Synthesis, Characterization, and Reactivity of Isocyanidephosphidoniobocene Derivatives: X-ray Diffraction Structures of New Isocyanideniobocene Complexes, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CNR)(PMePh_2)]I$, R = Xylyl, Cy

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Received March 30, 2006

The reaction of the hydride niobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(L)]$ [L = $CNBu^n$ (**1**), CNCy (**2**), and CNXylyl (**3**)] with $ClPPh_2$ yielded the cationic niobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(L)]Cl$ [L = $CNBu^n$ (**4**), CNCy (**5**), and CNXylyl (**6**)]. Treatment of these complexes with NaOH yielded a new family of phosphidoniobocene derivatives $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$ [L = $CNBu^n$ (**7**), CNCy (**8**), and CNXylyl (**9**)] by elimination of the hydrogen atom directly bonded to the phosphorus. The cationic d^2 species $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PRPh_2)(L)]X$ [R = Me, X = I, L = $CNBu^n$ (**10**), CNCy (**11**), and CNXylyl (**12**); R = CH_2Ph, X = Br, $CNBu^n$ (**13**), CNCy (**14**), and CNXylyl (**15**); R = CH_2CH_2Ph, X = Br, $CNBu^n$ (**16**), CNCy (**17**), and CNXylyl (**18**)] were prepared by the reaction of alkyl halides RX (R = Me, X = I; CH_2Ph, X = Br; CH_2CH_2Ph, X = Br) with **7**, **8**, or **9** by electrophilic attack on the phosphorus atom present in the phosphido terminal ligand. In the same way, the reaction of **9** with ICH_2CH_2I or iodine yielded the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CNXylyl)]I_3$ (**19**). The insertion reaction of carbon disulfide into the Nb−P bond of **7**, **8**, or **9** yielded a new family of diphenylphosphidodithioformato complexes with the niobocene system $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-}S\text{-}SC(S)(PPh_2))(L)]$ [L = $CNBu^n$ (**20**), CNCy (**21**), and CNXylyl (**22**)]. The molecular structures of **11** and **12** were determined by single-crystal X-ray diffraction studies.

Introduction

Hydride complexes of transition metals represent one of the most important classes of compounds due to their chemical reactivity and applications in catalysis.[1] In recent years our research group has published several papers concerning the synthesis, structural characterization, and reactivity of new niobocene hydrides. Our interest has been focused in important fields of inorganic and organometallic chemistry such as hydrogen exchange coupling in metallocene trihydride complexes,[2] σ-bond activation by niobocene hydrides,[3] insertion processes with heterocumulene molecules,[4] insertion processes with alkynes,[5] the synthesis of dihydrogen complexes in protonation processes,[6] and the synthesis of hydride-olefin niobocene complexes.[7]

Furthermore, phosphorus plays an important role in organometallic chemistry, a fact demonstrated by the huge number, and relevance, of the scientific publications related to compounds containing this element.[8] Of all the phosphorus ligands known in organometallic chemistry, the newest type—called the phosphido ligand—has not been widely studied in transition metal chemistry, particularly with respect to group 5 transition metal complexes.[9]

The number of isocyanideniobocene complexes that have been characterized by X-ray diffraction methods is very small.[10]

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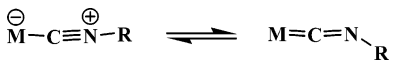
10.1021/om060283p CCC: $33.50
Publication on Web 06/13/2006

Scheme 1



The well-known equilibrium between the two extreme possibilities, isocyanide or carbene coordination mode for the metal−isocyanide bond,[11] has usually been studied by IR spectroscopy techniques, while X-ray diffraction methods provide unambiguous evidence concerning the coordination mode (Scheme 1).

With the aim of combining aspects of isocyanide and phosphidoniobocene chemistry, we decided to prepare new isocyanidephosphidoniobocene complexes starting from new hydridoisocyanideniobocene complexes in order to investigate both their reactivity and chemical similarity with the carbonylphosphidoniobocene derivatives in insertion and alkylation processes.[12] We also aimed to prepare a significant number of different isocyanide complexes in order to increase the number of structures of this kind of complexes resolved by X-ray diffraction studies.

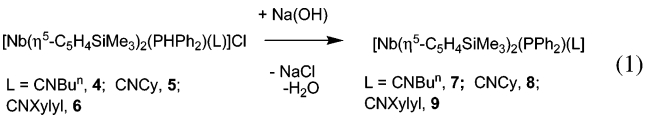
Starting from a well-known methodology[13,14] to prepare phosphidoniobocene complexes [Nb(η^5-$C_5H_4R)_2$(PPh_2)(L)], herein we report new isocyanide-containing niobocene derivatives, namely, [Nb(η^5-$C_5H_4SiMe_3)_2$(PPh_2)(CNR)], as well as their reactivity in alkylation and insertion[15−17] processes with electrophilic reagents RX and CS_2 to give cationic d^2 18-electron species [Nb(η^5-$C_5H_4SiMe_3)_2$($PRPh_2$)(L)]X and phosphinodithioformato-containing complexes [Nb(η^5-$C_5H_4SiMe_3)_2$(κ^1-*S*-SC(S)(PPh_2))(L), respectively.

Results and Discussion

We report the synthesis of new phosphorus-containing niobocene complexes using a new family of hydride isocyanide niobiocene complexes as starting materials, [Nb(η^5-$C_5H_4SiMe_3)_2$H(L)] [L = $CNBu^n$ (**1**), CNCy (**2**), and CNXylyl (**3**)]. These compounds were synthesized by heating [Nb(η^5-$C_5H_4SiMe_3)_2(H)_3$][2] in the presence of the corresponding isocyanide[7] (see Scheme 2).

$ClPPh_2$ was very smoothly inserted into the Nb−H bond of complexes **1**−**3** to give the ionic phosphine complexes [Nb(η^5-$C_5H_4SiMe_3)_2$($PHPh_2$)(L)]Cl [L = $CNBu^n$ (**4**), CNCy (**5**), and CNXylyl (**6**)]. Complexes **4**−**6** were isolated as air-sensitive red-orange crystalline solids in high yield (∼85%) and as red solids after precipitation from Et_2O. The ^{1}H NMR spectra of **4**−**6** reveal the equivalence of the two cyclopentadienyl rings, with an asymmetrical environment for the niobium center; four multiplets between δ = 5−7 ppm are observed for the protons of the Cp rings. In addition, the ^{1}H NMR spectra of **4**−**6** show a doublet for the P−H moiety ($^1J_{PH} \approx 370$ Hz). The IR spectra of **4**−**6** reveal the absence of a ν(Nb−H) band and the existence of ν(P−H) at ca. 2280 cm^{-1}. The $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{31}P NMR spectra are consistent with the observations outlined above (see Experimental Section).

In the study described here it was envisaged that [Nb(η^5-$C_5H_4SiMe_3)_2$(PPh_2)(L)] [L = $CNBu^n$ (**7**), CNCy (**8**), and CNXylyl (**9**)] would be obtained by deprotonation[13] of the P−H bond of **4**, **5**, and **6**. Indeed, the preparation of the phosphidoniobiocene complexes **7**, **8**, and **9** was achieved by deprotonation of the $PHPh_2$ ligand present in these complexes (eq 1).



(1)

Complexes **7**−**9** were isolated as air-sensitive yellow-brown oils, and they are soluble in most organic solvents such as thf, hexane, pentane, and toluene. Complexes **7**−**9** were characterized by IR and ^{1}H, $^{13}C\{^1H\}$, and ^{31}P NMR spectroscopy. The IR spectra of **7**−**9** contain one band between 1990 and 2111 cm^{-1}, and this corresponds to ν(C≡N), in agreement with the linear disposition of the isocyanide ligands. A band corresponding to ν(P−H) of the P−H bond was not observed in the IR spectra, which is consistent with the conversion of the coordinated diphenylphosphine ligand to a new phosphido ligand. Further evidence for this transformation was provided by the ^{1}H NMR spectra, which did not contain the doublet corresponding to the P−H bond at ca. 7 ppm that is present in the parent complexes **4**−**6**.[13] Evidence for the presence of a new phosphido ligand was provided by the ^{31}P NMR spectra, which contain a singlet at ca. δ −10.8 ppm due to the PPh_2 ligand.[12] This latter signal is at higher field than that in the corresponding $PHPh_2$ ligand in complexes **4**−**6**, which shows the higher electron density on the P atom in the neutral phosphido ligand. At low field the $^{13}C\{^1H\}$ NMR spectra exhibit one signal between δ 212 and 217 ppm for the carbon atoms of the *C*NR ligands. The spectroscopic data are in agreement with an 18-electron d^2 niobocene species in which the phosphido terminal ligand is coordinated as a monoanionic donor ligand. Thus, the phosphorus atom of the phosphido ligand retains one electron pair, and this makes it susceptible to further electrophilic attack. The niobium atom must adopt a pseudo-tetrahedral structure with both cyclopentadienyl rings bonded in a η^5-coordination mode to give the typical bent metallocene conformation.

Complexes **7**−**9** are excellent starting materials for the synthesis of a new family of 18 e^- cationic niobocene complexes. In the second part of this article we describe the reactivity of complexes **7**−**9** toward alkylation processes with several RX reagents as electrophilic species. The reaction of

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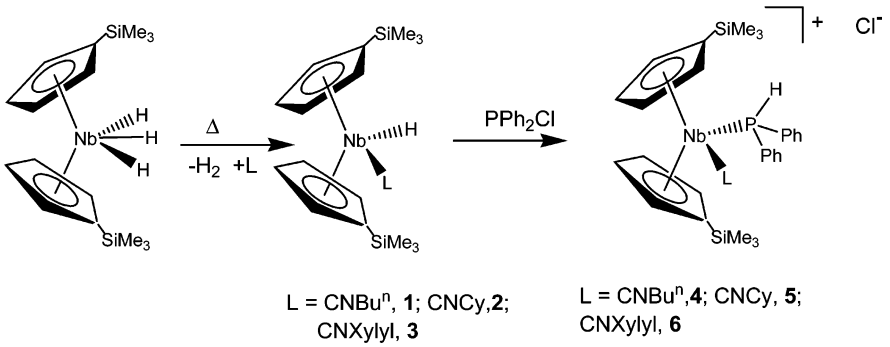
Scheme 2



complexes **7**−**9** with excess alkyl halide, such as methyl iodide (MeI), benzyl bromide (BzBr), and phenethyl bromide ($PhCH_2CH_2Br$), gives d^2 18 e^- cationic phosphinoniobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PRPh_2)(L)]X$ [R = Me, X = I, L = $CNBu^n$ (**10**), CNCy (**11**), and CNXylyl (**12**); R = CH_2Ph, X = Br, $CNBu^n$ (**13**), CNCy (**14**), and CNXylyl (**15**); R = CH_2CH_2Ph, X = Br, $CNBu^n$ (**16**), CNCy (**17**), and CNXylyl (**18**)] in high yield (see eq 2):

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)] \xrightarrow{+\ RX} [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PRPh_2)(L)]X \quad (2)$$

L = $CNBu^n$, **7** CNCy, **8**; CNXylyl, **9**

R = Me; X = I; L = $CNBu^n$, **10**; CNCy, **11**; CNXylyl, **12**
R = $PhCH_2$; X = Br; L = $CNBu^n$, **13**; CNCy, **14**; CNXylyl, **15**
R = $PhCH_2CH_2$ X = Br L = $CNBu^n$, **16** CNCy, **17**; CNXylyl, **18**

The formation of these complexes must be considered in terms of an alkylation process resulting from electrophilic attack of the alkyl halide on the nucleophilic P atom of the phosphido terminal ligand.[9a,12]

Complexes **10**−**18** were isolated as deep red air-sensitive crystalline solids. The low solubility of the complexes in hydrocarbons, ethers, and aromatic solvents enabled us to isolate the products very easily in analytically pure form.

Fortunately, all of the complexes are sufficiently soluble in acetone to allow their NMR spectra to be recorded. The ionic nature of complexes **10**−**18** was confirmed by measuring the molar conductivity (see Experimental Section), and the values are consistent with 1:1 electrolytes.[18]

Compounds **10**−**18** were characterized spectroscopically (see Experimental Section). The most significant bands in the IR spectra appear at ca. 2000 cm^{-1}, and these correspond to ν(C≡N) (see Experimental Section), in agreement with a linear disposition of the isocyanide ligands. The ^{31}P NMR spectra each contain a broad resonance, and these appear at ca. δ 50 ppm (see Experimental Section). These chemical shift values show the effect that alkylation has on the phosphorus by comparison with the ^{31}P NMR chemical shift of the phosphido terminal ligand in complexes **7**−**9**. This comparison shows the differences in electron density on the P atom. In agreement with the IR spectra, the $^{13}C\{^1H\}$ NMR spectra of **10**−**18** show low-field resonances for the carbon atom of the isocyanide ligand (ca. δ 200 ppm) as broad signals, probably due to the quadrupolar moment of the niobium atom.

The use of 1,2-diiodoethane (ICH_2CH_2I) as the alkylating reagent with **9** gave the cationic iodophosphinoniobocene triiodide complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CNXylyl)]I_3$ (**19**) rather than the expected dicationic derivative $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CNXylyl)\}_2(Ph_2P(CH_2CH_2)PPh_2)]I_2$ (see eq 3).

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CNXylyl)] \xrightarrow{I_2 \text{ or } 1,2\text{-diiodoethane}} [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CNXylyl)]I_3 \quad (3)$$

(**9**) (**19**)

The reaction of complex **9** with I_2/Et_2O was successful as an alternative method to obtain **19**. The new iododiphenylphosphine complex was isolated as a deep red air-sensitive solid. The ionic nature of complex **19** was confirmed by measurement of the molar conductivity (Λ_M = 105.6 Ω^{-1} cm^2 mol^{-1}), which is consistent with a 1:1 electrolyte.[18] The structural characterization was carried out by both spectroscopic and X-ray diffraction studies (see Experimental Section).

The IR spectrum shows one band at 2078 cm^{-1}, and this corresponds to ν(C≡N) of the C≡NXylyl ligand. In the NMR spectra (^1H and ^{13}C) the absence of a resonance in the typical region for the $Ph_2P(CH_2CH_2)PPh_2$ ligand, corresponding to the ethylene bridge of the $P(CH_2CH_2)P$ moiety, confirms that this ligand is not present. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance of the carbon atom of the *C*NXylyl ligand at δ 190.3 ppm. The ^{31}P NMR spectrum contains a signal at δ 85.2 ppm due to the iodophosphine ligand (see Experimental Section). These chemical shift values show the effect of the presence of the iodine atom by comparison with the data for complex **9**. This comparison is consistent with the decreasing electronic density in the phosphorus atom.[12]

X-ray Diffraction Study of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PMePh_2)(CNCy)]I$ (11) and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PMePh_2)(CNXylyl)]I$ (12). Crystallographic analyses were carried out on suitable single crystals of **11** and **12**. The aim of this crystallographic study was to establish the structures of **11** and **12** unambiguously and to ascertain the effect of steric hindrance of the isocyanide alkyl or aryl substitutes on the NbC−N−C bond angle of the isocyanide ligand. To the best of our knowledge, these molecular structures represent two of the few examples described for niobocene complexes containing an isocyanide moiety.

Single crystals of **11** and **12** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into dichloromethane solutions of the complexes. ORTEP views of the molecular structures of complexes **11** and **12** are shown in Figures 1 and 2, respectively, and selected bond distances and angles are given in Table 1.

The molecular structures of **11** and **12** are typical of bent metallocenes. The niobium geometry is distorted tetrahedral in which the centroids of the cyclopentadienyl rings are considered as occupying one unique coordination site and the phosphine and the isocyanide ligands occupy the other two sites. The

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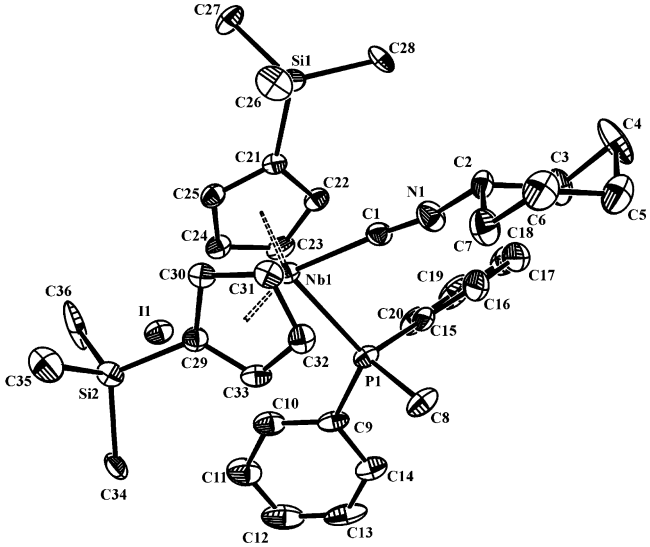

Figure 1. ORTEP view of the molecular structure of **11** with 30% probability ellipsoids. Hydrogen atoms have been omitted.

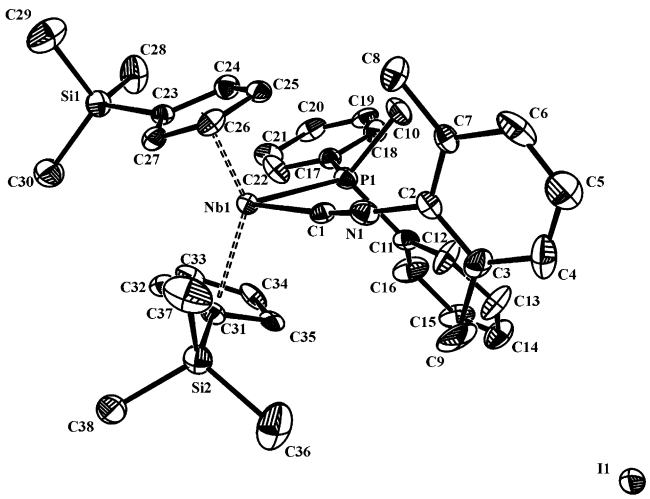

Figure 2. ORTEP view of the molecular structure of **12** with 30% probability ellipsoids. Hydrogen atoms have been omitted.

structural parameters for the $(Cp')_2Nb$ unit are very similar in both complexes (Table 2), and the mutual orientation of the two Cp′ rings is intermediate between eclipsed and staggered in both compounds. The Si(1)−Cent(1)−Cent(2)−Si(2) angles are 131.2° for **11** and 126.5° for **12**. The distances between the metal atom and the centroids of the Cp rings fall between 2.057(1) and 2.090(1) Å, and the value of the angle Cent(1)−Nb(1)−Cent(2) is between 139.39(3)° and 132.71(4)° [Cent(1) is the centroid of C(21)−C(25) for **11** and C(23)−C(27) for **12**; Cent(2) is the centroid of C(29)−C(33) for **11** and C(31)−C(35) for **12**]. These values are typical of bent niobocene derivatives. The Nb(1)−P(1) bond distances of 2.574(1) and 2.59(3) Å, respectively, are very close to the expected values for phosphinoniobocene derivatives.[19] The P(1) atom is pseudo-tetrahedral. The CH_3−P bond lengths of 1.824(6) Å for **11** and 1.84(1) Å for **12** fall into the expected range for other methyl−phosphorus bonds.[20] The C(1)−N(1) bond lengths of 1.177(7) and 1.16(1) Å are consistent with the presence of a carbon−nitrogen triple bond,[21] and the C(1)−N(1)−C(2) angles are 162.2(8)° and 164(1)°; that is, they clearly deviate from linearity. This confirms the back-donation of the niobium(III) d^2 center to the isocyanide ligand, with a triple bond remaining between

Table 1. Bond Lengths [Å] and Angles [deg] for 11 and 12

Bond Lengths

11		12	
Nb(1)−C(1)	2.099(5)	Nb(1)−C(1)	2.09(1)
Nb(1)−C(25)	2.353(5)	Nb(1)−C(31)	2.35(1)
Nb(1)−C(21)	2.356(5)	Nb(1)−C(25)	2.335(9)
Nb(1)−C(22)	2.356(5)	Nb(1)−C(26)	2.35(1)
Nb(1)−C(32)	2.361(5)	Nb(1)−C(32)	2.36(1)
Nb(1)−C(31)	2.367(5)	Nb(1)−C(27)	2.39(1)
Nb(1)−C(30)	2.393(5)	Nb(1)−C(35)	2.413(9)
Nb(1)−C(33)	2.414(5)	Nb(1)−C(33)	2.41(1)
Nb(1)−C(24)	2.421(5)	Nb(1)−C(34)	2.44(1)
Nb(1)−C(23)	2.433(5)	Nb(1)−C(24)	2.44(1)
Nb(1)−C(29)	2.446(5)	Nb(1)−C(23)	2.511(8)
Nb(1)−P(1)	2.574(1)	Nb(1)−P(1)	2.59(3)
P(1)−C(8)	1.824(6)	P(1)−C(11)	1.81(1)
P(1)−C(9)	1.829(6)	P(1)−C(17)	1.84(1)
P(1)−C(15)	1.840(6)	P(1)−C(10)	1.84(1)
N(1)−C(1)	1.177(7)	N(1)−C(1)	1.16(1)
N(1)−C(2)	1.46(1)	N(1)−C(2)	1.39(1)

Bond Angles

11		12	
C(1)−Nb(1)−P(1)	83.2(2)	C(1)−Nb(1)−P(1)	83.6(3)
C(8)−P(1)−C(9)	101.8(3)	C(11)−P(1)−C(17)	102.6(5)
C(8)−P(1)−C(15)	101.0(3)	C(11)−P(1)−C(10)	98.3(6)
C(9)−P(1)−C(15)	102.5(3)	C(17)−P(1)−C(10)	103.6(6)
C(8)−P(1)−Nb(1)	114.0(2)	C(11)−P(1)−Nb(1)	116.0(3)
C(9)−P(1)−Nb(1)	120.9(2)	C(17)−P(1)−Nb(1)	119.8(3)
C(15)−P(1)−Nb(1)	114.0(2)	C(10)−P(1)−Nb(1)	113.8(4)
C(1)−N(1)−C(2)	162.2(8)	C(1)−N(1)−C(2)	164(1)
N(1)−C(1)−Nb(1)	173.1(5)	N(1)−C(1)−Nb(1)	173.5(9)

Table 2. Crystal Data and Structure Refinement for 11 and 12

	11	12
empirical formula	$C_{36}H_{50}INNbPSi_2$	$C_{38}H_{48}INNbPSi_2$
fw	803.73	825.73
temperature (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/c$	orthorhombic, $P2_12_12_1$
a (Å)	11.143(5)	10.992(5)
b (Å)	14.322(1)	14.390(2)
c (Å)	24.444(3)	24.683(2)
β (deg)	97.40(1)	
volume (Å^3)	3868(2)	3904(2)
Z, calcd density (g/cm^3)	4, 1.380	4, 1.405
abs coeff (cm^{-1})	12.36	12.27
F(000)	1640	1680
cryst size (mm)	0.3 × 0.1 × 0.1	0.4 × 0.4 × 0.2
limiting indices	$0 \le h \le 14$ $0 \le k \le 18$ $-32 \le l \le 31$	$0 \le h \le 14$ $0 \le k \le 18$ $-32 \le l \le 32$
no. of reflns collected/unique	9299 [R(int) = 0.0276]	9411 [R(int) = 0.0314]
no. of data/restraints/params	9299/78/495	9411/0/406
goodness-of-fit on F^2	1.063	0.967
final R indices [$I > 2\sigma(I)$]	R1 = 0.0491, wR2 = 0.1403	R1 = 0.0592, wR2 = 0.1280
largest diff peak and hole (e·A^{-3})	0.924 and −0.806	0.729 and −0.709

(19) (a) Challet, S.; Kubicki, M. M.; Leblanc, J.-C.; Moise, C.; Nuber, B. *J. Organomet. Chem.* **1994**, *483*, 47. (b) Thiygarajan, B.; Michalczyk, L.; Bollinger, J. C.; Bruno, J. W. *Organometallics* **1996**, *15*, 2588. (c) Bailey, N. J.; Green, M. L. H.; Leech, M. A.; Saunders, J. F.; Tidswell, H. M. *J. Organomet. Chem.* **1997**, *538*, 111. (d) Humphries, M. J.; Douthwaite, R. E.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **2000**, 2952. (e) Nikonov, G. I.; Crishin, Y. K.; Lemenovskii, D. A.; Kazennova, N. B.; Kumina, L. G.; Howard, S. A. K. *J. Organomet. Chem.* **1997**, *547*, 183. (f) Nikonov, G. I.; Lemenovskii, Yudorogar, K.; Churakov, A. V. *Polyhedron* **1999**, *18*, 1159.

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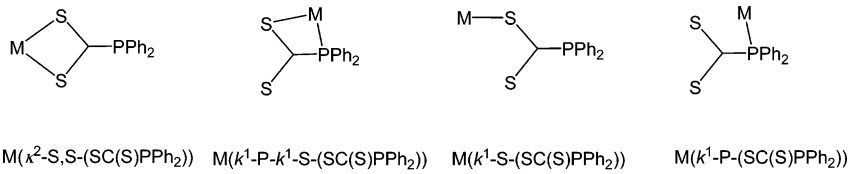
(21) Collazo, C.; Rodewald; D.; Schmidt H.; Rehder, D. *Organometallics* **1996**, *15*, 4884.

Scheme 3

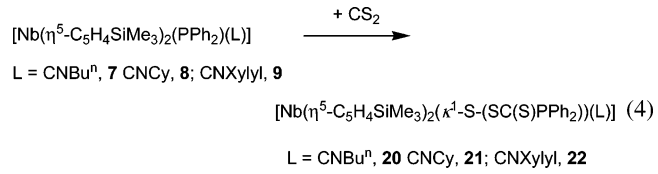


C(1)−N(1), but in these cases, the contribution of the carbene form in the interaction with the niobium center is small (see Scheme 1). The results of this analysis are in agreement with the IR data in solution (see Experimental Section).

The cyclohexylisocyanido and the xylylisocyanido ligands are bonded to niobium at a lateral position in the major coordination plane at the front sector of the bent-metallocene wedge [C(1)−Nb−C(11) = 107.3(3)°]. In both complexes the −C≡N substituent is oriented in an equatorial position in order to decrease steric repulsive interactions between the phenyl rings of the phosphine.

In the last part of this article we will describe the insertion reaction of CS_2 into the Nb−P bond of complexes **7**−**9** to yield the products in which the diphenylphosphinodithioformato ligand, $Ph_2P(S)CS^-$, is coordinated to the niobium center.[12] Of all the possible coordination modes to a metal center, the one expected for the diphenylphosphinodithioformato ligand[22] (see Scheme 3) is the S-monodentate coordination mode **c** that exists in the new diphenylphosphinodithioformatoniobocene [Nb(η^5-$C_5H_4SiMe_3)_2$(κ^1-SC(S)(PPh_2))(CNR)] [R = Bu^n (**20**), Cy (**21**), and Xylyl (**22**)].

The complexes were prepared by stirring of a mixture of **7** and **8** with carbon disulfide for few days. In this way, we were able to isolate complexes **20**−**22** as air-sensitive red solids after the appropriate workup. When the reaction mixture in thf was stirred over a longer period of time, the solution became green and the solvent was removed to give complex [Nb(η^5-C_5H_4-$SiMe_3)_2$(κ^2-*S*,*S*-SC(S)(PPh_2))], **23**.



(4)

The new diphenylphosphinodithioformatoniobocene derivatives **20**−**23** were isolated as air-sensitive solids and were characterized by IR and NMR spectroscopy (see Experimental Section).

The IR spectra of **20**−**22** display a characteristic band at ca. 1000 cm^{-1}, which corresponds to the ν(C═S),[4,13] and another band at 2040 cm^{-1} corresponding to the CNR group. The presence of a $Ph_2P(S)CS^-$ ligand is confirmed by a resonance in each of the $^{31}P\{^1H\}$ NMR spectra at δ 40.3, 27.2, and 18.6 for complexes **20**, **21**, and **22**, respectively (see Experimental Section).

Compared with the ^{31}P chemical shift for compounds **7**−**9**, the relatively low-field shift of each resonance for **20**−**22** is in agreement with the different chemical environments for the phosphorus atoms in the complexes.[12]

^1H NMR and ^{13}C NMR have demonstrated to be a useful tool to distinguish between the coordination modes of the dithioformate ligand in **20** and **21** versus **23**. The most significant difference between **20**/**21** and **23** in the spectra is the number of signals corresponding to the cyclopentadienyl ligands. In fact, the ^1H NMR spectra show four multiplet resonances for **20**−**22**, for the mentioned ligand, whereas only two are present for **23**; this observation is consistent with the absence or presence of a symmetry plane (σ_v) respectively through the niobium center. Similarly there are five and three signals for **20**−**22** and **23**, respectively, in the ^{13}C NMR spectra of the cyclopentadienyl ligand of the niobocene system. Both the ^1H NMR and ^{13}C NMR spectra are consistent with the formulas [Nb]-(κ^1-*S*-SC(S)(PPh_2)) for **20**−**22** and [Nb]-(κ^2-*S*,*S*-SC(S)(PPh_2)) for **23**.[12]

Two possibilities can explain the formation of the diphenylphosphinodithioformato ligand. (i) The insertion reaction goes via a four-centered transition state to give the corresponding new ligand. (ii) The transition state is formed by nucleophilic attack by the lone electron pair of the phosphorus atom at the carbon atom of the carbon disulfide, followed by the interaction of one of the noncoordinated sulfur atoms with the niobium metal center with simultaneous cleavage of the Nb−P bond.

As far as the mechanism for the formation of complex **23** is concerned, this could occur by attack of the noncoordinated S atom of the κ^1-*S*-diphenylphosphinodithioformato ligand in **20** and **21** to the Nb center and the simultaneous elimination of the CNR ligand to give the κ^2-*S*,*S*-diphenylphosphinodithioformato coordination mode in milder conditions as reported for other related compounds.[4,12,13]

Conclusions

We have prepared new phosphidoniobocenes **7** and **8**, which contain isocyanide as an ancillary ligand, starting from hydride niobocenes (**1**, **2**, or **3**) and $ClPPh_2$ through the formation of **4**, **5**, or **6** and subsequent reaction with sodium hydroxide. The electrophilic attack of alkyl halides on the phosphorus atom of the phosphido ligand in **7**, **8**, or **9** allowed the isolation of a new family of d^2 cationic niobocene species **10**−**19**. The X-ray molecular structures of **11** and **12** were determined, and they are members of a small family of metallocenes of early transition metals with isocyanide ligands. Finally, we studied the reactivity of phosphido-containing niobocene complexes **7**, **8**, and **9** toward CS_2. It was found that an insertion process into the Nb−P bond occurs to give complexes **20**, **21**, and **22**, in which a phosphinodithioformato ligand is present.

Experimental Section

General Procedures. All reactions were carried out 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. [Nb(η^5-$C_5H_4SiMe_3)_2$-$(H)_3$],[2] [Nb(η^5-$C_5H_4SiMe_3)_2$H(L)][6] (L = CNCy (**2**), CNXylyl (**3**)),

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$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(L)]Cl$[13] (L = CNXylyl (**6**)), and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$[23] (L = CNXylyl (**9**)) were prepared as described in the literature. Deuterated solvents were dried over 4 Å molecular sieves and degassed prior to use. $ClPPh_2$, $CNBu^n$, CS_2, MeI, $(C_6H_5)CH_2Br$, $(C_6H_5)CH_2CH_2Br$, and I_2 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.

Preparation of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(CNBu^n)]$ (1). $CNBu^n$ (0.091 mL, 0.067 g, 0.800 mmol) was added by syringe to a solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ (0.80 mmol) in THF (40 mL). The mixture was stirred at 343 K for 2 h. The resulting red-brown solution was filtered and evaporated to dryness. Complex **1** was isolated as a red oily material after maintaining it under vacuum for a lengthy period (yield: 95%).

Complex 1. IR (Nujol): ν (cm^{-1}) 1715 (Nb−H), 2089, 1811 (C≡N). ^1H NMR (500 MHz, C_6D_6): δ −5.85 (s, 1 H, Nb−H), 0.25 (s, 18 H, Si*Me*$_3$), 0.75 (t, $^3J_{HH}$ = 5 Hz, 3 H, C*H*$_3$), 1.25, 1.42 (m, 2 H, C*H*$_2$−C*H*$_2$), 3.20 (t, 2 H, CN−C*H*$_2$), 4.38, 4.56, 4.89, 5.13 (2H, each a complex signal, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 0.7 (Si*Me*$_3$), 13.6 (*C*H$_3$), 20.5, 30.5 (*C*H$_2$-*C*H$_2$), 51.0 (CN−*C*H$_2$), 87.7, 91.7, 92.0, 94.0 (C^{2-5}, exact assignment not possible, $C_5H_4SiMe_3$), 94.6 (C^1, $C_5H_4SiMe_3$), 264.0 ($CNBu^n$). Anal. Calcd for $C_{21}H_{36}NNbSi_2$: C, 55.85; H, 8.04; N, 3.10. Found: C, 55.76; H, 8.13; N, 3.20.

Preparation of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(L)]Cl$ [L = $CNBu^n$ (4) and CNCy (5)]. To a solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(L)]$ [L = $CNBu^n$ (**1**)] (0.55 mmol) in Et_2O (40 mL) was added $ClPPh_2$ (125 μL, 0.70 mmol) by syringe. A red-orange precipitate formed immediately. When sedimentation was complete, the solution was filtered and the residue was washed with Et_2O (2 × 20 mL) and dried in vacuo. Complex **4** was obtained as an orange solid in 80% yield. Complex **5** was obtained in 80% yield by following the same process as for **4**.

Complex 4. Λ_M (Ω^{-1} cm^2 mol^{-1}): 92.1. IR (Nujol): ν (cm^{-1}) 2245 (P−H), 2111 (C≡N). ^1H NMR (500 MHz, acetone-d_6): δ 0.02 (s, 18 H, Si*Me*$_3$), 0.95 (t, $^3J_{HH}$ = 5 Hz, 3 H, C*H*$_3$), 1.45, 1.76 (m, 2 H, C*H*$_2$−C*H*$_2$), 4.09 (t, 2 H, CN−C*H*$_2$), 5.11, 5.14, 5.41, 5.70 (2H, each a complex signal, $C_5H_4SiMe_3$), 7.27 (d, $^1J_{HP}$ = 357 Hz, P*H*Ph$_2$), 7.48 (m, 2 H, C_6H_5), 7.68 (m, 8 H, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ 0.0 (Si*Me*$_3$), 13.6 (*C*H$_3$), 20.5, 30.5 (*C*H$_2$−*C*H$_2$), 47.2 (CN−*C*H$_2$), 92.5, 99.0, 100.6 (C^{2-5}, exact assignment not possible, $C_5H_4SiMe_3$), 99.3 (C^1, $C_5H_4SiMe_3$), 122.7, 125.3, 131.2, 139.4 (C_6H_5). $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6): δ 32.8 (s, *P*HPh$_2$). ^{31}P NMR (202 MHz, acetone-d_6): δ 32.8 (d, $^1J_{PH}$ = 357 Hz, *P*HPh$_2$). Anal. Calcd for $C_{33}H_{46}ClNNbPSi_2$: C, 58.97; H, 6.85; N, 2.01. Found: C, 58.56; H, 6.23; N, 2.30.

Complex 5. Λ_M (Ω^{-1} cm^2 mol^{-1}): 108.1. IR (Nujol): ν (cm^{-1}) 2250 (P−H), 2108 (C≡N). ^1H NMR (500 MHz, $CDCl_3$): δ 0.15 (s, 18 H, Si*Me*$_3$), 0.80−2.06 (m, 10 H, C_6H_{11}), 4.10 (m, 1H, H^1, C_6H_{11}), 4.88, 4.95, 5.11, 5.48 (2H, each a complex signal, $C_5H_4SiMe_3$), 7.50 (d, $^1J_{HP}$ = 325 Hz, P*H*Ph$_2$), 7.40−7.68 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ 0.1 (Si*Me*$_3$), 23.6, 24.6, 32.8 (C_5H_{11}), 56.9 (C^1, C_5H_{11}), 90.8, 98.5, 98.6, 100.2 (C^{2-5}, exact assignment not possible, $C_5H_4SiMe_3$), 99.1 (C^1, $C_5H_4SiMe_3$), 128.9, 129.1, 130.4, 132.4 (C_6H_5). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 32.2 (s, *P*HPh$_2$). ^{31}P NMR (202 MHz, acetone-d_6): δ 32.2 (d, $^1J_{PH}$ = 325 Hz, *P*HPh$_2$). Anal. Calcd for $C_{35}H_{48}ClNNbPSi_2$: C, 60.20; H, 6.93; N, 2.01. Found: C, 59.96; H, 6.73; N, 2.10.

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Preparation of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$ [L = $CNBu^n$ (7) and CNCy (8)]. A solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(L)]Cl$ [L = $CNBu^n$ (**4**) and CNCy (**5**)] (0.87 mmol) in toluene (30 mL) was treated with 0.5 M aqueous NaOH (1.72 mL, 10% excess). The mixture was vigorously stirred. Within 4 h the precipitate had dissolved and the organic phase had turned dark brown. The toluene solution was filtered and evaporated to dryness. The product was obtained as a yellow-brown oil in 80% yield for both **7** and **8**.

Complex 7. IR (Nujol): ν (cm^{-1}) 2111, 1817 (C≡N). ^1H NMR (500 MHz, C_6D_6): δ 0.09 (s, 18 H, Si*Me*$_3$), 0.65 (t, $^3J_{HH}$ = 5 Hz, 3 H, C*H*$_3$), 1.02, 1.14 (m, 2 H, −C*H*$_2$−C*H*$_2$), 3.16 (t, $^3J_{HH}$ = 5 Hz, 2 H, CN−C*H*$_2$), 4.46, 4.70, 4.75, 5.31 (2H, each a complex signal, $C_5H_4SiMe_3$), 6.99, 7.14, 7.65 (each a complex signal, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 0.6 (Si*Me*$_3$), 13.6 (*C*H$_3$), 20.5, 32.5 (−*C*H$_2$−*C*H$_2$−), 51.1 (−CN−*C*H$_2$−), 87.7, 91.7, 92.1, 94.0 (C^{2-5}, exact assignment not possible, $C_5H_4SiMe_3$), 89.3 (C^1, $C_5H_4SiMe_3$), 115.0, 123.0 (C_6H_5), 153.6 (d, $^1J_{CP}$ = 30.0 Hz, C_{ipso} of C_6H_5), 214.1 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ −4.2 (s, *P*Ph$_2$). Anal. Calcd for $C_{33}H_{45}NNbPSi_2$: C, 62.34; H, 7.13; N 2.20. Found: C, 62.35; H, 7.21; N, 2.21.

Complex 8. IR (Nujol): ν (cm^{-1}) 2098, 1830 (C≡N). ^1H NMR (500 MHz, C_6D_6): δ 0.11 (s, 18 H, Si*Me*$_3$), 0.80−1.62 (m, 10 H, C_6H_{11}), 3.49 (m, 1H, H^1, C_6H_{11}), 4.54, 4.82, 4.84, 5.41 (2 H, each a complex signal, $C_5H_4SiMe_3$), 6.90, 7.15, 7.65 (m, each a complex signal, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 0.6 (Si*Me*$_3$), 23.9, 25.1, 33.3 (C_5H_{11}), 57.2 (C^1, C_6H_{11}), 91.9, 99.0, 99.3, 102.7 (C^{2-5}, exact assignment not possible, $C_5H_4SiMe_3$), 95.2 (C^1, $C_5H_4SiMe_3$), 124.1, 133.8, 134.1 (C_6H_5), 154.1 (d, $^1J_{CP}$ = 33.0 Hz, C_{ipso},C_6H_5), 212.2 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ −3.3 (*P*Ph$_2$). Anal. Calcd for $C_{35}H_{47}NNbPSi_2$: C, 63.52; H, 7.16; N, 2.12. Found: C, 63.45; H, 7.21; N, 2.28.

Preparation of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PRPh_2)(L)]X$ [R = Me, X = I, L = $CNBu^n$ (10), CNCy (11), and CNXylyl (12); R = CH_2Ph, X = Br, $CNBu^n$ (13), CNCy (14), and CNXylyl (15); R = CH_2CH_2Ph, X = Br, $CNBu^n$ (16), CNCy (17), and CNXylyl (18)]. To a solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(L)]$ [L = $CNBu^n$ (**7**), CNCy (**8**), and CNXylyl (**9**)] (0.83 mmol) in dry toluene (30 mL) was added an excess of the appropriate alkyl halide [**5**, methyl iodide (1:10) (1.17 g, 0.51 mL, ρ = 2.28 g/mL, 8.30 mmol); **6**, benzyl bromide, (1:10) (1.42 g, 0.98 mL, ρ = 1.44 g/mL, 8.30 mmol); and **7**, 1-(2-bromoethyl)benzene (1:10) (1.53 g, 1.14 mL, ρ = 1.34 g/mL, 8.30 mmol)]. In each case the reaction mixture was stirred at room temperature for 2 h. During this time the solution changed to a deep red color. The solvent was evaporated under vacuum to dryness. The resulting solid was recrystallized by dissolving it in dichloromethane and placing a layer of diethyl ether above it in a Schlenk tube. Deep red crystals began to grow within a few days. The resulting solid was filtered off to give a deep red solid in 80−85% yield for **10**, **11**, **12**, **13**, **14**, **15**, **16**, **17**, and **18**.

Complex 10. Λ_M (Ω^{-1} cm^2 mol^{-1}): 95.2. IR (Nujol): ν (cm^{-1}) 2053 (C≡N). ^1H NMR (500 MHz, acetone-d_6): δ 0.25 (s, 18 H, Si*Me*$_3$), 1.01 (t, $^3J_{HH}$ = 5.5 Hz, 3 H, −C*H*$_3$), 1.53, 1.92 (m, 2 H, −C*H*$_2$−C*H*$_2$−), 4.27 (t, $^3J_{HH}$ = 5.5 Hz, 2 H, CN−C*H*$_2$), 2.25 (d, $^2J_{HP}$ = 7.8 Hz, 3 H, *Me*), 4.37, 4.73, 5.02, 5.35 (2H, each a complex signal, $C_5H_4SiMe_3$), 7.53 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ 0.2 (Si*Me*$_3$), 15.2 (−*C*H$_3$), 22.6 (−CH$_2$−*C*H$_2$−CH$_3$), 24.5 (−CH$_2$−*C*H$_2$−CH$_2$), 48.1 (CN−*C*H$_2$−), 18.2 (d, $^1J_{CP}$ = 27 Hz, *Me*), 89.6 (C^1, $C_5H_4SiMe_3$), 90.8, 95.2, 96.3, 99.3 (C^{2-5}, exact assignment not possible, $C_5H_4SiMe_3$), 116−129 (C_6H_5), 133.8 (d, $^1J_{CP}$ = 33 Hz, C_{ipso} C_6H_5), 203.2 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6): δ 41.4 (*P*MePh$_2$). Anal. Calcd for $C_{34}H_{48}INNbPSi_2$: C, 52.51; H, 6.22; N, 1.80. Found: C, 52.79; H, 6.32; N, 1.70.

Complex 11. Λ_M (Ω^{-1} cm^2 mol^{-1}): 90.3. IR (Nujol): ν (cm^{-1}) 2074 (C≡N). ^1H NMR (500 MHz, acetone-d_6): δ 0.25 (s, 18 H, Si*Me*$_3$), 1.30−1.95 (m, 10 H, C_6H_{11}), 2.65 (d, $^2J_{HP}$ = 7.3 Hz, 3 H,

Me), 4.5 (m, 1 H, H^1 C_6H_{11}), 4.75, 5.09, 5.35, 5.67 (2H, each a complex signal, $C_5H_4SiMe_3$), 7.03, 7.34, 7.76 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ 0.0 (Si*Me*$_3$), 15.8 (d, $^1J_{CP}$ = 30 Hz, *Me*), 13.8, 20.4, 47.1 (exact assignment not possible, C_6H_{11}), 68.8 (C^1, C_6H_{11}), 98.8, 99.2, 100.5 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 92.5 (C^1, $C_5H_4SiMe_3$), 129.4 (d, $^3J_{CP}$ = 9 Hz, C_{meta} of C_6H_5), 131.2 (C_6H_5), 133.3 (d, $^2J_{CP}$ = 16 Hz, C_{ortho} of C_6H_5), 134.5 (d, $^1J_{CP}$ = 34 Hz, C_{ipso} of C_6H_5), 205.2 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6): δ 40.5 (*P*MePh$_2$). Anal. Calcd for $C_{36}H_{50}INNbPSi_2$: C, 53.80; H, 6.27; N, 1.74. Found: C, 53.70; H, 6.30; N, 1.72.

Complex 12. Λ_M (Ω^{-1} cm^2 mol^{-1}): 99.0. IR (Nujol): ν (cm^{-1}) 2031 (C≡N). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.18 (s, 18 H, Si*Me*$_3$), 2.16 (d, $^2J_{HP}$ = 8.0 Hz, 3 H, *Me*), 2.39 (s, 6 H, C*H*$_3$ of Xylyl), 4.58, 5.05, 5.15, 5.56 (2H, each a complex signal, $C_5H_4SiMe_3$), 7.18, 7.24, 7.39, 7.41 (m, each a complex signal C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.2 (Si*Me*$_3$), 19.3 (*C*H$_3$ Xylyl), 19.3 (d, $^1J_{CP}$ = 29 Hz, *Me*), 91.8, 98.9, 100.2, 100.6 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 101.9 (C^1, $C_5H_4SiMe_3$), 127.5, 128.7, 128.8, 128.9, 130.9, 131.1, 131.3 (exact assignment not possible, C_6H_5), 135.5 (d, $^1J_{CP}$ = 37.5 Hz, C_{ipso} C_6H_5), 198.1 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 38.3 (s, *P*MePh$_2$). Anal. Calcd for $C_{38}H_{48}INNbPSi_2$: C, 55.27; H, 5.86; N, 1.70. Found: C, 55.08; H, 5.72; N, 1.82.

Complex 13. Λ_M (Ω^{-1} cm^2 mol^{-1}): 92.0. IR (Nujol): ν (cm^{-1}) 2043 (C≡N). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.22 (s, 18 H, Si*Me*$_3$), 1.23 (t, $^3J_{HH}$ = 5.3 Hz, 3 H, −C*H*$_3$), 1.32, 1.52 (m, 2 H, −C*H*$_2$−C*H*$_2$−), 3.98 (t, $^3J_{HH}$ = 5.0 Hz, 2 H, CN−C*H*$_2$), 3.80 (d, $^2J_{HP}$ = 7.4 Hz, 2 H, −C*H*$_2$−Ph), 4.75, 5.19, 5.33, 5.74 (2H, each a complex signal, $C_5H_4SiMe_3$), 6.55, 7.35, 6.96, 7.05, 7.20 (m, exact assignment not possible C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.2 (Si*Me*$_3$), 15.5 (−*C*H$_3$), 23.4, 25.5 (−*C*H$_2$−*C*H$_2$−CH$_3$), 45.3 (−CN−*C*H$_2$−), 43.1 (d, $^1J_{CP}$ = 28 Hz, −*C*H$_2$−Ph), 89.3 (C^1, $C_5H_4SiMe_3$), 95.2, 96.6, 98.6, 102.5 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 129.0−133.0 (C_6H_5), 135.6 (d, $^1J_{CP}$ = 35.0 Hz, C_{ipso} C_6H_5), 202.5 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 56.4 (s, *P*(CH$_2$Ph)Ph$_2$). Anal. Calcd for $C_{40}H_{52}BrNNbPSi_2$: C, 59.55; H, 6.45; N, 1.74. Found: C, 59.80; H, 6.61; N, 1.72.

Complex 14. Λ_M (Ω^{-1} cm^2 mol^{-1}): 103.0. IR (Nujol): ν (cm^{-1}) 2058 (C≡N). ^{1}H NMR (500 MHz, acetone-d_6): δ 0.23 (s, 18 H, Si*Me*$_3$), 1.30−2.22 (m, 10 H, C_6H_{11}), 3.89 (m, 1 H, H^1 C_6H_{11}), 3.96 (d, $^2J_{HP}$ = 6.5 Hz, 2 H, −C*H*$_2$−Ph), 4.82, 5.09, 5.44, 5.70 (2 H, each a complex signal, $C_5H_4SiMe_3$), 6.71−7.90 (m, 15 H, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ 0.3 (Si*Me*$_3$), 15.8, 22.5, 42.3 (C_6H_{11}), 71.2 (C^1, C_6H_{11}), 41.4 (d, $^1J_{CP}$ = 25 Hz, −*C*H$_2$−Ph), 89.2, 93.8, 99.9, 103.5 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 94.7 (C^1, $C_5H_4SiMe_3$), 129.0−133.0 (C_6H_5), 135.6 (d, $^1J_{CP}$ = 35 Hz, C_{ipso} of C_6H_5). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 55.5 (s, *P*(CH$_2$Ph)Ph$_2$). Anal. Calcd for $C_{42}H_{54}BrNNbPSi_2$: C, 60.57; H, 6.54; N, 1.68. Found: C, 60.62; H, 6.68; N, 1.71.

Complex 15. Λ_M (Ω^{-1} cm^2 mol^{-1}): 95.5. IR (Nujol): ν (cm^{-1}) 2038 (C≡N). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.17 (s, 18 H, Si*Me*$_3$), 2.42 (s, 6 H, C*H*$_3$ Xylyl), 3.74 (d, $^2J_{HP}$ = 6.4 Hz, 2 H, −C*H*$_2$−Ph), 4.67, 5.13, 5.26, 5.72 (2H, each a complex signal, $C_5H_4SiMe_3$), 6.52, 6.91, 7.03, 7.39, 7.19, 7.17, 7.45, 7.32 (m, each a complex signal C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.7 (Si*Me*$_3$), 19.8 (*C*H$_3$ lyl), 39.9 (d, $^1J_{CP}$ = 29.0 Hz, −*C*H$_2$−Ph), 93.36, 98.95, 100.96, 101.59 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 102.14 (C^1, $C_5H_4SiMe_3$), 127.81 (C_{ipso} of Xylyl), 128.27, 128.65, 128.78 (C_{arom} of Xylyl), 130.63, 131.69, 133.70 (C_{ortho}, C_{meta}, and C_{para} of C_6H_5), 132.7 (d, $^1J_{CP}$ = 37.5 Hz, C_{ipso} of C_6H_5), 201.1 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 53.3 (s, *P*(CH$_2$Ph)Ph$_2$). Anal. Calcd for $C_{44}H_{52}BrNNbPSi_2$: C, 61.82; H, 6.13; N, 1.64. Found: C, 61.85; H, 5.99; N, 1.63.

Complex 16. Λ_M (Ω^{-1} cm^2 mol^{-1}): 96.7. IR (Nujol): ν (cm^{-1}) 2106 (C≡N). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.13 (s, 18 H, Si*Me*$_3$), 0.93 (t, $^3J_{HH}$ = 5.3 Hz, 3 H, −C*H*$_3$), 1.22, 1.42 (m, 2 H, −C*H*$_2$−C*H*$_2$−), 4.20 (t, $^3J_{HH}$ = 5.0 Hz, 2 H, CN−C*H*$_2$), 3.6 (d, $^2J_{HP}$ = 7.4 Hz, 4 H, −C*H*$_2$−C*H*$_2$−Ph), 4.83 (4H, a complex signal, $C_5H_4SiMe_3$), 5.01, 5.58 (2H, each a complex signal, $C_5H_4SiMe_3$), 6.55−7.70 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.2 (Si*Me*$_3$), 13.6 (−*C*H$_3$), 20.4, 25.5 (−*C*H$_2$−*C*H$_2$−), 47.6 (−CN−*C*H$_2$−), 34.0 (d, $^1J_{CP}$ = 28 Hz, −*C*H$_2$−*C*H$_2$−Ph), 93.5 (C^1, $C_5H_4SiMe_3$), 90.5, 99.1, 99.7, 99.9 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 126.0−134.0 (C_6H_5), 140.0 (d, $^1J_{CP}$ = 35.0 Hz, C_{ipso} C_6H_5), 181.7 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 50.6 (s, *P*(CH$_2$Ph)Ph$_2$). Anal. Calcd for $C_{43}H_{56}BrNNbPSi_2$: C, 60.98; H, 6.67; N, 1.65. Found: C, 60.81; H, 6.71; N, 1.72.

Complex 17. Λ_M (Ω^{-1} cm^2 mol^{-1}): 103.2. IR (Nujol): ν (cm^{-1}) 2047 (C≡N). ^{1}H NMR (500 MHz, acetone-d_6): δ 0.14 (s, 18 H, Si*Me*$_3$), 1.41−2.70 (m, 10 H, C_6H_{11}), 2.50 (s, 4 H, −CH$_2$−C*H*$_2$−Ph), 3.79 (m, 1 H, H^1 C_6H_{11}), 4.01 (d, $^2J_{HP}$ = 6.5 Hz, 2 H, −C*H*$_2$−CH$_2$−Ph), 4.72, 5.10, 5.53, 5.85 (2H, each a complex signal, $C_5H_4SiMe_3$), 6.90−7.90 (m, 15 H, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 0.2 (Si*Me*$_3$), 16.8, 22.4, 41.0 (C_6H_{11}), 66.1 (C^1, C_6H_{11}), 33.5 (−CH$_2$-*C*H$_2$−Ph), 44.3 (d, $^1J_{CP}$ = 25 Hz, −*C*H$_2$−CH$_2$−Ph), 92.4, 93.6, 102.4, 104.5 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 97.8 (C^1, $C_5H_4SiMe_3$), 128.0−131.1 (C_6H_5), 134.2 (d, $^1J_{CP}$ = 35 Hz, C_{ipso} C_6H_5), 201.4 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 53.2 (s, *P*(CH$_2$CH$_2$Ph)Ph$_2$). Anal. Calcd for $C_{43}H_{56}BrNbPSi_2$: C, 60.98; H, 6.67; N, 1.65. Found: C, 61.15; H, 6.54 3.21; N, 1.44.

Complex 18. Λ_M (Ω^{-1} cm^2 mol^{-1}): 95.0. IR (Nujol): ν (cm^{-1}) 2034 (C≡N). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.15 (s, 18 H, Si*Me*$_3$), 2.25 (s, 6 H, C*H*$_3$ of Xylyl), 2.56 (s, 2 H, −CH$_2$−C*H*$_2$−Ph), 3.38 (dt, $^2J_{HP}$ = 7.2 Hz, $^3J_{HH}$ = 5.8 Hz, −C*H*$_2$−CH$_2$−Ph), 4.68, 5.07, 5.23, 5.76 (2H, each a complex signal, $C_5H_4SiMe_3$), 6.96 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, H_{para} of C_6H_5), 7.20 (d, $^3J_{HH}$ = 7.2 Hz, 4 H, H_{ortho} of C_6H_5), 7.18 (s, 3 H, H_{arom} of Xylyl), 7.40 (t, $^3J_{HH}$ = 7.3 Hz, 4 H, H_{meta} of C_6H_5), 7.42−7.70 (m, 5 H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.1 (Si*Me*$_3$), 19.0 (*C*H$_3$ of Xylyl), 30.9 (d, $^2J_{CP}$ = 5.8 Hz, −CH$_2$−*C*H$_2$−Ph), 34.6 (d, $^1J_{CP}$ = 19.0 Hz, −*C*H$_2$−CH$_2$−Ph), 92.1, 98.7, 100.4, 100.9 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 101.6 (C^1, $C_5H_4SiMe_3$), 126.7, 127.9, 128.9, 133.0, 132, 129.2, 129.6, 130.0, 130.4 (C_{arom} of Xylyl), 132.3 (d, $^2J_{CP}$ = 15 Hz, C_{ortho} of C_6H_5), 134.8 (C_{ipso} of Xylyl), 140.3 (d, $^1J_{CP}$ = 30 Hz, C_{ipso} C_6H_5), 199.3 (*C*≡N). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 50.5 (s, *P*(CH$_2$CH$_2$Ph)Ph$_2$). Anal. Calcd for $C_{45}H_{54}BrNNbPSi_2$: C, 62.20; H, 6.26; N, 1.61. Found: C, 62.32; H, 5.98; N, 1.54.

Preparation of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(P(I)Ph$_2$)(CNXylyl)]I$_3$ (19). Method 1. To a solution of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(PPh$_2$)-(CNXylyl)](**9**) (0.45 g, 0.74 mmol) in dry toluene (30 mL) was added an excess of 1,2-diiodoethane [ICH$_2$CH$_2$I; (1:10) (2.23 g; 1.05 mL; ρ = 2.13 g/mL; 7.40 mmol)]. The reaction mixture was stirred at room temperature for 2 h. During this time the solution changed to a deep red color. The solvent was evaporated under vacuum to dryness. The remaining solid was crystallized by dissolving it in dichloromethane and placing a layer of diethyl ether above it in a Schlenk tube. Deep red crystals began to grow within a few days. The resulting product was filtered off to give a deep red solid in 85% yield.

Method 2. To a solution of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(PPh$_2$)-(CNXylyl)] (**9**) (0.50 g, 0.83 mmol) in dry toluene (30 mL) was added an excess of I$_2$ in diethyl ether (1:2) (0.42 g, 1.66 mmol). The reaction mixture was stirred at room temperature for 2 h. During this time the solution changed to a deep red color. The solvent was evaporated under vacuum to dryness. The resulting solid was crystallized by dissolving it in dichloromethane and placing a layer of diethyl ether above it in a Schlenk tube. Deep red crystals began to grow within a few days. The resulting solid was filtered off to give a deep red solid in 80% yield.

Complex 19. Λ_M (Ω^{-1} cm^2 mol^{-1}): 105.6. IR (Nujol): ν (cm^{-1}) 2078 (C≡N). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.33 (s, 18 H, Si*Me*$_3$), 2.56 (s, 6 H, C*H*$_3$ of Xylyl), 4.62, 5.91 (2H, each a complex signal, $C_5H_4SiMe_3$), 5.34 (4H, a complex signal, $C_5H_4SiMe_3$), 7.53 (m, 13 H, H_{arom} of C_6H_5 and Xylyl). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 1.0 (Si*Me*$_3$), 20.3 (*C*H$_3$ of Xylyl), 94.5, 101.8, 103.7 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 104.6 (C^1, $C_5H_4SiMe_3$), 128.6, 129.1, 133.6 (C_{arom} of Xylyl), 133.4 (C_1 of Xylyl), 129.3 ($C_{para\ and}$ C_{meta} of C_6H_5), 136.0 (d, $^2J_{CP}$ = 12 Hz, C_{ortho} of C_6H_5), 138.0 (d, $^1J_{CP}$ = 24 Hz, C_{ipso} of C_6H_5), 190.3 (*C*≡N). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 85.2 (s, *P*(I)Ph$_2$). Anal. Calcd for $C_{37}H_{45}I_4NNbPSi_2$: C, 37.30; H, 3.81; N, 1.18. Found: C, 37.26; H, 3.64; N, 1.09.

Preparation of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(κ^1-*S*-SC(S)(PPh$_2$))(L)] [L = CNBu^n (20), CNCy (21), and CNXylyl (22)]. A mixture of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(PPh$_2$)(L)] [L = CNBu^n (**7**), CNCy (**8**), and CNXylyl (**9**)] (0.93 mmol) was treated with a stoichiometric amount of CS_2 (0.07 g, 0.06 mL, ρ = 1.26 g/mL; 0.93 mmol), and the mixture was stirred in dry THF (30 mL) at room temperature for 4 h. During this time the solution changed color from yellow-brown to dark red. The solvent was evaporated under vacuum to dryness. The dark red oily residue was extracted with hexane (5 mL). The resulting solution was filtered and evaporated to dryness. The deep red oil was dissolved in hexane (5 mL) and kept at 5 °C for 10 h. A microcrystalline dark purple-red solid was obtained. The solid was filtered off to give 82%, 85%, and 80% yield for **20**, **21**, and **22**, respectively.

Complex 20. IR (Nujol): ν (cm^{-1}) 2098 (C≡N), 1100 (C═S), 630 (C−S). ^{1}H NMR (500 MHz, C_6D_6): δ 0.10 (s, 18 H, Si*Me*$_3$), 0.93 (t, $^3J_{HH}$ = 5.3 Hz, 3 H, −C*H*$_3$), 1.12, 1.42 (m, 2 H, −C*H*$_2$−C*H*$_2$−), 4.40 (m, 2 H, CN−C*H*$_2$), 4.63, 4.82, 5.20, 5.48 (2H, each a complex signal, $C_5H_4SiMe_3$), 6.90−7.70 (m, C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 0.2 (Si*Me*$_3$), 13.6 (−*C*H$_3$), 20.4, 25.5-(−*C*H$_2$−*C*H$_2$−), 47.6 (−CN−*C*H$_2$−), 34.0 (d, $^1J_{CP}$ = 28 Hz, −*C*H$_2$−*C*H$_2$−Ph), 92.6 (C^1, $C_5H_4SiMe_3$), 92.3, 94.0, 96.0, 99.9 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 126.0−134.0 (*C*$_6$H$_5$), 140.0 (d, $^1J_{CP}$ = 35.0 Hz, C_{ipso} *C*$_6$H$_5$), 185.5 (*C*≡N), 260.3 (d, $^1J_{CP}$ = 45.5 Hz, *C*S$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 40.3 (s, *P*(CH$_2$Ph)Ph$_2$). Anal. Calcd for $C_{34}H_{45}NNbPS_2Si_2$: C, 60.06; H, 5.97; N, 1.84. Found: C, 60.11, 33.35; H, 6.11, 3.21; N, 1.72.

Complex 21. IR (Nujol): ν (cm^{-1}) 2050 (C≡N), 1089 (C═S), 625 (C−S). ^{1}H NMR (500 MHz, C_6D_6): δ 0.06 (s, 18 H, Si*Me*$_3$), 0.90−1.60 (m, 10 H, C_6H_{11}), 3.39 (q, $^3J_{HH}$ = 5.0 Hz, 1 H, H_1 of C_6H_{11}), 4.79, 4.91, 5.27, 5.29 (2H, each a complex signal, $C_5H_4SiMe_3$), 7.00 (d, $^3J_{HH}$ = 7.0 Hz, 4 H, H_{ortho} of C_6H_5), 7.77 (t, $^3J_{HH}$ = 7.4 Hz, 4 H, H_{meta} of C_6H_5), 7.93 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, H_{para} of C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 0.4 (Si*Me*$_3$), 23.7, 23.9, 32.8 (*C*$_6$H$_{11}$), 58.5 (C_1 of C_6H_{11}), 92.6 (C^1, $C_5H_4SiMe_3$), 95.9, 100.9, 101.9, 103.7 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 125.6, 128.3, 129.2 (*C*$_6$H$_5$), 135.0 (d, $^1J_{CP}$ = 33.0 Hz, C_{ipso} of C_6H_5), 198.2 (*C*≡N), 261.5 (d, $^1J_{CP}$ = 45.5 Hz, *C*S$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 27.2 (s, *P*Ph$_2$). Anal. Calcd for $C_{36}H_{47}NNbPS_2Si_2$: C, 58.59; H, 6.42; N, 1.90. Found: C, 58.60; H, 6.45; N, 1.92.

Complex 22. IR (Nujol): ν (cm^{-1}) 2042 (C≡N), 1100 (C═S), 630 (C−S). ^{1}H NMR (500 MHz, C_6D_6): δ −0.03 (s, 18 H, Si*Me*$_3$), 2.19 (s, 6 H, C*H*$_3$ of Xylyl), 4.82, 5.09, 5.19, 5.38 (2H, each a complex signal, $C_5H_4SiMe_3$), 6.70 (s, 3 H, H_{arom} of Xylyl), 6.99 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, H_{para} of C_6H_5), 7.05 (d, $^3J_{HH}$ = 7.0 Hz, 4 H, H_{ortho} of C_6H_5), 7.75 (t, $^3J_{HH}$ = 7.2 Hz, 4 H, H_{meta} of C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 0.8 (Si*Me*$_3$), 19.9 (*C*H$_3$ of Xylyl), 97.1, 101.4, 102.9, 105.2 (C$^{2-5}$, exact assignment not possible, $C_5H_4SiMe_3$), 95.8 (C^1, $C_5H_4SiMe_3$), 127.7, 127.9, 129.7 (s, C_{para}, C_{meta}, and C_{ortho} of C_6H_5), 133.9, 135.4, 135.8 (s, C_{arom} of Xylyl), 141.2 (s, C_1 of Xylyl), 141.6 (d, $^1J_{CP}$ = 23 Hz, C_{ipso} of C_6H_5), 214.3 (s, *C*≡N), 262.6 (d, $^1J_{CP}$ = 46.5 Hz, *C*S$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 18.6 (s, *P*Ph$_2$). Anal. Calcd for $C_{38}H_{45}NNbPS_2Si_2$: C, 60.06; H, 5.97; N, 1.84. Found: C, 60.17; H, 6.11; N, 1.89.

Preparation of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(κ^2-*S*,*S*-SC(S)(PPh$_2$))] (23). A mixture of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(κ^1-*S*-SC(S)(PPh$_2$))(L)] [L = CNBu^n (**20**), CNCy (**21**), and CNXylyl (**22**)] (0.56 g, 0.82 mmol) and dry THF (20 mL) was stirred at room temperature for 15 days. During this time the solution changed color from dark red to dark green. The solvent was evaporated under vacuum to dryness. The dark green oily residue was extracted with hexane (5 mL). The solid was filtered off to give 90% yield of **23**.

Complex 23. IR (Nujol): ν (cm^{-1}) 1000 (*C*═*S*). ^{1}H NMR (500 MHz, C_6D_6): δ 0.23 (s, 18 H, Si*Me*$_3$), 4.94, 5.09 (m, 4 H each a complex signal, $C_5H_4SiMe_3$); 6.55 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, C_6H_5), 6.80 (d, $^3J_{HH}$ = 7.1 Hz, 4 H, C_6H_5), 7.53 (t, $^3J_{HH}$ = 7.1 Hz, 4 H, C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 0.4 (Si*Me*$_3$), 105.9 (C^1, $C_5H_4SiMe_3$), 97.8, 105.3 (C$^{2-3}$, exact assignment not possible, $C_5H_4SiMe_3$); 124.3, 125.7, 129.7 (*C*$_6$H$_5$), 141.8 (d, $^1J_{CP}$ = 23.00 Hz, *C*$_6$H$_5$), 244.0 (d, $^1J_{CP}$ = 20.00 Hz, *C*S$_2$). ^{31}P NMR (C_6D_6): δ 2.03 (*P*Ph$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 2.03 (q, $^3J_{PH}$ = 7.30 Hz, *P*Ph$_2$). Anal. Calcd for $C_{30}H_{39}NbPS_2Si_2$: C, 55.97; H, 6.11. Found: C, 56.00; H, 5.93.

X-ray Crystallographic Structure Determination of 11 and 12. Single crystals of a red block of **11** and red prismatic crystals of **12** were placed in a NONIUS-MACH3 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal data, data collection, structural solution, and refinement parameters for both compounds are given in Table 2. Intensity data were collected using an $\omega/2\theta$ scan technique. Examination of two standard reflections, monitored after 60 min, showed no sign of crystal deterioration. Data were corrected for Lorentz and polarization effects, and semiempirical absorption correction (psi-scans) was made.[24] The structures were solved by direct methods using the SIR92 computer program,[25] completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures (SHELXL97)[26] on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. Compound **11** exhibited a rotational disorder of the $SiMe_3$ groups with a 50:50 occupancy ratio. Furthermore the cyclohexylisocyanide ligand appeared disordered over two distinct sites in 50:50 ratio.

The single crystals obtained for compound **19** diffracted particularly poorly and were of rather poor quality. For this reason only a rough model of the structure could be obtained. Crystal data: monoclinic, $P2_1/n$, a = 21.397(2) Å, b = 11.022(2) Å, c = 19.600(3) Å, β = 107.19(1)°; V = 4416(1), Z = 4.

Acknowledgment. We gratefully acknowledge financial support from the Dirección General de Investigación Científica Spain (MEC Grant. No. BQU2002-04638-CO2-02) and the Junta de Comunidades de Castilla-La Mancha (Grant Nos. PAC-02-003, GC-02-010, PBI05-23, and PBI-05-029).

Supporting Information Available: Detailed X-ray crystallographic data of atomic positional parameters, bond distances and angles, and anisotropic thermal parameters for complexes **11** and **12**. Tables of X-ray crystallographic data for complexes **11** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060283P

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