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Article

Niobium/Rhodium Bimetallic Complexes: Synthesis, Structure, and Catalytic Hydrosilylation of Acetophenone and Benzaldehyde

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Reactions of a new imido phosphido complex, $Cp_2Nb(=NBu^t)(PPh_2)$ (**1**), with olefin complexes of rhodium afford two types of compounds. With $[(\mu\text{-Cl})Rh(C_2H_4)_2]_2$, an imido/phosphido-bridged complex, $Cp(Cl)Nb(\mu\text{-}NBu^t)(\mu\text{-}PPh_2)RhCp$ (**2**), characterized by NMR and X-ray diffraction, was prepared. Formation of **2** represents a rare example of a Cp/Cl exchange reaction in organometallic chemistry. When **1** reacts with $[(\mu\text{-Cl})Rh(COD)]_2$, the target phosphido-bridged bimetallic complex $Cp_2Nb(=NBu^t)(\mu\text{-}PPh_2)Rh(Cl)(COD)$ (**4**) is formed. The structure of this product was established by NMR and an X-ray diffraction study. Both **2** and **4** are catalyst precursors for hydrosilylation of benzaldehyde and acetophenone. The activity of the neutral complex **4** exceeds that of the cation $[Cp_2Nb(NBu^t)(PPh_2)Rh(COD)]^+$ derived from **4** by chloride anion abstraction.

Introduction

Heterobimetallic complexes[1] have recently received renewed attention because the cooperative action of both metal atoms allows them to activate robust bonds and mediate complex transformations.[2,3] All successful examples of active bimetallic systems are almost exclusively based on metals from the right (Rh, Pt, Cu, etc.) or middle part of transition series.[3] Despite the fact that complexes featuring both early and late transition metals, i.e., early late heterobimetallics (ELHB), have been the subject of intensive research over the last 25 years,[1] relatively little is known about their catalytic activity.[1b,4] Previous work in this area was primarily based on the idea that electron-deficient early transition metals should serve as intramolecular Lewis acidic centers of ELHB, assisting the transformation of organic molecules such as carbonyls in the coordination sphere of late transition metals (LTM), thus facilitating catalysis.[1a,4c] For this reason, the earlier design of most ELHB complexes was based on unsaturated group 4 metal moieties,[1,4] and relatively little is known about the behavior of group 5 derivatives.[4b,5]

Another approach to a rational design of a bimetallic catalyst consists in the incorporation of one of the metal atoms into the ligand framework of the other catalytically active center, which is usually a LTM center. This can facilitate chemical transformation on the LTM by means of fine adjustment of ligand bonding capabilities. Such an approach has previously recommended itself in the catalytic Suzuki−Miyaura reaction mediated by phosphido-bridged Re/Pd and Ru/Pd complexes.[6] In this case, the polarization of the $M^{\delta+}-P^{\delta-}$ bond (M = Re or Ru) makes the phosphorus atom a better donor to the palladium atom. One can expect that metallophosphides, MPR_2, based on the electropositive early transition metals will result in even greater polarization of the metal−phosphorus bond,[6a] which will further increase the bonding capabilities of the phosphido ligand toward a catalytically active late transition metal. Surprisingly, although a number of phosphido-bridged ELHBs are known,[1a,1b,7] their application to organic synthesis and catalysis is scarce.[4a]

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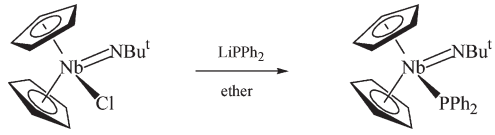
Hemilabile ligands play a prominent role in modern catalysis.[8] They usually feature a soft center (usually based on C, S, or P), which ensures strong binding to the metal, and a hard center (O or N based), which can bind loosely to a vacant metal site, thus creating a masked form of an unsaturated complex. We suggested that the attachment of hard and soft ligands such as imido and phosphido to an early transition metal would give rise to a new type of "spectator" metalloligand[9] that could be used as a hemilabile ligand to a catalytically active late transition metal. Herein we report the application of this concept to the preparation of imido phosphido niobocene $Cp_2Nb(=NBu^t)(PPh_2)$ (**1**) and the synthesis of some Nb/Rh heterobimetallics derived therefrom. In the course of our studies, we encountered an unusual exchange of Cp and chloride ligands between two metal centers. Application of the new Nb/Rh ELHB to catalytic hydrosilylation of acetophenone and benzaldehyde is also reported.

Results and Discussion

Preparation of $Cp_2Nb(=NBu^t)(PPh_2)$ (1). Our initial strategy to prepare complex **1** was based on the insertion/deprotonation method developed in this laboratory[10] and by the group of Moïse.[11] Namely, we anticipated that the reaction between $Cp_2Nb(=NBu^t)(H)$[12] and $ClPR_2$ would give the insertion product $[Cp_2Nb(=NBu^t)(PHR_2)]Cl$, which could be then deprotonated to furnish the phosphide **1**. Related cationic P−H phosphine complexes have been previously prepared by reactions of Cp_2MH_3 and $Cp_2MH(L)$ (M = Nb, Ta; L = two-electron ligand) with chlorophosphines.[10,11,13] In reality, it happens that $Cp_2Nb(=NBu^t)(H)$ reacts with $ClPEt_2$ to give $Cp_2Nb(=NBu^t)(Cl)$ and $HPEt_2$. We attribute the difference in chemical behavior between our imido hydride system and the previously studied trihydrides and monohydrides to the ease of phosphine displacement from the intermediate $[Cp_2Nb(=NBu^t)(PHR_2)]^+$, which generates an unsaturated intermediate, $[Cp_2Nb(=NBu^t)]^+$, amenable to coupling with the chloride.

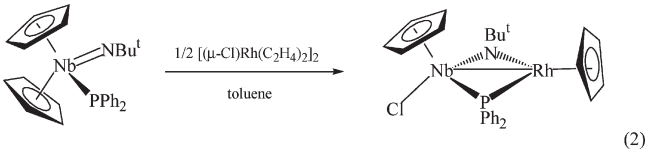
Eventually, complex **1** was prepared in moderate yield by reacting $Cp_2Nb(=NBu^t)(Cl)$ with $LiPPh_2 \cdot Et_2O$ in ether (eq 1). **1** was isolated as a yellow crystalline solid and characterized by multinuclear NMR spectroscopy. Similar chloride substitution by MeLi to give $Cp_2Nb(=NBu^t)(Me)$ has been previously described.[12] Although the ^{31}P NMR signal of **1** was not detectable due to the fast relaxation on the ^{93}Nb nucleus (spin $I = 9/2$, natural abundance 100%), its position can be established from a cross-peak in the $^1H-^{31}P$ HSQC NMR between the *ortho*-protons of the phenyl group and the phosphorus signal at $\delta = -0.2$ ppm.



(1)

1

Preparation of Bimetallic Complexes: Reaction with $[(\mu\text{-Cl})(Rh(C_2H_4)_2]_2$. Diolefin complexes of Rh(I) in combination with phosphine, NHC carbenes, or related two-electron donors are common catalysts of hydrosilylation of carbonyls.[14,15] Several families of related hemilabile ligands were applied in this catalytic system.[15c,15d] Bearing this in mind, we targeted the preparation of an adduct between the imido-phosphide **1** and $[(\mu\text{-Cl})(Rh(C_2H_4)_2]_2$. To our surprise, the reaction between **1** and 0.5 equiv of $[(\mu\text{-Cl})(Rh(C_2H_4)_2]_2$ in toluene resulted in the exchange compound $Cp((Cl)Nb(\mu\text{-}NBu^t)(\mu\text{-}PPh_2)RhCp$ (**2**) featuring the Cp ligand at rhodium and the chloride at niobium (eq 2). This is a very rare example of Cp ring substitution at an early transition metal center.[16] The ^1H NMR spectrum of **2** exhibits two Cp resonances, 4.88 and 5.42 ppm, of equal intensity that integrate as five protons each relative to the signals of the Ph and Bu^t groups. Correlation of these proton signals with the ^{13}C NMR signals at 87.3 and 104.4 ppm, respectively, supports their assignment. The ^1H signal of the Bu^t group at 1.72 ppm in **2** is shifted downfield relative to the corresponding resonance in **1** (1.02 ppm), indicating the presence of a bridging imido group in the former.



(2)

1 **2**

In order to get further insight into the structure of **2**, a crystal structure determination was carried out (Figure 1).

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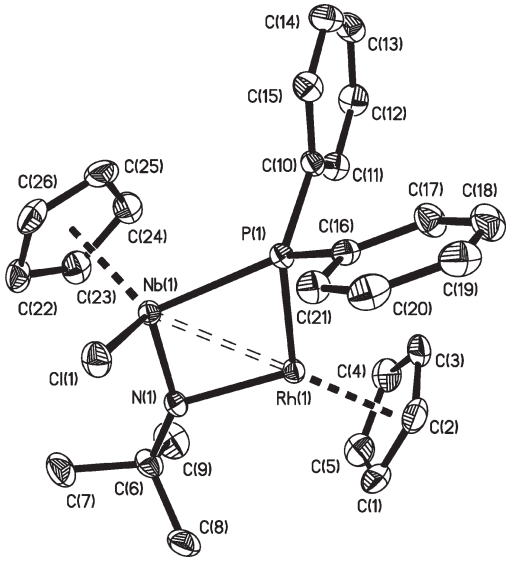

Figure 1. Molecular structure of compound **2**. Selected bond distances (in Å) and angles (in deg): Nb1−Rh1 2.6744(2), Nb1−N1 1.8643(17), Nb1−P1 2.4136(5), Nb1−Cl1 2.4349(5), Nb1−Cp 2.67(6), Rh1−N1 2.0817(16), Rh1−P1 2.2516(5), Rh1−Cp 2.06(10), N1−Nb1−Cl1 106.71(5), P1−Nb1−Cl1 100.998(18), N1−Nb1−P1 103.08(5), N1−Rh1−P1 101.91(5). Hydrogen atoms are omitted for clarity.

X-ray structure analysis proved unequivocally the formulation of **2** as the Cp/Cl exchange product Cp((Cl)Nb(μ-NBu^t)(μ-PPh$_2$)RhCp, but not the target complex Cp$_2$Nb(=NBu^t)(μ-PPh$_2$)RhCl(C$_2$H$_4$)$_2$. The molecular structure of **2** exhibits a three-leg piano-stool geometry for niobium and a two-leg piano-stool geometry for rhodium; both metal atoms are bridged by the imido and phosphido ligands. Our search in the Cambridge Structural Database[17] did not reveal any bimetallic rhodium complex with a μ_2-bridging imido ligand; thus complex **2** is the first representative of this class. However, its Rh−N bond of 2.082(2) Å is comparable with Rh−imido bonds in trimetallic complexes M$_2$Rh(μ_3-NR), in which the imido ligand bridges three metal centers (1.980−2.102 Å).[17] The Rh−P bond of 2.2516(5) Å in **2** is at the shorter end of a very wide spectrum of rhodium−phosphido distances (2.202−2.840 Å). Similarly, the Nb−N distance of 1.864(2) Å is the shortest in the class of imido-bridged Nb complexes (range 1.952−2.135 Å), and the Nb−P bond of 2.4136(5) is the shortest in the class of phosphido-bridged Nb complexes (range 2.487−2.717 Å). These structural features may be the consequence of a very short Nb−Rh distance (2.6744(2) Å), which indicates the presence of a direct Nb−Rh bond (compare with the sum of metal radii, 2.774 Å) and thus accounts for the diamagnetism of this complex.

Complex **2** is stable in the solid state but gradually decomposes in solution at room temperature to give unidentified products. It does not react with H$_3$SiPh over the course of 29 h. Attempted Cl/H exchange in **2** under the action of L-Selectride (Li[BH(CH(CH$_3$)C$_2$H$_5$)$_3$]) resulted in no reaction.

In an attempt to remove the chloride and to stop the Cp/Cl exchange leading to **2**, solutions of [Rh(μ-Cl)(C$_2$H$_4$)$_2$]$_2$ in THF were pretreated with L-Selectride before the addition of **1**. Although a reaction occurred, accompanied by the formation of a black precipitate, the benzene-soluble part contained only the starting phosphide **1** and a small amount of Cp$_2$Nb(NBu^t)Cl. Similar pretreatment of [Rh(μ-Cl)(C$_2$H$_4$)$_2$]$_2$ with Me$_2$PhSiH affords a new, fluxional Cp compound characterized by the ^{1}H NMR (C$_6$D$_6$) signal at 6.21 ppm. This product however decomposes overnight to furnish Cp$_2$Nb(NBu^t)Cl. No signals were observed in the ^{31}P NMR, suggesting that the phosphorus-containing co-product is either fluxional or insoluble in benzene.

When [Rh(μ-Cl)(C$_2$H$_4$)$_2$]$_2$ was pretreated with PPh$_3$, the fluxional complex [Rh(μ-Cl)(C$_2$H$_4$)(PPh$_3$)]$_2$ characterized by the Rh-coupled ^{31}P signal at 53.9 ppm (dd, J(Rh−P) = 184.6 Hz, J(Rh−P) = 6.0 Hz) was formed. Subsequent 1:1 reaction of this product with **1** results in a fast formation of a mixture containing a new ethylene compound, Cp$_2$Nb(=NBu^t)(μ-PPh$_2$)Rh(PPh$_3$)(C$_2$H$_4$)Cl (**3**), the exchange product **2**, and Cp$_2$Nb(NBu^t)Cl in the ratio 10:3.5:3.0. Complex **3** is unstable. After 1 h at room temperature, the signals due to **2** and **3** diminish, leaving Cp$_2$Nb(NBu^t)Cl as the main niobium product. Complex **3** is characterized by its ^{1}H NMR Cp signal at 6.06 ppm integrated as 10 protons, a broad ethylene signal at 2.13 ppm integrated as four protons, and a singlet at 0.66 ppm (Bu^t group) integrated as nine protons. The position of the latter signal suggests that the imido group remains terminal.

Preparation of Bimetallic Complexes: Reaction with [(μ-Cl)(Rh(COD)]$_2$. Reaction of **1** with 0.5 equiv of [(μ-Cl)(Rh(COD)]$_2$ (COD = 1,5 cyclooctadiene) in toluene afforded the target bimetallic complex Cp$_2$Nb(=NBu^t)(μ-PPh$_2$)Rh(Cl)(COD) (**4**) (Scheme 1). Complex **4** was isolated from toluene/hexane solution in the form of orange crystals of its hexane solvate (**4**·0.5hexane), and its structure was established by multinuclear NMR and X-ray diffraction analysis. The ^{1}H NMR spectrum of **4** in C$_6$D$_6$ shows, in addition to other signals, a doublet at 6.14 ppm (J(P−H) = 1.2 Hz) for the Cp ring integrated as 10 protons, two broad singlets at 5.62 and 3.15 ppm for nonequivalent olefin protons integrated as four each, and a singlet at 0.66 ppm for the terminal Bu^t-imido group. The downfield-shifted olefin signal at 5.62 ppm is coupled in the ^{1}H−^{31}P HSQC spectrum with the broad phosphorus resonance at 26.3 ppm (d, J(P−Rh) = 114.2 Hz), which suggests the mutual *trans* arrangements of these groups. The upfield olefin signal at 3.15 ppm, therefore, comes from the other double bond of COD that is *trans* to the chloride ligand, which is a weaker *trans* ligand than phosphide. These spectroscopic features are consistent with the presence of a four-coordinate Rh center bound to niobium via the phosphide bridge.

Complex **4** is stable in the solid state but gradually decomposes in solutions at room temperature (half-life approximately 4 days) to give Cp$_2$Nb(NBu^t)Cl and the known complex [Rh$_2$(μ-Cl)(μ-PPh$_2$)(COD)$_2$], identified by the ^{31}P NMR.[18] After a few days, the latter product partially rearranges to [Rh(μ-PPh$_2$)(COD)]$_2$.[19]

The X-ray structure analysis of **4** confirms the phosphido-bridged bimetallic structure (Figure 2). The niobium atom is in a typical disubstututed niobocene geometry.[20] The imido ligand remains terminal, forming a short Nb−N bond of 1.776(4) Å, which is close to the mean Nb=N bond of 1.782 Å found for the wide range of niobium−imido bonds

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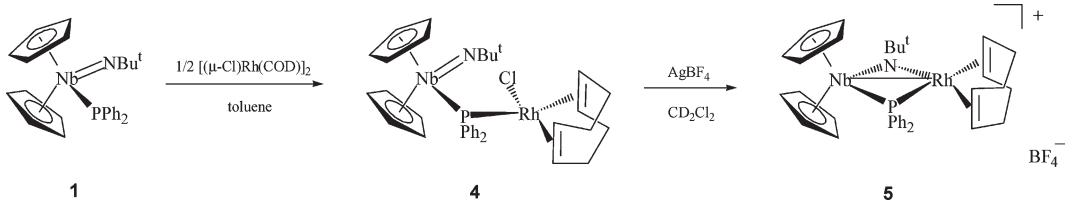
Scheme 1. Preparation of Complexes 4 and 5



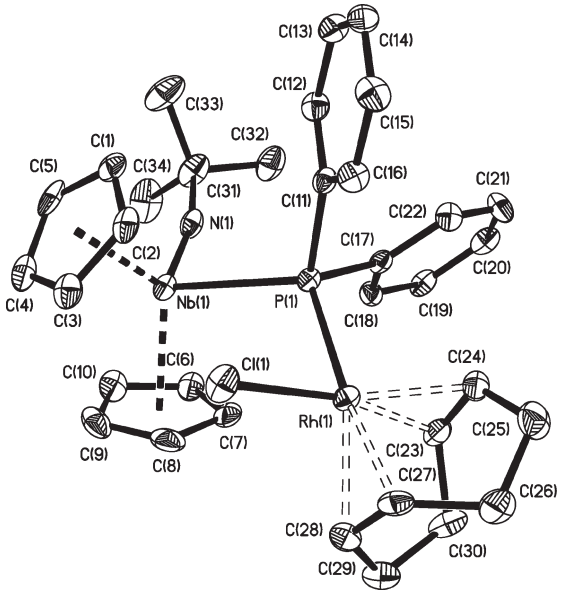


Figure 2. Molecular structure of the compound **4**·0.5hexane. Selected bond distances (in Å) and angles (in deg): Nb1−P1 2.6854(13), Rh1−P1 2.3790(12), Nb1−N1 1.776(4), Rh1−Cl1 2.3968(13), Rh1−C24 2.102(5), Rh1−C23 2.137(5), Rh1−C28 2.183(5), Rh1−C27 2.209(4), N1−Nb1−P1 94.10(13), C31−N1−Nb1 166.3(4), P1−Rh1−Cl1 92.27(4), C24−Rh1−P1 94.92(14), C23−Rh1−P1 93.28(13), C28−Rh1−P1 152.75(13), C27−Rh1−P1 170.35(14), C24−Rh1−Cl1 149.93(15), C23−Rh1−Cl1 168.88(14), C28−Rh1−Cl1 89.02(14), C27−Rh1−Cl1 86.80(14). Hydrogen atoms and the hexane solvate are omitted for clarity.

(1.672−2.051 Å).[17] For related niobocene imido complexes, a narrow range of Nb=N distances has been determined (1.737(6)−1.804(5) Å).[12,21] The bond angle Nb−N−Bu^t of 166.2(3)° is also quite normal for niobocene imido complexes.[21a] The Nb−P bond of 2.685(1) Å and the Rh−P bond of 2.379(1) Å are noticeably longer than the corresponding distances in compound **2** discussed above, which can be accounted for by the absence of direct Nb−Rh bonding at the long Nb−Rh separation of 4.266 Å. The Rh atom is ligated by the chloride ligand, two double bonds of COD, and the bridging phosphide, which together comprise the usual, square-planar geometry around the d^8 Rh center. Consistent with the NMR data, one double bond of the COD ligand is positioned *trans* to the phosphide, and the other one is *trans* to the chloride ligand. The Rh−C$_{COD}$ distances *trans* to the phosphide (2.183(5) and 2.209(4) Å) are longer than those *trans* to the chloride (2.102(5) and 2.137(5) Å), which highlights the stronger *trans* influence of the phosphide ligand.

Catalytic Studies. On the basis of literature precedents on catalytic hydrosilylation of carbonyls by cationic Rh complexes,[15b,15c,15e] we initially sought to study the catalytic activity of the cationic complex [Cp$_2$Nb(μ-NBu^t)(μ-PPh$_2$)-Rh(COD)]$^+$ (**5**), which could be prepared by chloride abstraction from **4**. We anticipated that the imido ligand would be able to occupy the bridging position, so that the fragment Cp$_2$Nb(NBu^t)(PPh$_2$) would serve as a hemilabile ligand to the cation [Rh(COD)]$^+$.

The cation **5** was generated in CD_2Cl_2 by reacting **4** with $AgBF_4$ (Scheme 1). Upon mixing the reagents, the color of the solution changed immediately from yellow to brown, accompanied by the formation of a brown precipitate. The ^{1}H NMR showed the formation of a new species, which however turned out to be too unstable to allow isolation. In light of this, hydrosilylation of acetophenone by $PhSiH_3$ catalyzed by the *in situ* formed **5** was attempted. The course of the reaction in CD_2Cl_2 was monitored by ^{1}H NMR spectroscopy. In 5 h, complete conversion was achieved, giving a mixture of mono- and bis(hydrosilylation) products ($PhSiH_2OCH(Me)Ph$ and $PhSiH(OCH(Me)Ph)_2$, respectively) in the ratio 38:62 (Table 1).

However, to our surprise, the parent neutral complex **4** showed even greater activity. The reaction was complete in 2 h, showing the same product composition (Table 1, entries 2 and 3). The change of solvent from methylene chloride to benzene had no effect on the rate of hydrosilylation or product distribution (Table 1, entries 2 and 3), whereas the nature of the silane does affect the reaction. With a secondary silane ($PhMeSiH_2$), the reaction took more time and up to 30% of a dehydrogenative silylation product, $PhSiHMeOC(Ph)=CH_2$, was formed (Table 1, entry 4). Tertiary silanes were not active in this reaction (Table 1, entries 5−7).

For comparison, hydrosilylation of acetophenone was attempted with the parent Rh complex [Rh(μ-Cl)(COD)]$_2$ in the absence of any added phosphide. [Rh(μ-Cl)(COD)]$_2$ turned out to be a better catalyst than **4** for the hydrosilylation with $PhMeSiH_2$ (Table 1, entry 4 vs entry 15), but a worse one for the hydrosilylation with $PhSiH_3$ (Table 1, entry 14 vs entry 2).

Even more surprisingly, the Cp/Cl exchange complex **2** also showed significant, although much reduced catalytic activity in the hydrosilylation of acetophenone (Table 1, entries 9−12). Again, the primary silane $PhSiH_3$ performed much better than the secondary one (Table 1, entry 8 vs entry 9), while tertiary silanes were not active (entries 10−12). Complex **2** does not catalyze the addition of Me_2PhSiH to 1-hexene. The isomerization to 2-hexene takes place instead.

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Table 1. Catalytic Hydrosilylation of Acetophenone by 2, 4, and 5 (3%) in C_6D_6

entry	catalyst	silane	time	yield (%)
1	**5**	$PhSiH_3$	5 h[a]	$PhSiH_2OCH(Me)Ph$: 32% $PhSiH(OCH(Me)Ph)_2$: 68%
2	**4**	$PhSiH_3$	2 h[a]	$PhSiH_2OCH(Me)Ph$: 40% $PhSiH(OCH(Me)Ph)_2$: 60%
3		$PhSiH_3$	2 h	$PhSiH_2OCH(Me)Ph$: 32% $PhSiH(OCH(Me)Ph)_2$: 68%
4		$MePhSiH_2$	5 h	$PhSiHMeOCH(Me)Ph$: 60% $PhSiHMeOC(Ph)=CH_2$: 30%
5		Me_2PhSiH	1 d	NR
6		Et_3SiH	1 d	NR
7		$(OEt)_3SiH$	1 d	NR
8	**2**	$PhSiH_3$	7 h 10 min	$PhSiH_2OCH(Me)Ph$: 20% $PhSiH(OCH(Me)Ph)_2$: 80%.
9		$MePhSiH_2$	1 d 22 h	$PhSiHMeOCH(Me)Ph$ 100%
10		Me_2PhSiH	1 d	NR
11		Et_3SiH	1 d	NR
12		$(OEt)_3SiH$	1 d	NR
14	$[Rh(\mu\text{-Cl})(COD)]_2$	$PhSiH_3$	7 h 30 min	$PhSiH_2OCH(Me)Ph$: 19% $PhSiH(OCH(Me)Ph)_2$: 81%
15	$[Rh(\mu\text{-Cl})(COD)]_2$	$MePhSiH_2$	2 h	$PhSiHMeOCH(Me)Ph$: 63% $PhSiHMeOC(Ph)=CH_2$: 34%.

[a] In CD_2Cl_2.

Complex **4** was also found to catalyze hydrosilylation of benzaldehyde with $PhSiH_3$ at a low catalyst load (1.5 mol %, 50 min for completeness), with the products being mono- and bis(addition) derivatives, $PhSiH_2OCH_2Ph$ and $PhSiH(OCH_2Ph)_2$,[22] in the ratio 36:64. At 3.0% catalyst load, the reaction was complete in 5 min, showing the selective formation of $PhSiH(OCH_2Ph)_2$ (94% yield).

In an attempt to gain more insight into these catalytic transformations, stoichiometric reactions were attempted. When complex **4** reacts with $PhSiH_3$ in a 1:1 ratio, decomposition occurs, leading to the formation of $Cp_2Nb(NBu^t)Cl$ and $Cp_2Nb(NBu^t)(PPh_2)$. With a stoichiometric amount of PhCHO, **4** decomposes to $Cp_2Nb(NBu^t)Cl$, but no new detectable Rh species could be identified in the reaction mixture by ^1H and ^{31}P NMR.

Conclusions

The new imido phosphido complex $Cp_2Nb(NBu^t)(PPh_2)$ (**1**) serves as a metallophosphine ligand to rhodium olefin fragments $\{ClRhL_2\}$, affording phosphido-bridged bimetallic complexes. The outcome of the reaction depends on the nature of the olefin L. With L = ethylene, the main product is an unusual Cp/Cl exchange complex, $Cp(Cl)Nb(\mu\text{-}NBu^t)(\mu\text{-}PPh_2)RhCp$ (**2**), featuring a bridging imido group in addition to bridging phosphido group. When L_2 is the chelating diolefin COD, the reaction of **1** with 0.5 equiv of $[(\mu\text{-Cl})RhCOD]_2$ proceeds as a simple phosphide addition to furnish the bimetallic product $Cp_2Nb(=NBu^t)(\mu\text{-}PPh_2)Rh(Cl)(COD)$ (**4**). Both **2** and **4** were found to be active precatalysts for hydrosilylation of acetophenone and benzaldehyde. The neutral complex **4** exhibits enhanced reactivity in comparison with the cationic derivative $[Cp_2Nb(NBu^t)(PPh_2)Rh(COD)]^+$, presumably because the latter has the imido ligand too tightly coordinating to the Rh center. Future research will be directed at the optimization of the starting imido-phopshido complex of Nb to make it a better hemilabile metalloligand.

Experimental Details

All manipulations were carried out, using conventional inert atmosphere glovebox and Schlenk techniques. Solvents were dried by Grubbs-type columns or by distillation from appropriate drying agents. NMR spectra were obtained with Bruker DPX-300 and Bruker DPX-600 instruments (^1H: 300 and 600 MHz; ^{13}C: 75.5 and 151 MHz; ^{29}Si: 119.2 MHz; ^{31}P: 121.5 and 243 MHz). IR spectra were measured on an ATI Mattson FTIR spectrometer. L-Selectride was purchased from Alfa Aesar, and $[Rh(\mu\text{-Cl})(COD)]_2$ and $[Rh(\mu\text{-Cl})(C_2H_4)]_2$ were from Strem. Silanes $PhSiH_3$, MePhSiH, and $MePh_2SiH$ were prepared by reducing the corresponding chlorides with $LiAlH_4$, and Et_3SiH and $(OEt)_3SiH$ were obtained from Aldrich. Complexes $Cp_2Nb(N^tBu)Cl$[12] and $Ph_2PLi\cdot Et_2O$[23] were prepared according to the literature methods.

Synthesis of $Cp_2Nb(NBu^t)(PPh_2)$ (1). $Ph_2PLi\cdot Et_2O$ (0.177 g, 0.665 mmol) dissolved in Et_2O (20 mL) was added under stirring to a solution of $Cp_2Nb(NBu^t)Cl$ (0.213 g, 0.646 mmol) in Et_2O (20 mL) at −30 °C. The color changed first from yellow to brown and then gradually turned to brown-green in the course of 2 h. The solution was allowed to warm to room temperature and then was stirred overnight, affording a brown suspension. After filtration through a microglass filter paper, volatiles were removed from the yellow solution *in vacuo* to give a yellow solid. The latter was washed with hexane and recrystallized from Et_2O at −20 °C, affording a yellow microcrystalline material in 77% yield (0.245 g, 0.511 mmol). ^1H NMR (300 MHz, C_6D_6, ppm): δ 1.02 (s, 9H, Bu^t), 5.52 (d, $J(P-H)$ = 0.6 Hz, 10H, Cp), 7.05 (t, $J(H-H)$ = 7.2 Hz, 2H, p-Ph), 7.19 (t, $J(H-H)$ = 7.2 Hz, 4H, m-Ph), 7.80 (dd, $J(H-H)$ = 7.2 Hz, $J(P-H)$ = 9.3 Hz, 4H, *o*-Ph). ^{13}C NMR (75.5 MHz, C_6D_6, ppm): δ 31.0 (Bu^t), 108.0 (d, $J(P-C)$ = 2.3 Hz, Cp), 125.7 (*p*-Ph), 127.8 (*m*-Ph), 135.0 (d, $J(C-P)$ = 16.6 Hz, *o*-Ph), 148.9 (d, $J(C-P)$ = 35.4 Hz, *i*-Ph). $^1H-^{31}P$ HSQC NMR (C_6D_6, ppm): δ −0.2 (s, PPh_2). Anal. Calcd for $C_{26}H_{29}NNbP$: C, 65.14; H, 6.10; N, 2.92. Found: C, 65.04; H, 6.16; N, 2.80.

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Synthesis of CpNbCl(μ-NBu^t)(μ-PPh$_2$)RhCp (2). A solution of complex **1** (0.101 g, 0.211 mmol) in toluene (5 mL) was added to a stirred solution of [Rh(μ-Cl)(C_2H_4)$_2$]$_2$ (0.035 g, 0.105 mmol) in toluene (5 mL). The resulting dark green solution was stirred for 15 min, after which time the volatiles were removed *in vacuo*. The green solid produced was washed with hexane and recrystallized from Et_2O, giving a green microcrystalline material in 81% yield (0.105 g, 0.170 mmol). ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 1.72 (s, 9H, Bu^t), 4.88 (s, 5H, Cp), 5.42 (d, J(P−H) = 0.6 Hz), 5H, Cp), 6.99 (m, 4H, m-Ph), 7.05 (m, 2H, *p*-Ph), 7.28 (m, 2H, *o*-Ph), 8.06 (dd, J(H−H) = 8.3 Hz, J(P−H) = 13.0 Hz, 2H, *o*-Ph). ^{13}C NMR (75.5 MHz, C_6D_6, ppm): δ 35.4 (Bu^t), 87.3 (Cp), 104.4 (Cp), 133.2, 134.1 (Ph). Anal. Calcd for $C_{26}H_{29}ClNNbPRh$: C, 50.55; H, 4.73; N, 2.27. Found: C, 51.04; H, 5.25; N, 1.83.

Generation of Cp$_2$Nb(=NBu^t)(μ-PPh$_2$)Rh(PPh$_3$)(C_2H_4)Cl (3). To [Rh(μ-Cl)(C_2H_4)$_2$]$_2$ (0.003 g, 0.009 mmol) in C_6D_6 (0.6 mL) was added PPh_3 (0.005 g, 0.019 mmol) to give an orange solution of [Rh(μ-Cl)(C_2H_4)(PPh_3)]$_2$ (^{31}P NMR (121.5 MHz, C_6D_6, ppm): δ 53.9 ppm (dd, J(Rh−P) = 184.6 Hz, J(Rh−P) = 6.0 Hz)). Then 0.009 g (0.019 mmol) of complex Cp$_2$Nb(N^{t}Bu)(PPh_2) (**1**) was added to the mixture, causing the color change to brown. NMR spectra revealed the formation of a mixture of compounds containing Cp$_2$Nb(=NBu^t)(μ-PPh$_2$)Rh(PPh$_3$)(C_2H_4)Cl (**3**), **2**, and Cp$_2$Nb(NBu^t)Cl in the ratio 10:3.5:3.0. Complex **3** decomposes in benzene solutions in the course of 1 h.

Selected NMR data for Cp$_2$Nb(=NBu^t)(μ-PPh$_2$)Rh(PPh$_3$)(C_2H_4)Cl (**3**): ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 6.06 (s, 10, H, Cp), 2.13 (bd, J(Rh−H) = 1.8 Hz, 4 H, C_2H_4), 0.66 (s, 9H, Bu^t). ^{31}P NMR (121.5 MHz, C_6D_6, ppm): δ 36.4 (d, J(Rh−P) = 128.8 Hz, PPh_3).

Synthesis of [Cp$_2$NbCl(NBu^t)(μ-PPh$_2$)RhCl(COD)]·0.5hexane (4·0.5hexane). A solution of complex **1** (0.100 g, 0.209 mmol) in toluene (5 mL) was added to a stirred solution of [Rh(μ-Cl)(COD)]$_2$ (0.052 g, 0.106 mmol) in toluene (5 mL). The resulting orange solution was stirred for 15 min, after which time the solvent was removed *in vacuo*. The orange solid produced was washed with hexane and recrystallized by layer diffusion of hexane into a toluene solution, giving orange crystals of **4**·0.5hexane in 91% yield (0.146 g, 0.190 mmol). ^{1}H NMR (600 MHz, toluene-d_8, 237 K, ppm): δ 0.69 (s, 9H, Bu^t), 0.95 (t, J(H−H) = 7.2 Hz, 3H, 0.5 hexane), 1.25 (m, 4H, 0.5 hexane) 1.65 (m, 2H, COD), 1.80 (m, 2H, COD), 2.34 (m, 4H, COD), 3.17 (s, 2H, COD), 5.62 (s, 4H, COD), 6.14 (s, 10H, Cp), 6.98 (m, 2H, *p*-Ph), 7.01 (m, 2H, Ph), 7.22 (m, 2H, Ph), 7.25 (m, 2H, Ph), 8.95 (bs, 2H, *o*-Ph). ^{1}H NMR (300 MHz, 295 K, C_6D_6, ppm): δ 0.66 (s, 9H, Bu^t), 1.59 (m, 2, COD), 1.72, (m, 2H, COD), 2.27 (m, 4H, COD), 3.15 (bs, 2H, COD), 5.62 (bs, 2H, COD), 6.14 (d, J(P−H) = 1.2 Hz, 10H, Cp), 6.98 (t, J(H−H) = 7.4 Hz, 2H, *p*-Ph), 7.01 (t, J(H−H) = 7.4 Hz, 4H, *m*-Ph), 8.11 (bs, 4H, *o*-Ph). ^{1}H NMR (300 MHz, 295 K, CD_2Cl_2, ppm): δ 0.81 (s, 9H,Bu^t), 1.77 (m, 2, COD), 1.92, (m, 2H, COD), 2.37 (m, 4H, COD), 2.93 (bs, 2H, COD), 5.09 (bs, 2H, COD), 6.21 (d, J(P−H) = 1.5 Hz, 10H, Cp), 7.17 (m, 2H, *p*-Ph), 7.25 (m, 4H, *m*-Ph), 7.8 (dd, J(H−H) = 7.5 Hz, J(H−P) = 7.5 Hz, 4H, *o*-Ph). ^{13}C NMR (150.9 MHz, C_6D_6, 239 K, ppm): δ 14.5 (hexane), 23.2 (hexane), 29.4 (bs, COD), 30.7 (Bu^t), 32.2 (hexane), 33.0 (bs, COD), 70.7 (bs, COD), 98.3 (bs, COD), 110.0 (Cp), 126.8 (*p*-Ph), 127.4 (m, Ph), 127.7 (*m*-Ph), 129.2 (Ph), 135.1 (*o*-Ph), 143.7 (d, J = 12.9 Hz, *i*-Ph). ^{31}P NMR (243.0 MHz, toluene-d_8, 239 K, ppm): δ 26.3 (d, J(Rh−P) = 114.2 Hz). Anal. Calcd for $C_{37}H_{48}ClNNbPRh$: C, 57.79; H, 6.29; N, 1.82. Found: C, 57.85: H, 6.18; N, 1.83.

General Procedure for the Hydrosilylation of PhC(O)CH$_3$ and PhC(O)H Catalyzed by 2 or 4 in Benzene. The catalyst (0.003 mmol, 2.3 mol %) was dissolved in 0.6 mL of C_6D_6. The silane (16 μL, 0.130 mmol) was added into the solution, followed by the carbonyl compound (0.128 mmol). The course of the reaction was monitored by ^{1}H NMR spectroscopy. The hydrosilylation products $PhSiH_2OCH_2Ph$,[24] $PhSiH(OCH_2Ph)_2$,[24] $PhSiH_2(OCH(Me)Ph)$,[25] and $PhSiH(OCH(Me)Ph)_2$[25] were characterized by NMR.

First Stereoisomer of PhSiHMeOCH(Me)Ph.[26] ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 0.30 (d, 3H, SiMe), 1.38 (d, 3H, Me), 5.29 (q, 1H, SiH), 7.61 (m, SiPh). ^{1}H−^{29}Si HSQC NMR (^{1}H: 300 MHz; ^{29}Si: 59.6 MHz, C_6D_6, J = 7 Hz, ppm): δ −4. ^{29}Si INEPT+ NMR (119.2 MHz, C_6D_6, J = 200 Hz, ppm): δ −4.3 (d, $^1J_{Si-H}$ = 210). ^{1}H−^{13}C HSQC NMR (^{1}H: 300 MHz; ^{13}C: 75.5 MHz, C_6D_6, J = 145 Hz, ppm): δ −1.0 (O*Me*Ph), 22.0 (Si*Me*).

Second Stereoisomer of PhSiHMeOCH(Me)Ph. ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 0.33 (d, 3H, Me), 1.41 (d, 3H, MeSi), 5.42 (q, 1H, SiH), 7.52 (m, SiPh). ^{1}H−^{29}Si HSQC NMR (^{1}H: 300 MHz; ^{29}Si: 59.6 MHz, C_6D_6, J = 7 Hz, ppm): δ −4.8 (d, $^1J_{Si-H}$ = 208 Hz). ^{1}H−^{13}C HSQC NMR (^{1}H: 300 MHz; ^{13}C: 75.5 MHz, C_6D_6, J = 145 Hz, ppm): δ −1.0 (O*Me*Ph), 22.0 (Si*Me*).

PhSiHMeOC(Ph)=CH$_2$.[27] ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 0.40 (d, 3H, SiMe), 4.57 (d, 1H, *C*=CH$_2$), 4.90 (d, 1H, *C*=CH$_2$), 5.47 (q, 1H, PhSi*H*Me). ^{1}H−^{29}Si HSQC NMR (^{1}H: 300 MHz; ^{29}Si: 59.6 MHz, C_6D_6, J = 7 Hz, ppm): δ −22. ^{1}H−^{13}C HSQC NMR (^{1}H: 300 MHz; ^{13}C: 75.5 MHz, C_6D_6, J = 145 Hz, ppm): δ 90 (C=*C*H$_2$).

General Procedure for the Hydrosilylation of PhC(O)CH$_3$ by PhSiH$_3$ Catalyzed by 4 or 4/AgBF$_4$ in CD$_2$Cl$_2$. Complex **4** (4.0 mg, 0.005 mmol, 3.0 mol %) or a mixture of **4** (4.0 mg, 0.005 mmol, 3.0 mol %) and $AgBF_4$ (1.0 mg, 0.005 mmol) was dissolved in 0.6 mL of CD_2Cl_2. $PhSiH_3$ (23 μL, 0.186 mmol) and $PhC(O)CH_3$ (22.0 μL, 0.188 mmol) were charged into the mixture. The course of the reaction was monitored by ^{1}H NMR spectroscopy.

Table 2. X-ray Crystal Data and Structure Refinement for 2 and 4·0.5hexane

	2	**4**·0.5hexane
formula	$C_{26}H_{29}ClNNbPRh$	$C_{37}H_{48}ClNNbPRh$
fw	617.74	769.00
color, habit	green, needle	yellow-orange, block
cryst size, mm	0.20 × 0.08 × 0.08	0.38 × 0.12 × 0.10
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	9.1504(3)	9.1766(6)
b, Å	16.5399(6)	18.6877(12)
c, Å	16.5001(6)	20.1635(12)
β, deg	103.540(1)	98.312(3)
V, Å^3	2427.83(15)	3421.5(4)
Z	4	4
T, °C	150	123
ρ_{calc}, g/cm^3	1.690	1.493
F(000)	1240	1580
μ, mm^{-1}	1.342	0.968
$2\theta_{max}$, deg	58.00	56.00
total no. of reflns	26 584	23 855
unique reflns	6445	8234
R_{int}	0.0324	0.0531
no. with $I \geq 2\sigma(I)$	5497	6317
no. of variables	280	379
R_1 ($I \geq 2\sigma(I)$)	0.0239	0.0587
wR_2 (all data)	0.0586	0.1113
GOOF	1.050	1.164

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Crystal Structure Determinations. X-ray quality crystals of **2** were obtained by low-temperature crystallization from ether, and crystals of **4**·0.5hexane were grown by layer diffusion of hexane into a toluene solution of **4**. In both cases, crystals were covered by polyperfluoro oil and mounted directly onto the Bruker Smart three-circle diffractometer with CCD area detector at 150 and 123 K, respectively. Experimental intensities were collected using Mo Kα radiation (0.71073 Å) in ω-scan mode. The crystallographic data and characteristics of structure solution and refinement are assembled in Table 2. The Bruker SAINT program[28] was used for data reduction. The structures were solved by direct methods[29] and refined by full-matrix least-squares procedures, using $w(|F_o^2| - |F_c^2|)^2$ as the refined function. In both structures, all non-hydrogen atoms were refined with anisotropic thermal parameters and all hydrogen atoms were placed in calculated positions and refined using a riding model.

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Supporting Information Available: Crystallographic information files (CIF) for compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

(28) *SAINT*, Version 6.02A; Bruker AXS Inc.: Madison, WI, 2001.
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