atoms were refined with anisotropic temperature parameters. The largest peak in the final difference Fourier map had an electron density of $0.747 \text{ e } \text{\AA}^{-3}$ and the lowest hole was of $-0.759 \text{ e } \text{\AA}^{-3}$. The location and magnitude of the residual electron density was of no chemical significance.

14. The green–brown crystals of **14** were grown from hexane solution. The crystals were covered by oil and mounted on an Enraf-Nonius CAD-4 diffractometer at -100°C . Crystallographic data are given in Table 3. The unit cell parameters were determined using 25 accurately centered reflections, 2 reflections were measured every 2 h for orientation and decay control. The structure amplitudes for 1765 independent reflections were obtained after the usual

Table 3
Crystal data, collection data and refinement parameters for **8** and **15**

	$\text{C}_{30}\text{H}_{32}\text{ClNbO}_2\text{P}_2$	$\text{C}_{16}\text{H}_{14}\text{PBrNb}$
Empirical formula	$\text{C}_{30}\text{H}_{32}\text{ClNbO}_2\text{P}_2$	$\text{C}_{16}\text{H}_{14}\text{PBrNb}$
Formula weight	526.76	421.15
Temperature (K)	153(2)	293
Wavelength	0.71073 Å	0.71073 Å
Space group	$\text{P2}_1/\text{c}$	$\text{C2}/\text{c}$
Unit cell dimensions		
a Å	9.5363(5)	25.779 (5)
b Å	14.7434(8)	8.820 (2)
c Å	16.2272(8)	15.537 (3)
β deg	99.440(1)	102.64(3)
Volume Å ³	2250.6(2)	3447.0(12)
Z	4	8
Density (calculated) Mg/m ³	1.555	1.623
Absorption coefficient mm ⁻¹	0.819	0.310
θ range ($^\circ$) for data collection	4.53 to 28.41	2.69 to 26.99
Index ranges	$-12 < h < 12$ $-19 < k < 12$ $-19 < l < 21$	$-32 < h < 32$ $0 < k < 11$ $0 < l < 19$
Max. and min. transmission (correction)	0.7465 and 0.6345	0.824 and 1.192
Goodness-of-fit on F^2	1.371	1.110
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0564$, $wR2 = 0.1271$	$R1 = 0.0378$, $wR2 = 0.1025$

Lorentz and polarization corrections. The structure was solved by direct methods [41] and refined by full-matrix least squares procedures [42], using $\omega(|F_o|^2 - |F_c|^2)$ as the refined function. After isotropic refinement for all non-hydrogen atoms, DIFABS [43] was applied for the absorption correction. In the final cycles of refinement, all the non-hydrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms were found from Fourier difference syntheses and were refined isotropically. The largest peak in the final difference Fourier map had an electron density of $0.402 \text{ e } \text{\AA}^{-3}$, and the lowest hole was of $-0.299 \text{ e } \text{\AA}^{-3}$. The location and magnitude of the residual electron density was of no chemical significance.

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