DOI: 10.1002/ejic.200800983

Insertion Reactions of Isothiocyanates into the Nb–P Bond of Phosphide–Niobocene Complexes

Antonio Antiñolo,*[a] Santiago García-Yuste,[a] Antonio Otero,*[a] and Rebeca Reguillo-Carmona[a]

Keywords: Insertion / Niobium / Phosphorus / Isothiocyanates / Phosphanes

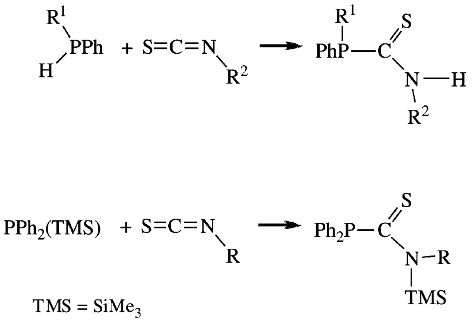
The reaction of the niobocene complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$ {L = CO (**1**), CNXylyl (**2**), and CNCy (**3**)} with isothiocyanates RNCS (R = *t*Bu or Ph) yielded new derivatives $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\kappa^1\text{-}S\text{-}SC(PPh_2)(=NR)\}(L)]$ {R = *t*Bu, L = CO (**4**), CNXylyl (**5**); R = Ph, L = CO (**6**), CNXylyl (**7**), CNCy (**8**)} by the insertion of the isothiocyanate group into the niobium–phosphorus bond of the phosphide ligand. Dinuclear complexes were also obtained by the reaction of complexes **1**–**3** with phenyldiisothiocyanate $\{1,4\text{-}(SCN)_2C_6H_4\}$ to yield $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(L)\}_2\{\mu\text{-}(\kappa^1\text{-}S\text{-}1,4\text{-}SC\{PPh_2\}\{=N\})_2(C_6H_4)\}]$ {L = CO (**9**), CNXylyl (**10**), CNCy (**11**)}.

Introduction

The interest in the use of phosphorus-containing ligands in transition-metal complexes is due to their ability to stabilize the metal center in the form of monomeric species while providing added control over the steric and electronic properties of the system.[1] As a result, the chemistry of early transition-metal complexes containing phosphorus ligands has received a great deal of attention.[2,3] For example, in the field of metallophosphanes, several studies on early transition-metal phosphido complexes have been reported.[3] However, examples of this kind of complex for group 5 elements and subsequent reactivity studies still remain scarce.[4,5]

In this context, our research group has previously reported the synthesis of new phosphido-containing niobocene complexes, and the insertion reaction of carbon disulfide into their Nb–P bond was studied.[6,7] The study of this reactivity allowed us to prepare a series of new niobocene complexes containing the anionic diphenylphosphanylthioformato ligand $Ph_2PCS_2^-$, κ^1- and κ^2-*S*-coordinated to the niobium center. These compounds represent good examples of the formation of a carbon–phosphorus bond mediated by transition-metal complexes. In particular, the formation of carbon–heteroatom bonds mediated by transition-metal complexes has emerged in its own right in recent years as an important step in organic synthesis.[8] More recently, we described the preparation of the niobacycles $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^1\text{-}C\text{-}C\{=N(Xylyl)\}C(CO_2Me)=C(R)(PPh_2)\text{-}\kappa^1\text{-}P)]$ by the insertion reaction of electron-deficient alkynes into the Nb–P bond.[9]

We subsequently became interested in studying the reactivity of the Nb–P bond in $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$ {L = CO (**1**),[6] CNXylyl (**2**), and CNCy (**3**)[7]} towards isothiocyanates. It is well known that the isothiocyanate functional group R–N=C=S has very interesting reactivity towards alkyl and arylphosphanes to give N-alkylated derivatives in which the phosphorus atom is bonded to the carbon atom to produce phosphanylthioformamide derivatives, particularly when a trimethylsilyl (TMS) group is incorporated into the phosphane or when a secondary phosphane is use in the process (Scheme 1).[10] The phosphanylthioformamides were first prepared in 1987 by the addition of diphenylphosphane across the C=N double bond of an aryl isothiocyanate.[11]



Scheme 1. Formation of phosphanylthioformamide derivatives.

In a previous paper in this area we reported the chemical reactivity of isothiocyanates and hydride–niobocene complexes and, as a result, a series of thioformamide-containing

---

[a] Departamento de Química Inorgánica, Orgánica y Bioquímica,
Facultad de Química, Universidad de Castilla-La Mancha,
13071 Ciudad Real, Spain
Fax: +34-926-295318
E-mail: antonio.antinolo@uclm.es
antonio.otero@uclm.es

niobocene complexes were prepared.[12] However, to the best of our knowledge a phosphanylthioformamide–niobium complex has not been reported in the literature.[13]

Herein, we report the synthesis of new phosphanylthioformamide niobocene complexes from phosphido complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$ {L = CO (**1**),[6] CNXylyl (**2**), and CNCy (**3**)[7]} by exploring the possibilities for the insertion reaction into the Nb–P bond using unsaturated isothiocyanates as reagents. This reactivity led to the preparation of new niobocene complexes containing the anionic diphenylphosphanylthioformamide ligand $\{SC(PPh_2)(=NR)\}$ coordinated to the niobium center.

The phosphanylthioformamide ligand contains three atoms (nitrogen, phosphorus, and sulfur) that have a lone electron pair capable of coordination to a metal center, and hence a large number of binding modes can be envisaged. One of the possibilities is the formation of polynuclear chemical entities when a bifunctional ligand is employed. Polynuclear complexes have been prepared by some of us using this synthesis strategy with carboxylic acid[14] or triazine[15] systems.

Results and Discussion

Synthesis and Characterization of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\kappa^1\text{-}S\text{-}SC(PPh_2)(=NR)\}(L)]$ {R = *t*Bu, L = CO (4), CNXylyl (5); R = Ph, L = CO (6), CNXylyl (7), CNCy (8)}

We had previously reported the synthesis of the complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$ {L = CO[6] (**1**), CNXylyl (**2**), CNCy[7] (**3**)} and their reactivity in nucleophilic attack on alkyl halides and in the insertion reaction of carbon disulfide (CS_2).[6,7]

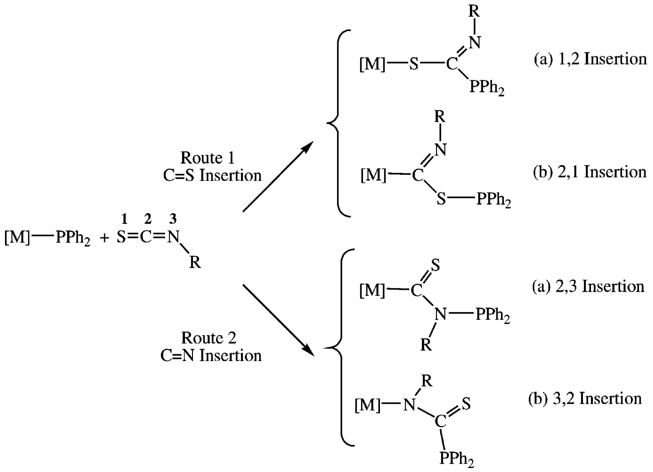
The work described herein concerns the study of the reactivity of complexes **1**–**3** towards isothiocyanates. The reaction of these complexes with the aforementioned reagents enabled the synthesis of new phosphanylthioformamide-niobocene derivatives, namely $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\kappa^1\text{-}S\text{-}SC(PPh_2)(=NR)\}(L)]$ {R = *t*Bu, L = CO (**4**), CNXylyl (**5**); R = Ph, L = CO (**6**), CNXylyl (**7**), CNCy (**8**)}, which were isolated, after the appropriate workup, as reddish-brown, air-sensitive solids that are soluble in thf and toluene [Equation (1)].

$$[\{Nb\}(PPh_2)(L)] \xrightarrow{S=C=N-R} [\{Nb\}\{\kappa^1\text{-}S\text{-}SC(=NR)(PPh_2)\}(L)] \qquad (1)$$

$\{Nb\} = Nb(\eta^5\text{-}C_5H_4SiMe_3)_2$
L = CO (**1**), CNXylyl (**2**), CNCy (**3**)

R = *t*Bu, L = CO (**4**), CNXylyl (**5**);
R = Ph, L = CO (**6**), CNXylyl (**7**), CNCy (**8**)

These complexes result from an insertion process of the appropriate isothiocyanide into the corresponding Nb–P bond of the phosphido moiety. It is well established that the insertion reaction of isothiocyanate into a metal–phosphorus bond could take place in different routes to give a wide variety of new ligands, depending on how the insertion reaction process occurs (Scheme 2).



Scheme 2. Possible insertion reactions of isothiocyanate into a metal–phosphorus bond.

The different complexes synthesized in this work were characterized by elemental analysis and by IR and NMR spectroscopy. The IR spectra of complexes **4**–**8** display the characteristic band of the ancillary ligand, namely the carbonyl band for **4** and **6**, at around ν(CO) = 1927 cm^{-1}, and the isocyanide band for **5**, **7**, and **8** at around ν(CN) = 2060 cm^{-1}. Additionally, the IR spectra show the characteristic band of the C=N bond of the thioformamide moiety, ν(C=N) at approximately 1590 cm^{-1}, according to the values observed for thioformamideniobocene complexes previously reported by our group.[12] In addition, the absence of a band corresponding to ν(C=S) at around 1100 cm^{-1} is consistent with the absence of a C=S bond in the resulting new ligand.

The ^1H NMR spectra of complexes **4**–**8** each contain a singlet due to the methyl groups of the $SiMe_3$ and four multiplets corresponding to the cyclopentadienyl ligands. This pattern of signals is consistent with an asymmetrical environment for the niobium center.[14] Further evidence for this situation is provided by the $^{13}C\{^1H\}$ NMR spectra, which contain five resonances for each complex, corresponding to the cyclopentadienyl ligands. The most interesting signal in each $^{13}C\{^1H\}$ NMR spectrum appears at a very low field, namely a doublet centered at δ = 145.9 ppm ($^1J_{CP}$ = 25.3 Hz) for **4** and at $\delta \approx$ 180.0 ppm ($^1J_{CP} \approx$ 50.0 Hz) for **6**–**8**. This signal is assigned to the quaternary carbon atom of the newly formed phosphanylthioformamide ligand, $^-SC(=NR)(PPh_2)$, a structure that is consistent with the $^{31}P\{^1H\}$ NMR spectra of these compounds (see below). Furthermore, the $^{13}C\{^1H\}$ NMR spectra contain a signal at $\delta \approx$ 250.0 ppm in **4** and **6** and at $\delta \approx$ 200.0 ppm in **7** and **8**, which is typical of the quaternary carbon atoms of carbonyl and isocyanide auxiliary ligands, respectively.

The $^{31}P\{^1H\}$ NMR spectra contain broad signals at chemical shifts between +50 and +70 ppm. These resonances appear in the same chemical shift region as the signal in the $^{31}P\{^1H\}$ NMR spectra of the anionic diphenylphosphanylthioformato ligand ($Ph_2PCS_2^-$) and are shifted downfield with respect to the phosphido ligands in complexes **1**–**3**.[6,7]

On the basis of the data outlined above, it can be suggested that the aforementioned insertion process involves the transformation of a C=S bond into a C–S bond, as well as the cleavage of a Nb–P bond and the formation of new a P–C bond, corresponding with the formation of a new phosphanylthioformamide ligand. The κ^1-*S* coordination of the new phosphanylthioformamide ligand to niobium also appears reasonable. In agreement with the spectroscopic data, the insertion reaction probably occurs through route 1(a), in which a 1,2-insertion process takes place and the C=S bond belonging to the isothiocyanate has been inserted into the Nb–P bond (see Scheme 2).

Unfortunately, it was not possible to establish the molecular structure as all attempts to prepare suitable crystals of **4**–**8** for X-ray crystal structure determinations were unsuccessful. However, the spectroscopic data for these compounds are in agreement with the formation of 18-electron niobocene complexes in which the niobium atom must adopt a pseudotetrahedral structure with the carbonyl or isocyanide and the phosphanylthioformamide ligand as shown in Figure 1.

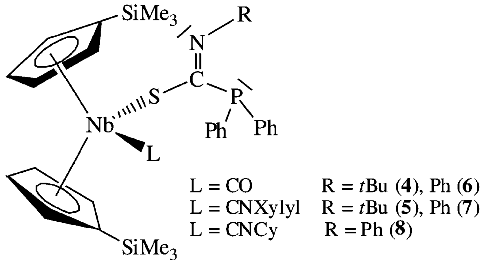


Figure 1. Proposed structure for complexes **4**–**8**.

Two stereoisomers could be present in the proposed structure; in the first one, depicted in Figure 1, the R and the PPh_2 fragments are arranged in a mutual *cis* disposition, whereas in the second possibility these groups are in a *trans* arrangement. In an attempt to determine unambiguously which stereoisomer is present, NOE NMR experiments were performed, but an NOE response was not observed. However, as the phosphorus atom still has a lone electron pair, as does the nitrogen atom, the repulsive interaction between these makes the former stereoisomer the most probable stable structure.

Synthesis and Characterization of $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(L)\}_2\{\mu\text{-}(\kappa^1\text{-}S\text{-}1,4\text{-}SC\{PPh_2\}\{=N\})_2(C_6H_4)\}]$ {L = CO (9), CNXylyl (10), CNCy (11)}

The reactions between complexes **1**–**3** and the dithioisocyanate $\{1,4\text{-}(SCN)_2(C_6H_4)\}$ were also carried out. It was found that **1**–**3** react with this dithioisocyanate to give new binuclear phosphanylthioformamideniobocene derivatives, namely $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(L)\}_2\{\mu\text{-}(\kappa^1\text{-}S\text{-}1,4\text{-}SC\{PPh_2\}\{=N\})_2(C_6H_4)\}]$ {L = CO (**9**), CNXylyl (**10**), CNCy (**11**)}, which were isolated as brown air-sensitive solids that are soluble in thf and toluene but insoluble in diethyl ether and hexane [Equation (2)]. These complexes evolve to uncharacterized substances when they are kept in solution for a long period of time.

$$[\{Nb\}(PPh_2)(L)] \xrightarrow{\{1,4\text{-}(S=C=N)_2\}(C_6H_4)} [\{NbL\}_2\{\mu\text{-}(\kappa^1\text{-}S\text{-}1,4\text{-}SC\{PPh_2\}\{=N\})_2(C_6H_4)\}] \tag{2}$$

L = CO (**1**), CNXylyl (**2**), CNCy (**3**)
$\{Nb\} = Nb(\eta^5\text{-}C_5H_4SiMe_3)_2$
L = CO (**9**), CNXylyl (**10**), CNCy (**11**)

Elemental analysis data are consistent with the isolation of binuclear species in which two niobocene units are bonded through a bridged phosphanylthioformamide moiety, $[1,4\text{-}\{SC(PPh_2)(=N)\}_2(C_6H_4)]^{2-}$.

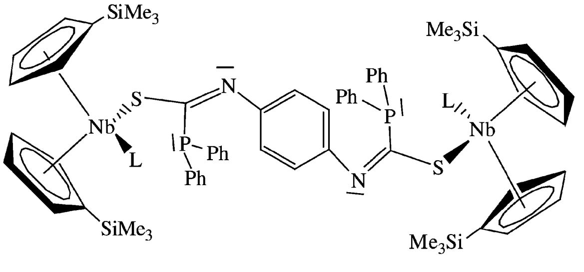
The IR spectra of complexes **9**–**11** contain characteristic bands due to the carbonyl group of **9** at ν(CO) = 1950 cm^{-1}, and the isocyanide groups of **10** and **11** at ν(CN) = 2051 and 2027 cm^{-1}, respectively. The characteristic band of the C=N bond of the phosphanylthioformamide is observed at ν(C=N) ≈ 1585 cm^{-1}. It is noteworthy that a band corresponding to ν(S=C=N) ≈ 2150–2050 cm^{-1} is not present in the IR spectra of complexes **9**–**11**, indicating that the two isothiocyanate functional groups are involved in the insertion processes. This situation is consistent with the proposal that the formation of a bridged phosphanylthioformamide unit takes place.

The ^1H NMR spectra for these complexes exhibit complex signals consistent with a C_s symmetry for the niobium center, namely a single signal for the methyl groups of the $SiMe_3$ and four multiplets corresponding to an ABCD spin system for the cyclopentadienyl ligands.

The $^{31}P\{^1H\}$ NMR spectra each show a single broad signal that is shifted downfield for each complex, at δ = 56.0 ppm for **9**, δ = 53.2 ppm for **10**, and δ = 61.9 ppm for **11**. This observation is consistent with the formation of a new phosphanylthioformamide ligand.

The rapid decompositions in solution of complexes **9** and **10** precluded the acquisition of good quality $^{13}C\{^1H\}$ NMR spectra. However, the spectrum of **11** provides evidence for the C_s symmetry of the niobocene moiety, as expected. The spectrum shows a single signal for the carbon atoms of the $SiMe_3$ groups and five signals for the cyclopentadienyl ligands. The signals for the quaternary carbon atoms are broad and appear as a doublet centered at δ = 189.3 ppm ($^1J_{CP}$ = 49.8 Hz) for the phosphanylthioformamide ligand and a singlet at δ = 188.0 ppm for the isocyanide.

We were unable to obtain crystals of **9**–**11** that were suitable for X-ray crystallography. However, on the basis of the analytical and spectroscopic data we can propose a binuclear species in which the diphenylphosphanylbis(thioformamide)-κ^1-*S* ligand acts as a bridge between two niobocene moieties. In the proposed structure, the niobium atoms would adopt a pseudotetrahedral disposition (Figure 2). Once again, the insertion reaction probably follows route 1(b) (Scheme 2), in which the C=S bond is inserted into the Nb–P bond (Scheme 1).



L = CO (**9**), CNXylyl (**10**), CNCy (**11**)

Figure 2. Proposed structure for complexes **9**–**11**.

The existence of only one system of signals in each of the NMR spectra demonstrates the equivalence of the two niobocene moieties and is consistent with the formation of only one isomer from all the potential isomers that could be formed. The newly formed bridging phosphanylthioamidate ligand is shown in Figure 2, in which the C_6H_4 group and each phosphorus atom are in a mutual *cis* disposition. Nevertheless, NOE NMR experiments were performed to determine unambiguously the nature of the species present. Unfortunately a response was not observed in these experiments. However, as the phosphorus atom still has a lone electron pair, as does the nitrogen atom, the repulsive interaction between them means that the former isomer is the most probable stable structure.

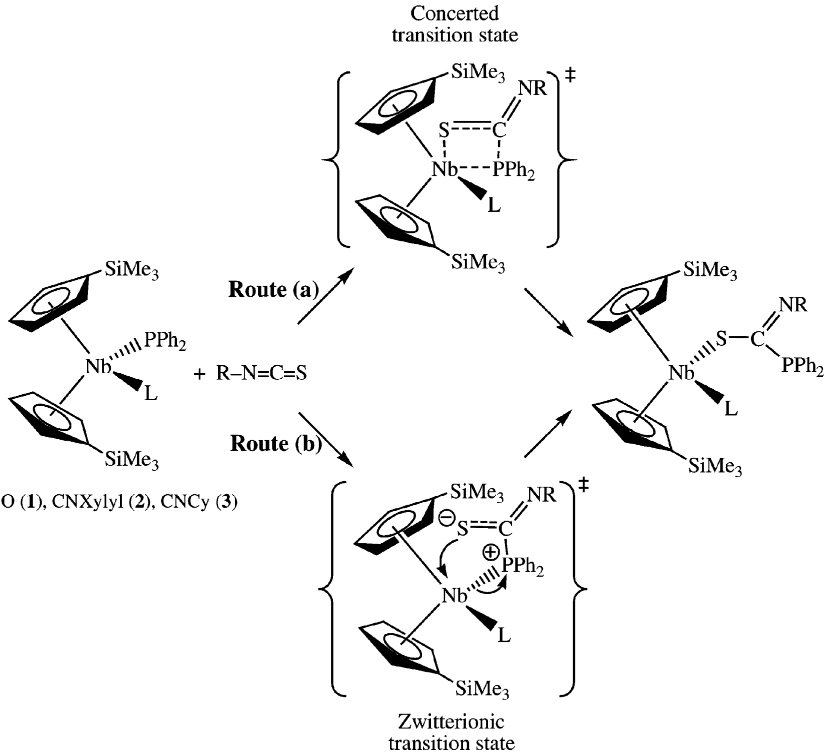
Proposed Pathway for Isothiocyanate Insertion into the Nb–P Bond

Mechanisms for insertion reactions of unsaturated molecules into M–H bonds have been widely studied.[15] In particular, insertion reactions with asymmetric heterocumulenes (X=C=Y) were studied with phosphidozirconocene complexes. In the resulting phosphanylthioformamide-containing complexes a κ^2-*N,S′* coordination mode of the ligand to the metal was always found.[16,17] On the basis of our previous results on the insertions of isothiocyanates into Nb–H bonds,[12] or the insertion of CS_2 into the Nb–P bond,[6,7] an analogous pathway is proposed for the insertion process studied in this work (Scheme 3).

The interaction between the Nb–PPh_2 moiety and the isothiocyanate could occur in two different ways. A four-centered concerted transition state can be obtained by an intermolecular insertion process involving the Nb–P bond and one of the C=S bonds [Scheme 3, route (a)] or, in the second possibility [route (b)], a zwitterionic intermediate could be formed by nucleophilic attack of the coordinated phosphido ligand onto the electron-deficient carbon atom of the isothiocyanate. Subsequent attack of the noncoordinated sulfur atom on the niobium would result in the simultaneous cleavage of the Nb–P bond.

Conclusions

In summary, we synthesized new phosphanylthioformamideniobocene complexes. The process involves the forma-



L = CO (**1**), CNXylyl (**2**), CNCy (**3**)

Scheme 3. Mechanistic proposal for complexes **4**–**11**.

tion of a C–P bond through reactions between a phosphidoisocyanide derivative and different isothiocyanates. The reaction proceeds through a 1,2-insertion process in which the C=S bond of the isothiocyanate is inserted into the Nb–P bond. These results represent the first example of the stabilization of phosphanylthioformamide-containing niobocene complexes.

Experimental Section

General Procedures: All reactions were carried out by using Schlenk techniques. Oxygen and water were excluded through the use of vacuum lines supplied with purified N_2. Toluene was distilled from sodium. Hexane was distilled from sodium/potassium alloy. Diethyl ether and thf were distilled from sodium benzophenone. All solvents were deoxygenated prior to use. The complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$ {L = CO (**1**), CNXylyl (**2**), CNCy (**3**)} were prepared as described in the literature.[6,7] Deuterated solvents were dried with 4 Å molecular sieves and degassed prior to use. PhNCS, *t*BuNCS, and 1,4-$(SCN)_2(C_6H_4)$ were used as supplied by Aldrich. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Innova 500 MHz spectrometer at ambient temperature unless stated otherwise. ^1H, ^{13}C, and ^{31}P NMR chemical shifts (δ values) are given in ppm relative to the solvent signal (^1H, ^{13}C) or standard resonances (^{31}P, external 85% H_3PO_4). IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer as Nujol mulls on CsI windows.

Syntheses of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\kappa^1\text{-}S\text{-}SC(PPh_2)(=NR)\}(L)]$ {R = *t*Bu, L = CO (4), CNXylyl (5)}: To a solution of the corresponding phosphidoniobocene complexes **1** and **2** (0.33 g, 0.53 mmol of **1**; 0.44 g, 0.61 mmol of **2**) was added *t*BuNCS (ρ = 0.908 g mL^{-1}, 0.06 g, 0.53 mmol and 0.07 g, 0.61 mmol of *t*BuNCS, respectively) in anhydrous toluene (30 mL) at room temperature. The mixture was heated at 85 °C for 6 h to give the new complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\kappa^1\text{-}S\text{-}SC(PPh_2)(=N\mathit{t}Bu)\}(L)]$ {L = CO (**4**), CNXylyl (**5**)}. The brown solids were filtered off and washed twice with anhydrous hexane (2 × 10 mL) at 0 °C. **4**: Yield: 0.32 g (80% rel. to **1**). IR (Nujol/polyethylene): ṽ = 1914 (C≡O), 1580 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ = 0.09 (s, 18 H, $SiMe_3$), 1.08 (s, 9 H, *t*Bu), 4.45, 5.32 (m, 2 H, C_5H_4), 4.89 (m, 4 H, C_5H_4), 6.41 (m, 4 H, PPh_2), 7.09 (m, 2 H, Ph), 8.71 (t, $^2J_{HP}$ = 8.5 Hz, 4 H, H_{ortho} Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 0.1 ($SiMe_3$), 30.2 (*t*Bu), 95.1, 96.8, 104.5, 104.9 (C_5H_4), 125.6–136.6 (Ph), 145.9 (d, $^1J_{CP}$ = 25.3 Hz, SCN), 260.2 (CO) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 66.66 ppm. $C_{34}H_{45}NNbOPSSi_2$ (695.84): calcd. C 58.69, H 6.52, N 2.01; found C 58.48, H 6.37, N 1.89. **5**: Yield: 0.40 g (80% rel. to **2**). IR (Nujol/polyethylene): ṽ = , 2055 (C≡N), 1590 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ = 0.11 (s, 18 H, $SiMe_3$), 1.08 (s, 9 H, *t*Bu), 2.31 (s, 6 H, CH_3 CNXylyl); 4.81, 4.88, 5.08, 5.16 (m, 2 H, C_5H_4), 7.01 (m, 6 H, PPh_2), 8.42 (t, $^2J_{HP}$ = 7.8 Hz, 4 H, *Ph*) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 68.9 ppm. $C_{42}H_{54}N_2NbPSSi_2$ (799.01): calcd. C 63.13, H 6.81, N 3.51; found C 63.01, H 6.75, N 3.61.

Syntheses of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\kappa^1\text{-}S\text{-}SC(PPh_2)(=NPh)\}(L)]$ {L = CO (6), CNXylyl (7), CNCy (8)}: The reaction of phosphidoniobocene complexes **1**–**3** with a stoichiometric amount of PhNCS (0.39 g, 0.63 mmol of **1**; 0.34 g, 0.47 mmol of **2**, 0.27 g, 0.39 mmol of **3**; ρ = 1.132 g mL^{-1}, 0.08 g, 0.63 mmol, 0.06 g, 0.47 mmol and 0.05 g, 0.39 mmol of PhNCS, respectively) in anhydrous toluene (30 mL) at room temperature gave, after 15 min for the reaction with **1**, 30 min for **2**, and 1 h for **3**, the complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{\kappa^1\text{-}S\text{-}SC(PPh_2)(=NPh)\}(L)]$ {L = CO (**6**), CNXylyl (**7**), CNCy (**8**)}. The brown solids were filtered off and washed with anhydrous hexane (2 × 10 mL) at 0 °C. **6**: Yield: 0.38 g (80% rel. to **1**). IR (Nujol/polyethylene): ṽ = 1947 (C≡O), 1590 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ = –0.03 (s, 18 H, $SiMe_3$), 4.33, 4.89, 4.99, 5.77 (m, 2 H, C_5H_4), 6.67 (m, 3 H, Ph), 6.97–7.63 (m, 6 H, Ph), 7.99 (t, $^2J_{HP}$ = 7.7 Hz, 4 H, Ph), 8.21 (d, $^2J_{HP}$ = 8.1 Hz, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 0.0 ($SiMe_3$), 96.6, 100.2, 101.2, 101.6 (C_5H_4), 120.9–135.8 (Ph), 153.5 (d, $^2J_{CP}$ = 28.5 Hz, C_{ortho} PPh_2), 172.2 (C_{ortho} *Ph*NCS), 186.6 (d, $^1J_{CP}$ = 25.3 Hz, SCN), 249.5 (CO) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 56.03 ppm. $C_{36}H_{41}NNbOPSSi_2$ (715.83): calcd. C 60.40, H 5.77, N 1.96; found C 60.33, H 5.68, N 1.88. **7**: Yield: 0.32 g (80% rel. to **2**). IR (Nujol/polyethylene): ṽ = 2063 (C≡N), 1589 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ = –0.01 (s, 18 H, $SiMe_3$), 2.19 (s, 6 H, CH_3 CNXylyl), 4.84, 4.90, 4.99, 5.44, 6.08 (m, 2 H, C_5H_4), 6.55 (m, 2 H, Ph), 6.67 (m, 1 H, Ph), 7.31 (t, $^2J_{HP}$ = 7.3 Hz, 4 H, Ph), 8.03 (m, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]toluene): δ = 0.2 ($SiMe_3$), 19.2 (CH_3 CNXylyl), 92.8, 99.3 (C_1 C_5H_4), 100.3, 101.8, 102.4 (C_5H_4), 121.0–129.4 (Ph), 139.8 (d, $^2J_{CP}$ = 33.5 Hz, Ph), 141.1, 153.2, 153.4 (Ph), 186.3 (d, $^1J_{CP}$ = 53.8 Hz, SCN), 201.7 (CN) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 50.8 ppm. $C_{44}H_{50}N_2NbPSSi_2$ (819.00): calcd. 64.53, H 6.15, N 3.42; found: C 64.41, H 5.98, N 3.34. **8**: Yield: 0.26 g (80% rel. to **3**). IR (Nujol/polyethylene): ṽ = 2100 (C≡N), 1589 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ = 0.02 (s, 18 H, $SiMe_3$), 0.12–1.77 (m, 10 H, CN*Cy*), 4.16 (m, H_1 Cy), 4.51, 4.89, 5.15, 5.79 (m, 2 H, C_5H_4), 6.53–7.94 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 0.38 ($SiMe_3$), 23.83, 25.06, 32.85, 57.41, 93.17 (Cy), 94.39 (C_1 C_5H_4), 97.88, 99.12, 100.31, 101.64 (C_5H_4), 121.84–135.88 (Ph), 187.32 (d, $^1J_{CP}$ = 50.1 Hz, SCN), 188.80 (CN) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 61.5 ppm. $C_{42}H_{52}N_2NbPSSi_2$ (796.99): calcd. C 63.29, H 6.58, N 3.51; found C 63.12, H 6.47, N 3.46.

Syntheses of $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(L)\}_2\{\mu\text{-}(\kappa^1\text{-}S\text{-}1,4\text{-}SC\{PPh_2\}\{=N\})_2(C_6H_4)\}]$ {L = CO (9), CNXylyl (10), CNCy (11)}: As described for the synthesis of complexes **4**–**8**, the reaction of phosphidoniobocene complexes **1**–**3** (0.39 g, 0.62 mmol of **1**, 0.61 g, 0.84 mmol of **2**, and 0.24 g, 0.34 mmol of **3**) in toluene with a 2:1 stoichiometric amount of $\{1,4\text{-}(SCN)_2\}(C_6H_4)$ (0.06 g, 0.31 mmol, 0.08 g, 0.42 mmol and 0.03 g, 0.17 mmol, respectively) at room temperature for **9** and **10** and 0 °C for **11** gave, after 15 min for **9** and 30 min for **10** and **11**, the complexes $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(L)\}_2\{\mu\text{-}(\kappa^1\text{-}S\text{-}1,4\text{-}SC\{PPh_2\}\{=N\})_2(C_6H_4)\}]$ {L = CO (**9**), CNXylyl (**10**), CNCy (**11**)}. The brown solids were filtered off and washed with anhydrous hexane (2 × 10 mL) at 0 °C. **9**: Yield: 0.75 g (90% rel. to **1**). IR (Nujol/polyethylene): ṽ = 1950 (C≡O), 1588 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ = –0.01 (s, 18 H, $SiMe_3$), 4.31, 4.86, 4.99, 5.70 (m, 2 H, C_5H_4), 6.89 (d, $^2J_{HP}$ = 8.8 Hz, 1 H, Ph), 7.94 (d, $^2J_{HP}$ = 8.8 Hz, 1 H, Ph), 7.06 (m, 6 H, Ph), 7.93 (m, 4 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 54.03 ppm. $C_{66}H_{76}N_2Nb_2O_2P_2S_2Si_4$ (1353.21): calcd. C 58.56, H 5.66, N 2.07; found C 58.50, H 5.54, N 2.01. **10**: Yield: 1.18 g (90% rel. to **2**). IR (Nujol/polyethylene): ṽ = 2051 (C≡N), 1588 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ = –0.01 (s, 18 H, $SiMe_3$), 2.16 (CH_3 CNXylyl), 4.79, 4.87, 5.33, 6.02 (m, 2 H, C_5H_4), 6.97 (m, 10 H, Ph), 6.79 (d, $^2J_{HP}$ = 8.4 Hz, 4 H, Ph), 7.78 (d, $^2J_{HP}$ = 8.4 Hz, 4 H, Ph), 7.92 (m, 3 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 53.24 ppm. $C_{82}H_{94}N_4Nb_2P_2S_2Si_4$ (1559.88): calcd. C 61.80, H 6.52, N 3.70; found C 61.71, H 6.46, N 3.63. **11**: Yield: : 0.40 g (80% rel. to **3**). IR (Nujol/polyethylene): ṽ = 2027 (C≡N), 1586 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ = , 0.04 (s, 18 H, $SiMe_3$), 0.90, 1.15, 1.38, 1.71 (m, Cy), 4.06 (m, H_1 Cy), 4.51, 4.82, 5.15, 5.73 (m, 2 H, C_5H_4), 6.83 (d, $^4J_{HP}$ = 8.4 Hz, 1 H, Ph), 7.60 (d, $^4J_{HP}$ = 8.4 Hz, 1 H, Ph), 7.09 (m, 6 H, Ph), 7.86 (t, $^3J_{HP}$ = 6.6 Hz, 4 H, H_{ortho} Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 0.1 ($SiMe_3$), 23.7, 24.9, 32.7 (Cy), 57.3 (C_1 C_5H_4), 93.0, 97.9, 99.1, 101.6 (C_5H_4), 100.1 (C_1 C_5H_4), 123.7–135.5 (Ph), 127.1 (d, J_{CP} = 8.5 Hz, Ph), 153.6 (d, J_{CP} = 27.1 Hz, Ph), 189.3 (d, $^1J_{CP}$ = 49.8 Hz, SCN), 188.0 (CN) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 61.9 ppm. $C_{78}H_{98}N_4Nb_2P_2S_2Si_4$ (1487.86): calcd. C 62.97, H 6.64, N 1.88; found C 62.71, H 6.46, N 1.93.

Acknowledgments

We gratefully acknowledge financial support from the Dirección General de Investigación Científica Spain (Grant MEC No. CTQ2005-08123-CO2-01/BQU), the Junta de Comunidades de Castilla La Mancha (Grant Nos. PCI08-0010 and PCI08-0032) and the program Consolider-Ingenio 2010 (Grant ORFEO No. CSD2007-00006).

---

[1] J. P. Collman, L. S. Hegedus, R. E. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, **1987**.

[2] D. W. Stephan, *Angew. Chem. Int. Ed.* **2000**, *39*, 314–329.

[3] E. Hey-Hawkins, *Chem. Rev.* **1994**, *94*, 1661–1717.

[4] a) G. I. Nikonov, D. A. Lemenovskii, J. Lorberth, *Organometallics* **1994**, *13*, 3127–3133; b) N. Etkin, M. T. Benson, S. Courtenay, M. J. McGlinchey, A. D. Bain, D. W. Stephan, *Organometallics* **1997**, *16*, 3504–3510; c) S. Blaurock, E. Hey-Hawkins, *Eur. J. Inorg. Chem.* **2002**, 2975–2984.

[5] G. Bonnet, O. Lavastre, J. C. Leblanc, C. Moïse, *New J. Chem.* **1988**, *12*, 551–552.

[6] a) A. Antinolo, F. Carrillo-Hermosilla, J. Fernandez-Baeza, S. García-Yuste, A. Otero, J. Sánchez-Prada, E. Villaseñor, *Eur. J. Inorg. Chem.* **2000**, 1437–1443; b) A. Antiñolo, S. Garcia-Yuste, A. Otero, J. C. Pérez-Flores, R. Reguillo Carmona, A. M. Rodriguez, E. Villaseñor, *Organometallics* **2006**, *25*, 1310–1316.

[7] A. Antiñolo, D. Evrard, S. Garcia-Yuste, A. Otero, J. C. Pérez-Flores, R. Reguillo Carmona, A. M. Rodriguez, E. Villaseñor, *Organometallics* **2006**, *25*, 3670–3677.

[8] See for example: B. M. Trost, M. U. Frederiksen, M. T. Rudd, *Angew. Chem. Int. Ed.* **2005**, *44*, 6630–6666.

[9] A. Antiñolo, S. Garcia-Yuste, A. Otero, I. López-Solera, J. C. Pérez-Flores, R. Reguillo Carmona, E. Villaseñor, *Dalton Trans.* **2006**, *12*, 1495–1496.

[10] A. R. Katritzky, O. Meth-Cohn, C. W. Rees, *Comprehensive Organic Functional Group Transformation*, Pergamon, Oxford, **1995**, vol. 6, p. 581.

[11] U. Kunze, R. Tittmann, *Z. Naturforsch., Teil B* **1987**, *42*, 77–83.

[12] A. Antiñolo, F. Carrillo, M. Fajardo, S. García-Yuste, M. Freitas, A. Otero, S. Prashar, E. Villaseñor, *Inorg. Chim. Acta* **1997**, *259*, 101–105.

[13] J. R. Dilworth, N. Wheatley, *Coord. Chem. Rev.* **2000**, *199*, 89–158.

[14] L. Salvi, A. Vallat, H. Cattey, Y. Mugnier, A. Antinolo, A. Otero, S. García-Yuste, I. Del Hierrro, I. López-Solera, J. C. Pérez-Flores, *J. Organomet. Chem.* **2005**, *690*, 3134–3141.

[15] A. Antiñolo, S. Garcia-Yuste, A. Otero, J. C. Pérez-Flores, I. López-Solera, A. M. Rodriguez, *J. Organomet. Chem.* **2007**, *692*, 3328–3339.

[16] U. Segerer, J. Sieler, E. Hey-Hawkins, *Organometallics* **2000**, *19*, 2445–2449.

[17] U. Segerer, E. Hey-Hawkins, *Polyhedron* **1997**, *16*, 2537–2545.

Received: October 7, 2008