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Lewis base character of the phosphorus atom in phosphanido-niobocene complexes. Synthesis of new early–early homo- and heterobimetallic entities[†]

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The reaction of phosphanido complexes $[Nb(\eta^5-C_5H_4SiMe_3)_2(L)(PPh_2)] [L = CO (1), CNXylyl (2)]$ with early transition metal halides in high oxidation states has been carried out. New bimetallic niobocene complexes $[{Nb(\eta^5-C_5H_4SiMe_3)_2(L)}(\mu-PPh_2)(MCl_5)] [M = Nb, L = CO (3), L = CNXylyl (4); M =$ Ta, L = CO (5), L = CNXylyl (6] have been successfully synthesized by the reaction with $[MCl_5]_2$ (M = Nb or Ta). In a similar way $[{Nb(\eta^5-C_5H_4SiMe_3)_2(L)}(\mu-PPh_2)(MCl_4)] [M = Ti, L = CO (13), CNXylyl$ $(14); M = Zr, L = CO (15), CNXylyl (16)] were synthesized using MCl_4 (M = Ti or Zr). Solutions of$ $complexes 4–6 in chloroform produced new ionic derivatives <math>[Nb(\eta^5-C_5H_4SiMe_3)_2(P(H)Ph_2)(L)] [MCl_6]$ [M = Nb, L = CO (7), L = CNXylyl (8); M = Ta, L = CO (9), L = CNXylyl (10)]. Ionic complexes $<math>[Nb(\eta^5-C_5H_4SiMe_3)_2(P(Cl)Ph_2)(L)] [NbCl_4O(thf)] [L = CO (11), CNXylyl (12)] were formed from$ solutions in th – rapidly in the case of 3 but more slowly for 4. New heterometallic complexes $<math>[Nb(\eta^5-C_5H_4SiMe_3)_2(L)(\mu-PPh_2){(Ti(\eta^5-C_5R_5)Cl_3}] [R = H, L = CO (17), CNXylyl (18); R = CH_3, L =$ $CO (19), CNXylyl (20)] were synthesized by the reaction of 1 or 2 with <math>[Ti(\eta^5-C_5R_5)Cl_3] (R = H or$ $CH_3)$. All of these compounds were characterized by IR and multinuclear NMR spectroscopy, and the molecular structures of 9 and 12 were determined by single-crystal X-ray diffraction.

Introduction

In the last three decades the chemistry of early/late heterobimetallic complexes (ELHBs) has been extensively developed,¹ mainly due to the synergistic effect produced in this type of system by the simultaneous presence of a hard Lewis acid early-metal centre and a soft Lewis base late-metal centre. In this field, phosphanidobridged heterobimetallic compounds are well documented and in a good rational approach they have been prepared by the incorporation of an appropriate late metal moiety into a metallophosphide, MPR₂, unit of the early transition metal. The first examples of this type of complex were described several years ago by Stelzer et al.² Although most of the complexes have been based on group 4 phosphanido-containing moieties,³ similar types of complexes containing group 5 metal moieties have been prepared, particularly in the pioneering work of Moïse et al. in the 1990s, by using both niobocene(tantalocene)-phosphanido systems and $M(CO)_x$ (M = Fe, Mo, W) as building blocks.⁴ More recently, Nikonov et al.5 used an imido-phosphanido niobocene for the construction of Nb/Rh heterobimetallic complexes that have proven to be active precatalysts for the hydrosilylation of ketones and aldehydes. In addition, Hey-Hawkins et al.6 have prepared a series of dimeric phosphinidene-bridged Ta^v complexes, a rare example of homobimetallic group 5 species containing bridged-phosphanido or related moieties. In the last decade we have developed a series of studies focused on the reactivity of phosphanido-containing niobocene complexes; thus, the insertion reaction of carbon disulfide into the Nb–P bond gave a series of new niobocene complexes that contained the anionic phosphanylthioformato ligand $R_2PCS_2^{-.7}$ More recently, we described the preparation of a series of niobacycles that involved the insertion reaction of electron-deficient alkynes into the Nb–P bond.⁸ We became interested in analyzing the behavior of our phosphanido-containing niobocene complexes as metallophosphides towards group 4 and 5 metal moieties in order to prepare new types of hetero- and homobimetallic early-early organometallic entities.

Herein we report the synthesis of several new dinuclear d^2 - d^0 , homo- and heterobimetallic mono-bridged complexes [Nb(μ -PPh₂)M] (M = Nb, Ta, Ti, Zr). This approach takes advantage of the ability of the niobium(III) phosphanido complexes [Nb(η^5 -C₅H₄SiMe₃)₂(L)(PPh₂)] (1 and 2) to act as Lewis bases toward a series of halide group 4 and 5 transition metal species MCl_x that can act as Lewis acids.

Results and discussion

The reaction of toluene solutions of 1 or 2 with the Lewis acids $(MCl_5)_2$, where M = Nb or Ta, gave the new bimetallic complexes **3–6** as red solids, in which the two metals on each complex are in a different oxidation state, *i.e.* Nb(III) and M(v). TiCl₄ and ZrCl₄ yielded the heterobimetallic complexes **13–16** and with monocyclopentadienyl Ti(Iv) trichloride the new complexes

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R = H; L = CO (17), CNXylyl (18) R = CH₃; L = CO (19), CNXylyl (20)

Scheme 1

17–20 were isolated as orange-red solids in high yield after the appropriate workup (see Scheme 1).

Complexes **4–6** and **13–20** were characterized by elemental analysis, IR and multinuclear NMR spectroscopy in solution.

The low solubility of complex **3** in hydrocarbons, ethers or aromatic solvents and its high reactivity toward chloroform or dichloromethane precluded characterization by NMR techniques.

The IR spectra for **3**, **5**, **13**, **15**, **17** and **19** contain a characteristic band due to the carbonyl ligand v($C \equiv O$) at 1950 (1949–1956) cm⁻¹ (a typical value for niobium(III) metallocenes⁷), and for **4**, **6**, **14**, **16**, **18**, and **20** there is a band corresponding to the isocyanide v($C \equiv N$) at 2060 (2073–2050) cm⁻¹.

The ³¹P{¹H} NMR spectra of these complexes in deuterated chloroform show a single broad signal for each complex, at 27.4 ppm for **4**, 29.9 ppm for **5** and 77.3 ppm for **6**. These resonances were shifted downfield with respect to those of the phosphanido ligand in complexes **1** or **2**. This change is consistent with the expected decrease in electron density on the phosphorus atom upon coordination to another metal centre. Furthermore, all the resonances are in the expected region for a phosphanido bridge with donation of the phosphanido lone pair to some of the empty orbitals in MCl₅ (M = Nb or Ta). Two conformational dispositions are possible in the bimetallic complexes as a consequence of this interaction (Scheme 2); the *exo* conformer in which the new MCl₅ entity is located away from the niobocene moiety, and the *endo* conformer in which this moiety and the metallic halide are closer and may interact to form a new metal–metal bond. These



conformational preferences have been described previously^{4a,9} and can be distinguished by the ³¹P NMR chemical shift. In fact, in all cases where the metal-metal bond exists the chemical shift of the signal for the phosphorus is found between +300 and 50 ppm, whereas when a metal-metal bond does not exist this signal appears between +50 and -300 ppm.

The ³¹P NMR chemical shifts found for 4 and 5 are in the region corresponding to the *exo* conformer. However, in the case of 6 the observed value is in the boundary region for the two conformers, and it is not possible to distinguish between the two possibilities.

However, the chemical shifts of the signals observed in the ${}^{31}P{}^{1}H$ NMR spectra of complexes 13, 14 and 16 (157.2, 166.1 and 165.8 ppm, respectively) are consistent 4a,9 with an interaction between the lone pair of the niobium(III) atom and the empty orbital of the other metal centre, as shown in Scheme 3 II. This additional metal-metal bonding interaction must provide





further stabilization for these complexes, in which the coordination number of Ti or Zr can be increased to six. In the case of complex **15** the value of the chemical shift for phosphorus is 28.7 ppm, which indicates that an interaction does not occur between the two metal centres, as shown in the Scheme 2 I. This situation could be because the lone pair of the d² niobocene system is mainly involved in π back-donation to the carbonyl ancillary ligand and an additional Nb–Zr interaction is therefore probably not present in complex **15**. Assuming an *exo* conformation for this complex (see Scheme 1), the zirconium centre increases its coordination number to five (bpt), and two isomers are possible (**I.a** and **I.b**, see Scheme 3).

There are few examples where the coordination number of five appears for titanium(IV) or zirconium(IV) complexes, and in these cases it displays a coordination environment intermediate between square-pyramidal and trigonal-bipyramidal.¹⁰

In the case of complexes **17–20** the ${}^{31}P{}^{1}H$ NMR are particularly informative, since the chemical shifts observed between 12.8 and 26.6 ppm (see Experimental section) are consistent^{4a,9} with a structural disposition bearing a phosphanido bridge between the two metal centres without any additional interaction.

The ¹H NMR spectra of complexes **4–6** and **13–20** provide evidence for the C_s symmetry of the niobocene moiety, and contain a singlet for the methyl groups of the SiMe₃ at *ca.* 0.20 ppm and four multiplets corresponding to the cyclopentadienyl protons, which adopt an ABCD spin system, in the range 4.58–5.80 ppm. The ¹H NMR spectra of **4–6** and **13–20** also contain signals corresponding to the phenyl groups, and the spectra of **4**, **6**, **14**, **16**, **18** and **20** contain a singlet for the methyl groups of the CNXylyl at *ca.* 2.3 ppm and a multiplet at *ca.* 7.3 ppm for the phenyl ring of the same group. Furthermore, the ¹H NMR spectra of **17** and **20** each contain a singlet signal at *ca*. 6.71 ppm corresponding to the C_5H_5 fragment for **17** and **18** or a signal at *ca*. 2.19 ppm corresponding to the methyl group of the C_5Me_5 unit for **18** and **20**.

The spectroscopic data are all consistent with the structural disposition depicted in Scheme 1, where the two metal centres are connected by a phosphanido-bridging moiety bearing the niobocene unit as a metallophosphide coordinated to the titanium centre, which exhibits the well known four-legged piano-stool structure.¹¹

The low stability in solution of complexes **3–6** precludes their characterization by ${}^{13}C{}^{1}H$ NMR; in fact, solutions of complex **3–6** in chloroform give rise to new ionic derivatives [Nb($\eta^{5}-C_{5}H_{4}SiMe_{3}$)₂(P(H)Ph₂)(L)] [MCl₆] [M = Nb; L = CO (7), CNXylyl (**8**); M = Ta, L = CO (9), CNXylyl (**10**)], probably due to attack by HCl arising from the solvent. In fact when complex **3–6** were solved in deuterated chloroform, the deuterated phosphonium complexes was identified by NMR; thus, the ³¹P NMR spectrum shows a 1:1:1 triplet resonance due to coupling with the deuterium atom (${}^{1}J_{PD}$ *ca.* 34 Hz). This signal allowed us to confirm the existence of the P–D bond as reported previously.^{7a}

The ionic nature of complexes **7–10** was confirmed by conductivity measurements on solutions of the complexes in acetone. The values obtained were between 116 and 121 Ω^{-1} cm² mol⁻¹ and these are consistent with 1 : 1 electrolytes.¹²

The spectroscopic data for complexes **7–10** [IR, ³¹P{¹H} NMR, ¹H and ¹³C{¹H} NMR spectra] are consistent with the formula [Nb(η^5 -C₅H₄SiMe₃)₂(P(H)Ph₂)(L)]⁺ (L = CO, CNXylyl), as reported previously.^{7a} In fact, these cations can also be synthesized by reaction of [Nb(η^5 -C₅H₄SiMe₃)₂(P(H)Ph₂)(L)]Cl (L = CO, CNXylyl)^{7a} with [MCl₅]₂ (M = Nb or Ta) in chloroform (Scheme 4). Additionally, complex **9** was characterized by X-ray diffraction.



Table 1Selected bond lengths (Å) and angles (°) for complex 9

| Bond lengths (Å) | | Bond angles (°) | | |
|------------------|---------|---------------------------------|-----------|--|
| $Nb(1)-Cp(1)^a$ | 2.07 | Cent(1)–Nb–Cent(2) ^b | 140.4 | |
| $Nb(1)-Cp(2)^a$ | 2.06 | C(1) - Nb(1) - P(1) | 82.9(10) | |
| Nb(1)-C(1) | 2.11(4) | Nb(1)-P(1)-C(31) | 117.6(8) | |
| Nb(1) - P(1) | 2.56(1) | Nb(1) - P(1) - C(41) | 122.5(8) | |
| C(1) - O(1) | 1.14(4) | C(31) - P(1) - C(41) | 104.2(12) | |
| P(1) - C(31) | 1.81(3) | Cl(1) - Ta(1) - Cl(2) | 178.0(3) | |
| P(1) - C(41) | 1.80(2) | Cl(1) - Ta(1) - Cl(3) | 88.8(4) | |
| Ta(1)– $Cl(1)$ | 2.33(1) | Cl(1) - Ta(1) - Cl(4) | 89.2(4) | |
| Ta(1)-Cl(2) | 2.35(1) | Cl(1) - Ta(1) - Cl(5) | 91.4(4) | |
| Ta(1)-Cl(3) | 2.32(1) | Cl(2)-Ta(1)-Cl(3) | 89.9(4) | |
| Ta(1)-Cl(4) | 2.32(1) | Cl(2)-Ta(1)-Cl(4) | 89.3(3) | |
| Ta(1) - Cl(5) | 2.30(1) | Cl(3) - Ta(1) - Cl(4) | 92.2(3) | |
| Ta(1) - Cl(6) | 2.37(1) | Cl(4) - Ta(1) - Cl(5) | 176.9(5) | |

^{*a*} Refers to the average bond distance between Nb(1) and the carbon atoms of the C₅ ring of the corresponding cyclopentadienyl moiety. ^{*b*} Cent(1) and Cent(2) are the centroids of C(11)–C(15) and C(21)–C(25), respectively.

A microcrystalline sample of **9**, which was suitable for Xray diffraction, was obtained by crystallization from chloroform. Structure is depicted in Fig. 1. Selected bond distances and angles are listed in Table 1.



Fig. 1 Structure of complex 9. Hydrogen atoms (except H1) have been omitted for clarity.

The structure of **9** shows the typical bent metallocene conformation with both cyclopentadienyl rings bound to the metal centre in a η^5 fashion. The niobium atom is also coordinated to the phosphane and the carbonyl ligands. The niobium–carbon bond length (carbonyl ligand), Nb(1)–C(1), is 2.11(4) Å, which is in the range found for other metallocene complexes with terminal carbonyl ligands.⁷ The carbonyl ligand is linear, with an O(1)–C(1)–Nb(1) angle of 174(3)° and an O(1)–C(1) distance of 1.14(4) Å, both values that are close to those found for the terminal carbonyl ligand in other niobocene complexes.⁷

The phosphorus atom is in a distorted tetrahedral environment, and the Nb(1)–P(1) bond length of 2.56(1) Å is similar to

those found in other niobium-phosphane complexes previously reported by our group.⁷

The positive charge of the metallocene is stabilized by the hexachlorotantalate(v) anion, in which the tantalum atom has an octahedral geometry. $^{\rm 13}$

The characterization of the niobiocene cation has already been described by our group through different spectroscopic techniques,⁷ but this structure represents the first example of a diphenylphosphanyl–niobiocene species to be characterized by Xray diffraction.

The behavior of the Lewis acid $[NbCl_5]_2$ in thf solution has recently been reported,¹⁴ and it was found that the niobium(v) centre promoted activation of the thf. As a result, we assessed the ability of complexes **3** and **4** to interact with this solvent. Thus, dissolution of **3** and **4** in thf at room temperature led to the formation of a precipitate after a reaction time of 30 min in each case. The appropriate workup led to the isolation of red solids, which were identified as complexes **11** and **12** (eqn (1)).

 $[\{Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(L)(\mu-PPh_{2})\}(MCl_{5})] \xrightarrow{\text{thf}}$ $[Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(P(Cl)Ph_{2})(L)][NbCl_{4}O(thf)]$ (1) where L=CO (3), CNXylyl (4), CO (11), CNXylyl (12)

Furthermore, the ionic complexes $[Nb(\eta^5-C_5H_4SiMe_3)_2-(P(Cl)Ph_2)(L)]$ $[NbCl_4O(thf)]$ [L = CO (11), CNXylyl (12)] were also isolated quickly from 1 or more slowly from 2 when solutions of these compounds in thf were treated with $[NbCl_5]_2$ at room temperature; in this reaction the probably formed 3 or 4 undergoes the halogenations of the phosphorous atom to give the corresponding cationic chlorophosphane complexes, while the $[NbCl_4O(thf)]^-$ is formed¹⁵ by the interaction with thf. In fact, as mentioned above, when 3 or 4 previously isolated were solved in thf at room temperature led to the formation of 11 or 12.

Complexes 11 and 12 were fully characterized by elemental analysis, IR and multinuclear NMR spectroscopy in solution. Complex 12 was also characterized by X-ray diffraction.

The ionic nature of complexes 11 and 12 was confirmed by conductivity measurements on solutions in acetone (see Experimental section). The spectroscopic data for 11 and 12 also confirm their ionic nature. For example, the ³¹P{¹H} NMR spectra show a single broad signal at 27.1 ppm for 11 and at 34.2 ppm for 12 for the chlorophosphane ligand. These resonances were shifted downfield with respect to those in the corresponding phosphanido ligand in complexes 1 and 2, but at high field with respect to the signal at 80 ppm presented by free¹⁶ PCIPh₂. These findings are consistent with the expected decrease in electron density on the phosphorus atom with respect to 1 and 2, and the increase in electron density with respect free PCIPh₂ by mean of the electron withdrawal from the niobium(III) centre. This behavior are in agreement with the ³¹P chemical shift observed in other halophosphanes coordinated to niobium.^{7c}

The IR spectra of complexes **11** and **12** contain the characteristic band due to the carbonyl ligand v(C \equiv O) at *ca.* 1950 cm⁻¹ for **11** and the band corresponding to v(C \equiv N) at *ca.* 2067 cm⁻¹ for **12**. Additionally, a strong band was also observed at *ca.* 957 cm⁻¹ in the expected region for v(Nb \equiv O).¹⁷

The ¹H NMR spectra of complexes **11** and **12** evidence the lack of symmetry of the niobocene moiety and contain two singlets for the methyl groups of the two different SiMe₃ groups at *ca*. 0.25 ppm

and eight multiplets in the range 5.23-5.31 ppm corresponding to the two cyclopentadienyl protons, each of which adopts an ABCD spin system. The different NMR behavior of the two cyclopentadienyl ring might be due to hindered rotation about the Nb–P bond or hindered rotation about the two Cp'–Nb axes; the rotation about the two Cp'–Nb axes could be hindered by steric reasons or some interaction between the terminal oxygen atom present in the anion [NbCl₄O(thf)] and one of the cyclopentadienyl rings through one of the methyl of the SiMe₃ groups. This interaction has been also observed in the solid state in the Xray studies carried out for the complex **12**. However, hindered rotation about the Nb–P bond related to the bigger size of the chloride atom in comparison with the hydrogen atom must be taken into account.

Furthermore, the spectrum of **12** contains two signals for the methyl groups of the CNXylyl ligand at 2.34 and 2.50 ppm and a multiplet at *ca*. 7.3 ppm for the phenyl ring; finally, in the spectra of **11** and **12** two resonances at 1.85 and 3.86 ppm are observed, and these are due to the methylene protons of the thf coordinated to the niobium center.

The ${}^{13}C{}^{1}H$ NMR spectra of complexes **11** and **12** also provide evidence for the lack of symmetry of the niobocene moiety. Two singlets are observed for the carbon atoms of the SiMe₃ groups and ten signals for the cyclopentadienyl rings. Signals due to the quaternary carbon atom of the ancillary ligand are not observed.

A red microcrystalline sample of **12**, which was suitable for X-ray diffraction, was obtained by crystallization from thf/hexane by cooling the solution at -20 °C for three days.

An ORTEP diagram of **12** is depicted in Fig. 2. Selected bond distances and angles are listed in Table 2.

The niobium atom has a distorted tetrahedral environment with two positions occupied by the cyclopentadienyl rings and the other two by the phosphane and the isocyanide ligands.⁷

The distance between the nitrogen and the carbon atoms of the isocyanide ligand, N(1)–C(1) 1.17(1) Å, and the angle N(1)–C(1)–Nb(1), 175.4(9)°, indicate the presence of a triple C=N bond and an almost linear coordination with the metal center. The Nb(1)–P(1) bond length is in the range of values observed in other phosphane–niobocene complexes described previously by our group.⁷

 Table 2
 Selected bond lengths (Å) and angles (°) for complex 12

| Bond lengths (Å) | | Bond angles (°) | | |
|--------------------------|---------|------------------------------------|-----------|--|
| Nb(1)–Cp(1) ^a | 2.05 | Cent(1)–Nb(1)–Cent(2) ^b | 140.3 | |
| $Nb(1)-Cp(2)^a$ | 2.06 | P(1)-Nb(1)-C(1) | 85.0(3) | |
| Nb(1)-P(1) | 2.55(1) | Nb(1)-P(1)-Cl(1) | 114.5(2) | |
| Nb(1)-C(1) | 2.13(1) | Nb(1)-P(1)-C(41) | 116.0(3) | |
| P(1) - Cl(1) | 2.04(1) | Nb(1)-P(1)-C(51) | 122.5(4) | |
| N(1) - C(1) | 1.17(1) | Cl(1) - P(1) - C(41) | 98.5(4) | |
| Nb(2)–O(1) | 1.69(1) | Cl(1)-P(1)-C(51) | 99.0(4) | |
| Nb(2)–O(2) | 2.39(1) | C(41)-P(1)-C(51) | 102.7(5) | |
| Nb(2)-Cl(2) | 2.38(1) | C(1)-N(1)-C(31) | 175.9(12) | |
| Nb(2)-Cl(3) | 2.39(1) | Nb(1)-C(1)-N(1) | 175.4(9) | |
| Nb(2)-Cl(4) | 2.37(1) | O(1)-Nb(2)-O(2) | 178.3(4) | |
| Nb(2)-Cl(5) | 2.41(1) | | | |

^{*a*} Refers to the average bond distance between Nb(1) and the carbon atoms of the C₅ ring of the corresponding cyclopentadienyl moiety. ^{*b*} Cent(1) and Cent(2) are the centroids of C(11)–C(15) and C(21)–C(25), respectively.



Fig. 2 ORTEP view of complex **12**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level.

The phosphorus atom is also in a distorted tetrahedral environment, as indicated by the values of the angles formed by the phenyl rings and the chlorine atom; C(51)-P(1)-Cl(1) 99.0(4)°, C(41)-P(1)-Cl(1) 98.5(4)°, C(41)-P(1)-C(51) 102.7(5)° and Nb(1)-P(1)-Cl(1) 114.5(2)°.

The positive charge of the metallocene is stabilized by the tetrachloro-oxo-tetrahydrofuran-niobate(v) anion. The structure of this anion has been described previously.¹⁷ The Nb(2)–O(1) bond distance of 1.69(1) Å is consistent with the presence of a double Nb=O bond. The ion has four chlorine atoms arranged in the equatorial plane of the molecule at distances of *ca*. 2.39 Å (see Table 1). The niobium atom is 0.29 Å out of the equatorial plane formed by the four chlorine atoms, which are oriented away from the oxygen atom of the oxo ligand. The niobium atom completes its coordination sphere with a molecule of thf, with a Nb(2)–O(2) bond length of 2.39(1) Å.

The crystal is stabilized by an extensive weak hydrogeninteraction network, the geometrical features of which are shown in Table 3. A noticeable feature of this structure is the observed hydrogen-bonding interaction¹⁸ between one methyl of the (trimethylsilyl)cyclopentadienyl ring and the oxygen atom of the tetrachloro-oxo-tetrahydrofuran-niobate(V) anion, which correspond to the atoms represented as C5–H5…O1 in the ORTEP diagram (Fig. 3).



Fig. 3 Selected hydrogen bonds of complex 12.

| D-H | d(D-H) (Å) | $d(\mathbf{H}\cdots\mathbf{A})(\mathbf{\mathring{A}})$ | ∠DHA (°) | $d(\mathbf{D}\cdots\mathbf{A})(\mathbf{\mathring{A}})$ | Symmetry ^a |
|----------------------|------------|--|----------|--|-----------------------|
| C5–H5a · · · O1 | 0.96 | 2.19 | 154.9 | 3.09(2) | x, y, z |
| C44–H44…O1 | 0.93 | 2.49 | 173.4 | 3.42(2) | 1-x, 1-y, 1-z |
| C37–H37a · · · Cl1 | 0.96 | 2.89 | 140.8 | 3.69(1) | x, y, z |
| $C7-H7c \cdots C13$ | 0.96 | 2.81 | 150.4 | 3.68(1) | x, y - 1, z |
| C34–H34····Cl3 | 0.93 | 2.76 | 156.8 | 3.63(1) | 2-x, 1-y, 1-z |
| $C37-H37c\cdots Cl3$ | 0.96 | 2.82 | 148.3 | 3.67(1) | x, y - 1, z |
| C23–H23····Cl5 | 0.98 | 2.87 | 160.0 | 3.80(1) | 1 - x, 1 - y, -z |

 Table 3
 Hydrogen bonds for compound 12

Although some organometallic halophosphane complexes have been described previously,^{7,19-21} to the best of our knowledge complex **12** is the first chlorophosphanyl–metallocene complex to be characterized by X-ray diffraction.

Concluding remarks

In conclusion, we have studied the reactivity of phosphanido complexes 1 and 2 with early transition metal halides in high oxidation states, and have successfully synthesized new homo- and heterobimetallic d^2-d^0 early–early complexes with a diphenylphosphanido-bridging moiety. Analysis of the possible conformational preferences in these complexes based on spectroscopic data was also carried out. Additionally, the formation of ionic complexes 7–10 based on cationic niobocene moieties and hexahalometallates was achieved. The molecular structures of 9 and 12 were determined by single-crystal X-ray diffraction.

Experimental

General

All reactions were carried out using Schlenk techniques. Oxygen and water were excluded through the use of vacuum lines supplied with purified N₂. Toluene was distilled from sodium. Hexane was distilled from sodium/potassium alloy. All solvents were deoxygenated prior to use. Complexes $[Nb(\eta^5-C_5H_4SiMe_3)_2(PPh_2)L][L =$ CO (1), CNXylyl (2)] were prepared by literature procedures.⁷ Niobium pentachloride, tantalum pentachloride, titanium tetrachloride, zirconium tetrachloride and $[Ti(\eta^5-C_5R_5)Cl_3]$ (R = H, CH₃) were used as received from Aldrich and were manipulated in a glovebox (model MBRAUN). Deuterated solvents were supplied by SDS, dried over 4 Å molecular sieves and degassed prior to use. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian Inova 500 MHz spectrometer at ambient temperature unless stated otherwise. ¹H, ¹³C and ³¹P NMR chemical shifts (δ values) are reported in parts per million (ppm) and trace amounts of protonated solvents (1H, 13C) or standard resonances (³¹P, external 85% H₃PO₄) were used as references. IR spectra in the region 200–4000 cm⁻¹ were recorded on a Perkin-Elmer 883 spectrophotometer. The samples were prepared as Nujol mulls and the spectra were collected on Nujol/polyethylene.

Preparations

 $[\{Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(L)\}(\mu-PPh_{2})(MCl_{5})], M = Nb, L = CO (3), CNXylyl (4); M = Ta, L = CO (5), CNXylyl (6). A solution$

of **1** (0.50 g, 0.86 mmol) or **2** (0.58 g, 0.86 mmol) in anhydrous toluene (30 mL) was added to a cooled (-78 °C) suspension of a stoichiometric amount of niobium pentachloride (0.23 g, 0.86 mmol) or tantalum pentachloride (0.30 g, 0.86 mmol) (1:1 ratio) in the same solvent. The addition gave a deep green solution, which was allowed to reach room temperature and stirred for 1 h. A red solid was observed in the solution after this time. The red precipitate was filtered off and dried under vacuum, yielding the new niobocene complexes [{Nb(η^{5} -C₅H₄SiMe₃)₂(L)}(μ -PPh₂)(MCl₅)] [M = Nb, L = CO (3), CNXylyl (4); M = Ta, L = CO (5), CNXylyl (6)], which were isolated as red solids in *ca.* 70% yield.

3. (0.52, 65%) Found: C, 39.89; H, 4.31; Calc. for $C_{29}H_{36}Cl_5Nb_2POSi_2$: C, 40.94; H, 4.26%. IR (Nujol/polyethylene): v (cm⁻¹); 1958 (C=O). The low solubility of complex **3** in hydrocarbons, ethers or aromatic solvents and its high reactivity toward chloroform or dichloromethane precluded characterization by NMR techniques.

4. (0.59 g, 80%) Found: C, 46.32; H, 4.56; N, 1.39. Calc. for C₃₇H₄₅Cl₅NNb₂PSi₂: C, 46.58; H, 4.75; N, 1.47%. IR (Nujol/polyethylene): *ν* (cm⁻¹); 2062 (C≡N). ¹H NMR (CDCl₃): δ (ppm); 0.29 (s, 18H, Si*Me*₃), 2.51 (s, 6H, C*H*₃ of CNXylyl), 4.58, 5.29, 5.32, 5.80 (m, 2H, C₅*H*₄), 7.89 (m, 13H, *Ph*). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 27.4 (s). ³¹P NMR (CDCl₃): δ (ppm); 27.4 (m).

5. (0.52, 65%) Found: C, 36.89; H, 3.71; Calc. for $C_{29}H_{36}Cl_5NbPOSi_2Ta$: C, 37.10; H, 3.86%. IR (Nujol/polyethylene): v (cm⁻¹); 1955 (C=O). ¹H NMR (CDCl₃): δ (ppm); 0.19 (s, 18H, Si Me_3), 4.58, 5.31, 5.57, 5.65 (m, 2H, C_5H_4), 7.05 (m, 10H, Ph). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 29.9 (s). ³¹P NMR (CDCl₃): δ (ppm); 29.9 (m).

6. (0.70 g, 79%). Found: C, 42.52; H, 4.26; N, 1.28; Calc. for C₃₇H₄₅Cl₅NNbPSi₂Ta: C, 42.65; H, 4.35; N, 1.34%; IR (Nujol/polyethylene): *ν* (cm⁻¹); 2050 (C≡N). ¹H NMR (CDCl₃): δ (ppm); 0.21 (s, 18H, Si*Me*₃), 2.33 (6H, C*H*₃ of CNXylyl), 4.89, 5.09, 5.25, 5.67 (m, 2H, C₅*H*₄), 7.34 (m, 13H, *Ph*). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 77.3 (s). ³¹P NMR (CDCl₃): δ (ppm); 77.3 (m).

[Nb(η⁵-C₅H₄SiMe₃)₂(P(H)Ph₂)(L)][MCl₆], M = Nb, L = CO (7), CNXylyl (8); M = Ta, L = CO (9), CNXylyl (10). A saturated solution of complexes 3–6 (*ca.* 1 mmol) in chloroform yielded red crystals after three days at room temperature. The red crystals were filtered off and dried under vacuum, yielding the new niobocene complexes [Nb(η⁵-C₅H₄SiMe₃)₂(P(H)Ph₂)(L)][MCl₆] [M = Nb, L = CO (7), CNXylyl (8); M = Ta, L = CO (9), CNXylyl (10)].

Complexes 7–10 can also be obtained by reaction of a solution of complex $[Nb(\eta^5-C_5H_4SiMe_3)_2(P(H)Ph_2)(L)]Cl^{7a}$ (L = CO,

CNXylyl) in anhydrous chloroform (30 mL) with stoichiometric amounts of MCl_5 (M = Nb or Ta). The reaction mixture was stirred for 1 h and the resulting red precipitate was filtered off and dried under vacuum, yielding the new complexes 7–10 in *ca.* 90% yield.

7 and **9**: 7: (0.80 g, 90%). Found: C, 39.55; H, 4.02; Calc. for $C_{29}H_{37}Cl_6Nb_2OPSi_2$: C, 39.26; H, 4.20%. **9**: (0.87 g, Yield: 90%) Found: C, 35.47; H, 3.65; Calc. for $C_{29}H_{37}Cl_6NbOPSi_2Ta$: C, 35.71; H, 3.82%; IR (Nujol/polyethylene): v (cm⁻¹); 1941 (CO), 2280 (P–H). ¹H NMR (CDCl₃): δ (ppm); 0.07 (s, 18H, Si Me_3), 5.35 (m, 4H, C_5H_4), 5.66, 6.00 (m, 2H, C_5H_4), 7.25 (m, 10H, C_6H_5), 7.30 (d, ¹ J_{HP} = 367.6 Hz, PHPh₂). ¹³C{¹H} NMR (CDCl₃): δ (ppm); -0.1 (Si Me_3), 97.0, 98.0, 99.1, 99.6 (C_5H_4), 101.3 (C₁ of C_5H_4), 129.3 (d, ³ J_{CP} = 9.90 Hz, C_6H_5), 130.9 (C_6H_5), 132.4 (d, ² J_{CP} = 9.90 Hz, C_6H_5), 130.4 (d, ¹ J_{CP} = 43.49 Hz, C_{ipso} of C_6H_5), 250.0 (CO). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 27.6 (s). ³¹P NMR (CDCl₃): δ (ppm); 27.7 (d, ¹ J_{PH} = 367.6 Hz).

8 and **10**: **8**: (0.88 g, 90%) Found: C, 45.47; H, 4.65; Calc. for C₃₇H₄₆Cl₆Nb₂PSi₂: C, 45.51; H, 4.75%. **10**: (0.96 g, Yield: 90%) Found: C, 41.67; H, 4.23; Calc. for C₃₇H₄₆Cl₆NbPSi₂Ta: C, 41.75; H, 4.36%; IR (Nujol/polyethylene): *v* (cm⁻¹); 2280 (P–H), 2058 (C≡N). ¹H NMR (CDCl₃): δ (ppm); 0.17 (s, 18H, Si*Me*₃), 2.31 [CN(2,6-*Me*₂C₆H₃)], 5.36 (m, 2H, C₅H₄), 5.55 (m, 2H, C₅H₄), 6.65 (m, 2H, C₅H₄), 6.11 (m, 2H, C₅H₄), 7.35 (m, 13H, C₆H₅ and C₆H₃), 8.70 (d, ¹J_{HP} = 387.0 Hz, PHPh₂). ¹³C{¹H} NMR (CDCl₃): δ (ppm); -0.1 (Si*Me*₃), 19.4 (CH₃ of CNXylyl), 92.3, 100.0, 100.8, 102.4 (*C*₅H₄), 100.2 (C₁ of *C*₃H₄), 127.6 (d, ³J_{CP} = 9.83 Hz, *C*₆H₅), 129.0 (*C*₆H₅), 133.0 (d, ²J_{CP} = 9.90 Hz, *C*₆H₅), 132.5 (d, ¹J_{CP} = 43.49 Hz, *C*_{1ppot} of *C*₆H₅), 248.0 (CNXylyl). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 38.50 (s). ³¹P NMR (CDCl₃): δ (ppm); 38.50 (d, ¹J_{PH} = 387.0 Hz).

Synthesis of $[Nb(\eta^5-C_5H_4SiMe_3)_2(P(Cl)Ph_2)(L)][NbCl_4O(thf)],$ L = CO (11), CNXylyl (12). A solution of 1 (0.31 g, 0.50 mmol) or 2 (0.42 g, 0.58 mmol) in anhydrous thf (30 mL) was added to a cooled (-78 °C) 1:1 stoichiometric suspension of niobium pentachloride (0.14 g, 0.50 mmol for 1; 0.16 g, 0.58 mmol, for 2) in the same solvent. The reaction mixture, which was deep green, was allowed to reach room temperature and stirred for 1 h (until a red solid appeared). The solid was filtered off and washed twice with anhydrous hexane (10 mL). The red solids were dried under vacuum, yielding the new complexes 11 and 12.

Complex 11 can also be obtained by stirring a solution of complex 3 in anhydrous thf (30 mL) for 30 min. The resulting red solid was filtered off and washed twice with anhydrous hexane (10 mL). The product was isolated in 90% yield and corresponded with complex 11.

11. (0.42 g, 90%) Found: C, 41.98; H, 4.67; Calc. for $C_{33}H_{44}Cl_5Nb_2O_3PSi_2$: C, 42.21; H, 4.72%; Electric conductivity: $\Lambda_M(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$; 116.4. IR (Nujol/polyethylene): *v* (cm⁻¹); 1950 (C=O), 955 (Nb=O). ¹H NMR (CDCl₃): δ (ppm); 0.25, 0.26 (s, 9H, Si*Me*₃), 1.84 (m, 4H, C*H*₂ of thf), 3.89 (m, 4H, C*H*₂O of thf), 4.58, 4.68, 5.30, 5.32, 5.48, 5.57 (m, 1H, C₅*H*₄), 5.67 (m, 2H, C₅*H*₄), 7.39 (m, 10H, *Ph*). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 27.1 (s). ³¹P NMR (CDCl₃): δ (ppm); 27.1 (m).

12. (0.54 g, 89%) Found: C, 47.02; H, 5.06; N, 1.31; Calc. for C₄₁H₅₃Cl₅NNb₂O₂PSi₂: C, 47.26; H, 5.13; N, 1.34%; Electric conductivity: $\Lambda_{\rm M}(\Omega^{-1} \, {\rm cm}^2 \, {\rm mol}^{-1})$; 121.0. IR (Nujol/polyethylene): *v* (cm⁻¹); 2067 (C=N), 957 (Nb=O). ¹H NMR (CDCl₃): δ (ppm);

0.04, 0.08 (s, 9H, Si Me_3), 1.85 (m, 4H, C H_2 of thf), 2.34, 2.50 (3H, C H_3 of CNXylyl), 3.86 (m, 4H, C H_2 O of thf), 4.58, 4.86, 5.12, 5.25, 5.27, 5.33, 5.64, 5.79 (m, 1H, C₃ H_4), 7.20 (s, 2H, Ph), 7.26 (s, 3H, Ph), 7.49 (m, 8H, Ph). ¹³C{¹H} NMR (CDCl₃): δ (ppm); 0.2, 0.9 (Si Me_3), 19.1 (CH₃ of CNXylyl), 25.5 (CH₂ of thf), 68.6 (CH₂O of thf), 91.2, 93.0, 99.8, 100.1, 100.5, 101.1, 101.9, 102.3, 103.8 (C_3H_4), 128.9–132.3 (Ph). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 34.2 (s). ³¹P NMR (CDCl₃): δ (ppm); 34.2 (m).

Synthesis of [{Nb(η^5 -C₅H₄SiMe₃)₂(L)}(μ -PPh₂)(MCl₄)], M = Ti, L = CO (13), CNXylyl (14). An appropriate volume of titanium tetrachloride (ρ = 1.73 g mL; 0.12 g, 0.34 mmol for 1; 0.14 g; 0.75 mmol for 2) was added in 1 : 1 molar ratio to a cooled (-78 °C) solution of 1 (0.21 g, 0.34 mmol) or 2 (0.55 g, 0.75 mmol) in anhydrous hexane (30 mL). The solution became green. The reaction mixtures were kept at low temperature for 1 h (until a red precipitate appeared) and were then allowed to reach room temperature. The solid was filtered off and washed twice with anhydrous hexane (10 mL) and dried under vacuum. Complexes 13 and 14 were isolated as orange-red and red solids, respectively, in *ca.* 83% yield.

13. (0.24 g, 83%) Found: C, 45.42; H, 4.81%. Calc. for C₂₉H₃₆Cl₄NbOPSi₂Ti: C, 45.22; H, 4.71%. IR (Nujol/polyethylene): v (cm⁻¹); 1956 (C=O). ¹H NMR (CDCl₃): δ (ppm); 0.26 (s, 18H, Si*Me*₃), 4.44, 5.39, 5.62, 5.91 (m, 2H, C₃*H*₄), 7.55 (m, 10H, *Ph*). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 157.2 (s). ³¹P NMR (CDCl₃): δ (ppm); 157.2 (m).

14. (0.57 g, 84%) C, 50.99; H, 5.24; N 1.61%. Calc. for $C_{37}H_{45}Cl_4NNbPSi_2Ti: C, 50.88; H, 5.19; N 1.60%. IR (Nujol/polyethylene): <math>v$ (cm⁻¹); 2073 (C=N). ¹H NMR (CDCl₃): δ (ppm); 0.27 (s, 18H, Si Me_3), 2.50 (6H, CH_3 CNXylyl), 4.63, 5.75 (m, 2H, C_3H_4), 5.30 (m, 4H, C_5H_4), 7.36 (m, 13H, Ph). ¹³C{¹H} NMR (CDCl₃): δ (ppm); 0.3 (Si Me_3), 19.5 (CH₃ CNXylyl), 92.3, 100.0, 100.2, 101.3 (C_5H_4), 128.8, 131.1, 132.5, 132.6 (Ph), 129.6 (d, ² J_{CP} = 9.21 Hz, Ph), 195.7 (CN) ³¹P{¹H} NMR (CDCl₃): δ (ppm); 166.1 (s). ³¹P NMR (CDCl₃): δ (ppm); 166.1 (m).

Synthesis of $[\{Nb(\eta^5-C_5H_4SiMe_3)_2(L)\}(\mu-PPh_2)(MCl_4)], M = Zr, L = CO (15), CNXylyl (16). A suspension of zirconium tetrachloride (0.16 g, 0.70 mmol for 1, 0.15 g, 0.63 mmol for 2) in anhydrous hexane was added to a cooled (-78 °C) solution of 1 (0.44 g, 0.70 mmol) or 2 (0.45 g, 0.63 mmol) in anhydrous hexane (30 mL). After the appropriate workup (see complexes 13 and 14), orange-red solids corresponding to 15 and 16 were isolated in$ *ca*. 80% yield.

15. (0.50 g, 81%). C, 42.81; H, 4.71%. Calc. for C₂₉H₃₆Cl₄NbOPSi₂Zr: C, 42.93; H, 4.79%; IR (Nujol/polyethylene): v (cm⁻¹); 1949 (C=O). ¹H NMR (CDCl₃): δ (ppm); 0.27 (s, 18H, SiMe₃), 4.65, 5.25, 5.35, 5.63 (m, 2H, C₅H₄), 6.95 (m, 10H, Ph). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 28.7 (s). ³¹P NMR (CDCl₃): δ (ppm); 28.7 (m).

16. (0.48 g, 81%). C, 48.82; H, 4.99; N 1.58%. Calc. for $C_{37}H_{45}Cl_4NNbPSi_2Zr$: C, 48.74; H, 4.95; N 1.53%. IR (Nujol/polyethylene): v (cm⁻¹); 2058 (C=N). ¹H NMR (CDCl₃): δ (ppm); 0.27 (s, 18H, Si Me_3), 2.50 (6H, CH_3 CNXylyl), 4.70, 5.29, 5.31, 5.71 (m, 2H, C_5H_4), 7.24 (s, 3H, Ph), 7.48 (m, 6H, Ph), 7.54 (m, 4H, Ph). ¹³C{¹H} NMR (CDCl₃): δ (ppm); 0.3 (Si Me_3), 19.5 (CH₃ CNXylyl), 91.6, 100.1, 100.3, 100.8 (C_3H_4), 128.7, 132.6,

132.7, 134.1 (*Ph*), 129.5 (d, J_{CP} = 9.49 Hz, *Ph*), 194.8 (*CN*). ³¹P{¹H} NMR (CDCl₃): δ (ppm); 165.8 (s). ³¹P NMR (CDCl₃): δ (ppm); 165.8 (m).

Synthesis of $[Nb(\eta^5-C_5H_4SiMe_3)_2(L)(\mu-PPh_2){(Ti(\eta^5-C_5R_5)Cl_3)]}, R = H, L = CO (17), CNXylyl (18). A solution of cyclopentadienyltrichlorotitanium(IV) (0.13 g, 0.59 mmol for 1, 0.15 g, 0.70 mmol for 2) in anhydrous hexane was added to a cooled (-78 °C) solution of 1 (0.36 g, 0.59 mmol) or 2 (0.51 g, 0.70 mmol) in anhydrous hexane (30 mL). After the appropriate workup (see complexes 13 and 14) red solids corresponding to 17 and 18 were isolated in$ *ca.*86% yield.

17. (0.42 g, 86%) Found: C, 49.12; H, 5.02; Calc. for $C_{34}H_{41}Cl_4NbOPSi_2Ti$: C, 49.05; H, 4.95%. IR (Nujol/polyethylene): v (cm⁻¹); 1944 (C=O). ¹H NMR (C₆D₆): δ (ppm); 0.07 (s, 18H, Si Me_3), 4.28, 5.31, 5.60, 5.94 (m, 2H, C₅ H_4), 6.75 (s, 5H, C₅ H_5), 6.89 (s, 2H, Ph), 7.36 (s, 8H, Ph). ³¹P{¹H} NMR (C₆D₆): δ (ppm); 26.6 (s). ³¹P NMR (C₆D₆): δ (ppm); 26.6 (m).

18. (0.57 g, 87%) Found: C, 53.63; H, 5.24; N, 1.42; Calc. for C₄₂H₅₀Cl₄NNbPSi₂Ti: C, 53.75; H, 5.37; N 1.49%. IR (Nujol/polyethylene): *v* (cm⁻¹); 2061 (C=N). ¹H NMR (C₆D₆): δ (ppm); 0.01 (s, 18H, Si*Me*₃), 2.14 (s, 6H, CH₃ CNXylyl), 4.90, 5.31, 5.34, 5.71 (m, 2H, C₅H₄), 6.40 (s, 5H, C₅H₅), 6.76 (s, 4H, *Ph*), 6.95 (s, 2H, *Ph*), 7.04 (t, 4H, *J*_{HP} = 6.95 Hz, *Ph*), 7.65 (m, 5H, *Ph*). ¹³C{¹H} NMR (C₆D₆): δ (ppm); 0.3 (Si*Me*₃), 19.7 (CH₃ CNXylyl), 92.3, 100.0, 100.2, 101.3 (*C*₃H₄), 121.8 (*C*₅H₅), 127.0, 128.7, 130.6, 131.8, 132.0 (*Ph*), 196.0 (*C*N). ³¹P{¹H} NMR (C₆D₆): δ (ppm); 20.1 (m).

 Table 4
 Crystal data and structure refinement for complexes 9 and 12

Synthesis of $[Nb(\eta^5-C_5H_4SiMe_3)_2(L)(\mu-PPh_2){(Ti(\eta^5-C_5R_5)Cl_3)]}$, $R = CH_3$, L = CO (19), CNXylyl (20). The same procedure was performed as for the synthesis of complexes 17 and 18, starting with solutions of 1 (0.38 g, 0.61 mmol) or 2 (0.34 g, 0.47 mmol) and solutions of pentamethylcyclopentadienyltrichlorotitanium(IV) (0.18 g, 0.61 mmol for 1, 0.13 g, 0.47 mmol for 2). Red solids corresponding to 19 and 20 were isolated in *ca*. 87% yield.

19. (0.48 g, 88%) Found: C, 51.92; H, 5.72; Calc. for $C_{39}H_{51}Cl_4NbOPSi_2Ti$: C, 51.73; H, 5.68%; IR (Nujol/polyethylene): v (cm⁻¹); 1944 (C=O). ¹H NMR (C₆D₆): δ (ppm); 0.14 (s, 18H, SiMe₃), 2.19 (s, 15H, C_5Me_5), 4.48, 5.88, 5.97, 6.87 (m, 2H, C_5H_4), 6.95 (t, 4H, $J_{HP} = 6.59$ Hz, *Ph*), 7.14 (m, 4H, *Ph*), 7.74 (t, 2H, $J_{HP} = 8.06$ Hz, *Ph*). ³¹P{¹H} NMR (C₆D₆): δ (ppm); 21.6 (s). ³¹P NMR (C₆D₆): δ (ppm): 21.6 (m).

20. (0.41 g, 86%) Found C, 56.05; H, 6.03; N, 1.41; Calc. for $C_{47}H_{60}Cl_4NNbPSi_2Ti$: C, 55.96; H, 6.00; N,1.39%; IR (Nujol/polyethylene): v (cm⁻¹); 2056 (C=N). ¹H NMR (C₆D₆): δ (ppm); 0.12 (s, 18H, Si Me_3), 2.03 (s, 15H, C_5Me_3), 2.20 (s, 6H, CH_3 CNXylyl), 5.25, 5.90 (m, 2H, C_5H_4), 5.69 (m, 4H, C_5H_4), 6.78 (s, 3H, *Ph*), 7.03 (m, 6H, *Ph*), 7.84 (m, 4H, *Ph*). ³¹P{¹H} NMR (C₆D₆): δ (ppm); 12.8 (s). ³¹P NMR (C₆D₆): δ (ppm); 12.8 (m).

Crystallographic data

Crystals of compound 9 were of poor quality. We have attempted to repeat the crystallization many times and we have mounted several crystals, but we were unable to obtain better data. However, considering the importance of the structure, it was solved despite the aforementioned problems. Data for complexes 9 and 12 were

| Complex | 9 | 12 |
|---|--|---------------------------------|
| Empirical formula | C ₂₉ H ₃₇ Cl ₆ NbOPSi ₂ Ta | $C_{41}H_{53}Cl_5NNb_2O_2PSi_2$ |
| MŴ | 975.30 | 1042.06 |
| T/K | 250(2) | 180(2) |
| Wavelength/Å | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1$ | $P\overline{1}$ |
| a/Å | 10.515(3) | 12.025(2) |
| b/Å | 12.939(3) | 12.159(2) |
| c/Å | 13.888(4) | 15.964(2) |
| α (°) | 90 | 90.091(2) |
| β (°) | 95.035(6) | 93.465(2) |
| γ (°) | 90 | 90.778(3) |
| Volume/Å ³ | 1882.1(9) | 2329.5(6) |
| Ζ | 2 | 2 |
| Density (calcd)/g cm ⁻³ | 1.721 | 1.486 |
| μ/cm^{-1} | 3.764 | 0.899 |
| F(000) | 956 | 1064 |
| Crystal size/mm | $0.43 \times 0.17 \times 0.13$ | $0.53 \times 0.25 \times 0.18$ |
| Index ranges | $-9 \le h \le 9$ | $-12 \le h \le 12$ |
| e e | $-12 \le k \le 12$ | $-12 \le k \le 12$ |
| | $-12 \le l \le 13$ | $-16 \le l \le 16$ |
| Reflections collected | 6395 | 10199 |
| Independent reflections | 3206 [<i>R</i> (int) 0.0973] | 5041 [<i>R</i> (int) 0.0503] |
| No. of data/restraints/params. | 3206/61/266 | 5041/18/495 |
| Goodness-of-fit on F^2 | 1.044 | 1.314 |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.0723$ | $R_1 = 0.0760$ |
| _ | $wR_2 = 0.1344$ | $wR_2 = 0.2046$ |
| Largest diff peak hole/e Å ⁻³ | 0.889 and -0.509 | 0.973 and -1.297 |

collected on a Bruker X8 APPEX II CCD-based diffractometer, equipped with a graphite-monochromated Mo-K α radiation source (λ =0.71073 Å). The crystal data, data collection, structural solution, and refinement parameters are summarized in Table 4. Data were integrated using SAINT²² and an absorption correction was performed with the program SADABS.²³ The structure was solved by direct methods using SHELXTL²⁴ and refined by fullmatrix least-squares methods based on F^2 . All non-hydrogen atoms were refined with anisotropic thermal parameters (except aromatic rings in complex **9**, which were refined isotropically). Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

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