Organometallics **2005,** *24,* 2061−2064

A Novel Constrained-Geometry Niobocene Complex with a Phosphanidoalkylcyclopentadienyl Ligand: $[Nb(N^tBu)\{(\eta^5\text{-}C_5H_4)CMe_2PPh\text{-}\kappa P\}\{(\eta^5\text{-}C_5H_4)CMe_2PHPh\}]$

Santiago Gómez-Ruiz,[†,‡] Thomas Höcher,[†] Sanjiv Prashar,[‡] and
Evamarie Hey-Hawkins*,[†]

*Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29,
D-04103 Leipzig, Germany, and Departamento de Tecnología Química, Ambiental y de los
Materiales, ESCET, Universidad Rey Juan Carlos, 28933 Móstoles (Madrid), Spain*

Received January 14, 2005

$Li[(C_5H_4)CMe_2PHPh]$ reacts with $[Nb(N^tBu)Cl_3(py)_2]$ with formation of $[Nb(N^tBu)\{(\eta^5\text{-}C_5H_4)CMe_2PPh\text{-}\kappa P\}\{(\eta^5\text{-}C_5H_4)CMe_2PHPh\}]$ (**1**), which exhibits a PH-functionalized phosphanylalkylcyclopentadienyl and a chelating phosphanidoalkylcyclopentadienyl ligand. Complex **1** was characterized by NMR spectroscopy. Only two of the four possible diastereomers are present in solution. X-ray crystallography showed that only the $R_{Nb},S_{Pcoord},R_{Pnon}/S_{Nb},R_{Pcoord},S_{Pnon}$ isomer is present in the unit cell.

Introduction

After the discovery of α-olefin polymerization,[1] numerous metallocene and monocyclopentadienyl derivatives with different steric and electronic properties were synthesized and employed as catalysts in polymerization reactions. *ansa*-Metallocene dichlorides of Ti, Zr, and Hf (especially chiral ones) are important catalysts for the methylalumoxane-promoted isotactic polymerization of olefins. Therefore, intensive research is being carried out toward the synthesis of improved catalysts.[2−5] Recently, monocyclopentadienyl derivatives in which the cyclopentadienyl ring has a heteroatom-functionalized side chain were prepared and employed in the polymerization and copolymerization of olefins.[6] These studies were also extended to phospholyl ligands.[7]

While numerous cyclopentadienyl ligands with O- and N-functionalized side chains are known, the number of cyclopentadienes with a P-functionalized alkyl or silyl side chain is still small,[8] and it was only in 1994 that Jutzi et al. reported the first compound in which the P atom bears a reactive P−H bond;[9] we and others have extended this class of compounds to other derivatives in 1999.[10,11] The lithium salts $[Li(TMEDA)]_2[(C_5H_4)CMe_2PPh]$[12] and $[Li(TMEDA)][(C_5H_4)CMe_2PR_2]$ (R = Ph, Me),[13] $1\text{-}SiMe_2PHMes^*C_5Me_4H$ and its dimeric dipotassium salt $[K(THF)_2]_2[(C_5Me_4)SiMe_2PMes^*]$ ($Mes^* = 2,4,6\text{-}^tBu_3C_6H_2$)[14] have been structurally characterized. Such compounds should be useful precursors for dianionic bifunctional ligands in transition-metal chemistry. In addition, the presence of a P-containing group is advantageous for reactivity studies by ^{31}P NMR spectroscopy.

We previously reported the synthesis of the PH-functionalized chromium(III) complexes $[CrCl_2\{(\eta^5\text{-}C_5H_4)CMe_2PHR\}(PMe_2Ph)]$ (R = Ph, ^tBu),[15] the ferrocene derivatives *rac*-$[Fe\{(\eta^5\text{-}C_5H_4)CMe_2PHR\}_2]$ (R = Ph, $2,4,6\text{-}Me_3C_6H_2$ (Mes)),[16] the monosubstituted phosphanylalkylcyclopentadienyl complexes of group 4 met-

---

[†] Universität Leipzig.

[‡] Universidad Rey Juan Carlos.

(1) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 541−547.

(2) Schneider, N.; Huttenloch, M. E.; Stehling, U.; Kirsten, R.; Schaper, F.; Brintzinger, H. H. *Organometallics* **1997**, *16*, 3413−3420 and references therein.

(3) Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995**, *497*, 181−193.

(4) Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171−180.

(5) (a) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* **1985**, *97*, 507−508. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507−508. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem.* **1995**, *107*, 1255−1282. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (c) Fink, G.; Mülhaupt, R.; Brintzinger, H. H. *Ziegler Catalysts−Recent Scientific Innovations and Technological Improvements*; Springer-Verlag: Berlin, Heidelberg, New York, 1995.

(6) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. (c) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140−4142. (d) Alt, H. G.; Föttinger, K.; Milius, W. *J. Organomet. Chem.* **1999**, *572*, 21−30. (e) Galan-Fereres, M.; Koch, T.; Hey-Hawkins, E.; Eisen, M. S. *J. Organomet. Chem.* **1999**, *580*, 145−155. (f) McKnight, A. L. Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598. (g) Canich, J. A. M. Eur. Patent 420 436, 1991. (h) Schmidt, G. F.; Timmers, F. J.; Knight, G. W.; Lai, S.-Y.; Nickias, P. N.; Rosen, R. K.; Stevens, J. C.; Wilson, D. R. Eur. Patent 416 815, 1991.

(7) (a) Brown, S. J.; Gao, X.; Harrison, D. G.; Koch, L.; Spence, R. E. V. H.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5445−5447. (b) Mathey, F. *Chem. Rev.* **1988**, *88*, 429−453. (c) Janiak, C.; Lange, K. C. H.; Versteeg, U.; Lentz, D.; Budzelaar, P. *Chem. Ber.* **1996**, *129*, 1517−1529. (d) Janiak, C.; Versteeg, U.; Lange, K. C. H.; Weimann, R.; Hahn, E. *J. Organomet. Chem.* **1995**, *501*, 219−234.

(8) Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527−1564.

(9) Heidemann, T.; Jutzi, P. *Synthesis* **1994**, 777−778.

(10) Koch, T.; Hey-Hawkins, E. *Polyhedron* **1999**, *18*, 2113−2116 and references therein.

(11) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233−350.

(12) Bildmann, U. J.; Müller, G. *Z. Naturforsch., B* **2000**, *55*, 895−900.

(13) Bildmann, U. J.; Winkler, M.; Müller, G. *Z. Naturforsch., B* **2000**, *55*, 1005−1010.

(14) Tardif, O.; Hou, Z.; Nishiura, M.; Koizumi, T.; Wakatsuki, Y. *Organometallics* **2001**, *20*, 4565−4573.

(15) Höcher, T.; Salisbury, B. A.; Theopold, K.; Hey-Hawkins, E. *Polyhedron* **2004**, *23*, 1393−1399.

(16) Höcher, T.; Blaurock, S.; Hey-Hawkins, E. *Eur. J. Inorg. Chem.* **2002**, 1174−1180.

10.1021/om0500319 CCC: \$30.25

als [$ZrCl_3\{(\eta^5\text{-}C_5H_4)SiMe_2PHR\}$] (R = Ph, Cy) and [$MCl_3\{(\eta^5\text{-}C_5H_4)CMe_2PH^tBu\}$] (M = Ti, Zr),[17] and the metallocene derivatives [$ZrCl_2\{(\eta^5\text{-}C_5H_4)CMe_2PHR\}_2$] and [$TiCl\{(\eta^5\text{-}C_5H_4)CMe_2PHR\}_2$] (R = Ph, ^{t}Bu). The metallocene derivatives mentioned last slowly decompose on recrystallization from THF, Et_2O, or toluene with formation of [$MCl_2\{(\eta^5\text{-}C_5H_4)_2CMe_2\}$] (M = Zr, Ti), $(PR)_n$ (R = Ph, $n = 4$–6; R = ^{t}Bu, $n = 4$), and PH_2R.[18] Recently, Erker et al. reported the synthesis of the constrained-geometry catalysts [$M(NR_2)_2\{(C_5H_4)CMe_2PCy\text{-}\kappa P\}$] (M = Ti, R = Me; M = Zr, R = Et) and their catalytic properties in the polymerization of olefins,[19] while Hou et al. reported the synthesis of [$LnL_n\{(\eta^5\text{-}C_5Me_4)SiMe_2PMes^*\text{-}\kappa P\}$] (Ln = Sm: L = THF, $n = 1, 3$; L = $MeOCH_2CH_2OMe$, $n = 2$; L = $PO(NMe_2)_3$, $n = 2$; Ln = Yb, L = THF, $n = 3$; Mes* = 2,4,6-$^tBu_3C_6H_2$) and the polymerization of ethene, ϵ-caprolactone, and 1,3-butadiene with the Sm^{II} mono-THF complex.[14] Another rare example of complexes with a chelating phosphanidoalkylcyclopentadienyl ligand is the constrained-geometry chromium complex [$CrCl\{(\eta^5\text{-}C_5H_4)CMe_2PPh\text{-}\kappa P\}$]$_2$.[15]

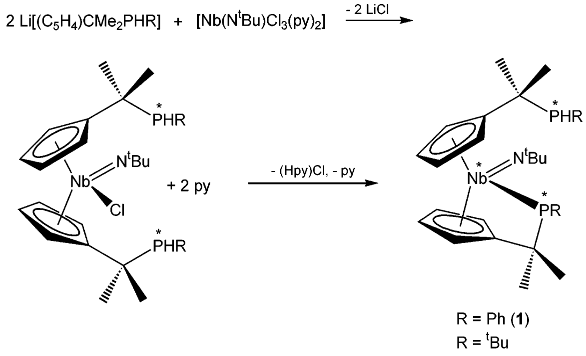
Like zirconocene derivatives, niobocenes and tantalocenes, especially *ansa*-metallocenes, were studied as model complexes for catalysts in polymerization reactions.[20] However, only a small number of niobocenes and tantalocenes with P-functionalized cyclopentadienyl rings are known; here, the phosphanyl group is directly bound to the cyclopentadienyl ring.[21] We now report the synthesis of the first niobocene(V) complex which exhibits a PH-functionalized phosphanylalkylcyclopentadienyl ligand and a chelating phosphanidoalkylcyclopentadienyl ligand, [$Nb(N^tBu)\{(\eta^5\text{-}C_5H_4)CMe_2PHPh\}\{(\eta^5\text{-}C_5H_4)CMe_2PPh\text{-}\kappa P\}$].

Results and Discussion

Niobocene(V) derivatives are not accessible from cyclopentadienides and $NbCl_5$, while the corresponding metallocene(IV) derivatives can be prepared from $NbCl_4$. However, the paramagnetism of these products complicates their characterization, but they can be oxidized, for example, with chlorine.[22] This synthetic approach also proved successful for the synthesis of a niobocene(IV) derivative with PH-functionalized cyclopentadienyl ligands. Thus, $NbCl_4$ reacts with the lithium reagent Li[$(C_5H_4)CMe_2PHR$], which is readily accessible by reaction of LiPHR (R = ^{t}Bu,[18] Ph[10]) with 6,6-dimethylfulvene, to give an inseparable mixture of two niobocene(IV) complexes, presumably [$NbCl_2\{(\eta^5\text{-}C_5H_4)CMe_2PHR\}_2$] and the HCl elimination product [$NbCl\{(\eta^5\text{-}C_5H_4)CMe_2PHR\}\{(\eta^5\text{-}C_5H_4)CMe_2PR\text{-}\kappa P\}$], which were characterized by mass spectrometry and EPR spectroscopy.[23]

A more suitable starting material is the niobium(V) imido complex [$Nb(N^tBu)Cl_3(py)_2$],[24] which has already been employed for the synthesis of niobocene(V) derivatives with P-functionalized cyclopentadienyl rings.[21]

The lithium reagent Li[$(C_5H_4)CMe_2PHPh$][10] reacts with [$Nb(N^tBu)Cl_3(py)_2$] (eq 1) to give the first niobium(V) phosphanido complex with three chiral centers, [$Nb(N^tBu)\{(\eta^5\text{-}C_5H_4)CMe_2PPh\text{-}\kappa P\}\{(\eta^5\text{-}C_5H_4)CMe_2PHPh\}$] (**1**), which exhibits a PH-functionalized phosphanylalkylcyclopentadienyl and a chelating phosphanidoalkylcyclopentadienyl ligand. Similarly, Li[$(C_5H_4)CMe_2PH^tBu$] reacts with [$Nb(N^tBu)Cl_3(py)_2$] to give the corresponding niobocene(V) complex [$Nb(N^tBu)\{(\eta^5\text{-}C_5H_4)CMe_2P^tBu\text{-}\kappa P\}\{(\eta^5\text{-}C_5H_4)CMe_2PH^tBu\}$] (^{31}P NMR: −23.7 (br), 41.5 (d, $^1J_{PH} = 197.0$ Hz), 39.2 ppm (d, $^1J_{PH} = 200.0$ Hz)), which is highly soluble in all common solvents but could not be obtained in pure form.



(1)

Elimination of lithium chloride and hydrogen chloride apparently occurs in this reaction. Complex **1** was characterized by multinuclear NMR spectroscopy and X-ray diffraction.

As shown in eq 1, compound **1** has three chiral centers: the free phosphanyl group (P_{non}), the coordinated phosphanido group (P_{coord}), and the niobium atom. Thus, four diastereomers can be formed ($R_{Nb},S_{Pcoord},R_{Pnon}/S_{Nb},R_{Pcoord},S_{Pnon}$, $R_{Nb},R_{Pcoord},R_{Pnon}/S_{Nb},S_{Pcoord},S_{Pnon}$, $R_{Nb},S_{Pcoord},S_{Pnon}/S_{Nb},R_{Pcoord},R_{Pnon}$, and $R_{Nb},R_{Pcoord},S_{Pnon}/S_{Nb},S_{Pcoord},R_{Pnon}$). However, only three signals are observed in the $^{31}P\{^1H\}$ NMR spectrum of **1**, two of which are singlets, while the third is a broad signal; this indicates the presence of only two diastereomers in solution. The two sharp singlets at 10.1 and 9.6 ppm correspond to the noncoordinating phosphanyl group, and they are shifted to low field by ca. 10 ppm compared to the lithium reagent. On proton coupling, the sharp singlets split into doublets with a $^1J_{PH}$ value of ca. 182 Hz. The broad signal at −66 ppm ($\nu_{1/2}$ ca. 122 Hz) can be assigned to the phosphanido group, which is bonded to niobium. Due to the quadrupole moment of niobium the two signals for the two diastereomers are not resolved but occur as one broad signal. The high-field

---

(17) Koch, T.; Hey-Hawkins, E.; Galan-Fereres, M.; Eisen, M. S. *Polyhedron* **2002**, *21*, 2445–2450.

(18) Koch, T.; Blaurock, S.; Somoza, F. B., Jr.; Voigt, A.; Kirmse, R.; Hey-Hawkins, E. *Organometallics* **2000**, *19*, 2556–2563.

(19) Kunz, K.; Erker, G.; Döring, S.; Fröhlich, R.; Kehr, G. *J. Am. Chem. Soc.* **2001**, *123*, 6181–6182.

(20) Chirik, P. J.; Zubris, D. L.; Ackerman, L. J.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *Organometallics* **2003**, *22*, 172–187. Ackerman, L. J.; Green, M. L. H.; Green, J. C.; Bercaw, J. E. *Organometallics* **2003**, *22*, 188–194.

(21) (a) Antinolo, A.; Fernández-Galán, R.; Orive, I.; Otero, A.; Prashar, S. *Eur. J. Inorg. Chem.* **2002**, *9*, 2470–2476. (b) Antinolo, A.; Exposito, T.; del Hierro, I.; Lucas, D.; Mugnier, Y.; Orive, I.; Otero, A.; Prashar, S. *J. Organomet. Chem.* **2002**, *655*, 63–69. (c) Poulard, C.; Boni, G.; Richard, P.; Moïse, C. *J. Chem. Soc., Dalton Trans.* **1999**, 2725–2730.

(22) Fakhr, A.; Mugnier, Y.; Broussier, R.; Gautheron, B. *J. Organomet. Chem.* **1985**, *279*, C15–C18.

(23) Gómez-Ruiz, S.; Prashar, S.; Hanner, M.; Kirmse, R.; Hey-Hawkins, E. Unpublished results.

(24) Sundermeyer, J.; Putterlik, J.; Foth, M.; Field, J. S.; Ramesar, N. *Chem. Ber.* **1994**, *127*, 1201–1212.

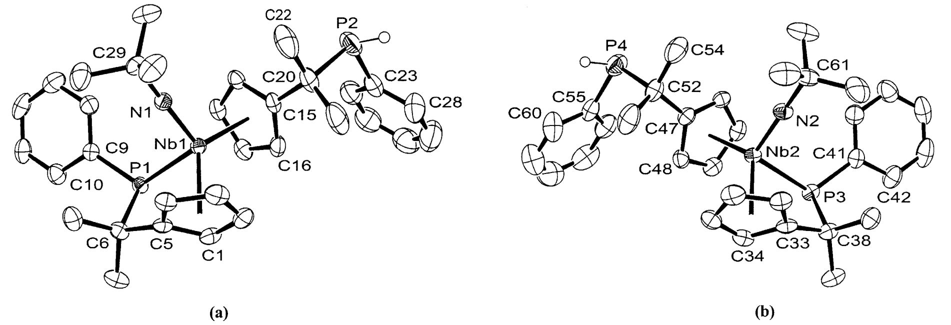


Figure 1. Molecular structure of [Nb(N^{t}Bu){(η^5-C$_5$H$_4$)CMe$_2$PPh-κP}{(η^5-C$_5$H$_4$)CMe$_2$PHPh}] (**1**), showing the atom-numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP):[34] (a) R_{Nb},S_{Pcoord},R_{Pnon} isomer; (b) S_{Nb},R_{Pcoord},S_{Pnon} isomer. Hydrogen atoms (other than PH) are omitted for clarity.

shift is due to the strained four-membered ring (C, P, Nb, and center of the C$_5$H$_4$ ring; “small ring effect”).[25]

The ^{1}H and ^{13}C NMR spectra are rather complex, due to the presence of two diastereomers and two differently coordinating cyclopentadienyl ligands and extensive overlap of the signals. In the ^{1}H{^{31}P} NMR spectrum, one signal is observed for the PH proton of each diastereomer at ca. 5 ppm. In the ^{13}C NMR spectrum, all of the aliphatic carbon atoms are observed and could be assigned by means of an HMQC NMR spectrum (see Experimental Section). The inequivalent methyl groups of the phosphanido ligands are observed at 24.45 and 36.71 or 36.74 ppm (in the ^{1}H NMR spectrum at 1.32 and 1.85 or 1.87 ppm).

Only 18 signals are observed for the C$_5$H$_4$ rings (20 expected). The missing signals are those of the ipso carbon atoms, which are obscured by the solvent, C$_6$D$_6$. The ipso carbon atoms of the phenyl rings of the phosphanido ligand are shifted to low field by ca. 5 ppm compared to the lithium salt, and the $^1J_{\mathrm{PC}}$ coupling constant of 57 Hz is much larger.

Molecular Structure of 1. X-ray-quality crystals of **1** were obtained from *n*-hexane as yellow platelets; separation of the two diastereomers by fractional crystallization was unsuccessful in aliphatic hydrocarbon solvents (*n*-hexane, *n*-pentane, 40−60 °C petroleum ether),[26] while no crystals were obtained from THF, toluene, diethyl ether, or chlorinated solvents, in which **1** is highly soluble. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two enantiomers of one diastereomer (R_{Nb},S_{Pcoord},R_{Pnon} and S_{Nb},R_{Pcoord},S_{Pnon}) in the asymmetric unit and four molecules in the unit cell. Both enantiomers are shown in Figure 1. The P−Nb bond lengths (2.6242(9) and 2.6240(9) Å; Table 1) are in the range observed for other Nb−P bonds (2.610(2)−2.644(3) Å; Table 2).[27] In niobocene complexes with primary phosphines, PH$_2$R, the Nb−P bond is shorter by ca. 0.1 Å.[28] The atoms P(1), C(6), Nb(1) or P(3), C(38), Nb(2) and the center of the C$_5$H$_4$ ring form a rectangle with bond angles of close to 90°.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 1

P(1)−Nb(1)	2.6242(9)	P(3)−Nb(2)	2.6240(9)
N(1)−Nb(1)	1.779(2)	N(2)−Nb(2)	1.780(2)
C(6)−P(1)	1.902(3)	C(38)−P(3)	1.904(3)
C(9)−P(1)	1.830(3)	C(41)−P(3)	1.836(3)
C(20)−P(2)	1.892(4)	C(52)−P(4)	1.889(4)
C(23)−P(2)	1.821(4)	C(55)−P(4)	1.819(4)
C(29)−N(1)	1.461(4)	C(61)−N(2)	1.464(4)
C(9)−P(1)−Nb(1)	115.8(1)	C(41)−P(3)−Nb(2)	113.2(1)
C(6)−P(1)−Nb(1)	91.75(9)	C(38)−P(3)−Nb(2)	91.3(1)
C(9)−P(1)−C(6)	106.1(1)	C(41)−P(3)−C(38)	106.8(1)
C(23)−P(2)−C(20)	105.3(2)	C(55)−P(4)−C(52)	104.6(2)
C(29)−N(1)−Nb(1)	171.9(2)	C(61)−N(2)−Nb(2)	170.9(2)
C(5)−C(6)−P(1)	94.2(2)	C(46)−C(41)−P(3)	123.3(3)
C(7)−C(6)−P(1)	114.5(2)	C(42)−C(41)−P(3)	118.8(3)
C(8)−C(6)−P(1)	112.1(2)	C(33)−C(38)−P(3)	95.1(2)
C(14)−C(9)−P(1)	123.5(2)	C(39)−C(38)−P(3)	115.0(2)
C(10)−C(9)−P(1)	117.6(2)	C(40)−C(38)−P(3)	111.4(2)
C(15)−C(20)−P(2)	108.5(2)	C(47)−C(52)−P(4)	107.8(2)
C(21)−C(20)−P(2)	110.1(2)	C(53)−C(52)−P(4)	111.1(3)
C(22)−C(20)−P(2)	104.2(3)	C(54)−C(52)−P(4)	104.3(3)
C(28)−C(23)−P(2)	122.5(3)	C(56)−C(55)−P(4)	121.5(3)
C(24)−C(23)−P(2)	120.0(3)	C(60)−C(55)−P(4)	120.8(3)
N(1)−C(29)−C(31)	109.0(3)	N(2)−C(61)−C(64)	109.8(3)
N(1)−C(29)−C(32)	109.9(3)	N(2)−C(61)−C(62)	109.0(3)
N(1)−C(29)−C(30)	109.0(2)	N(2)−C(61)−C(63)	108.9(3)

The CE−Nb−CE (CE = center of C$_5$H$_4$ ring) angle of 128.6 or 128.9° in **1** is larger by ca. 2 or 6° than the corresponding angle in [Nb(N^{t}Bu)Cp$_2$(PMe$_3$)][SO$_3$CF$_3$] (126.8°)[29] or [Nb(N^{t}Bu)ClCp$_2$].[30]

The Nb−N bond length of 1.779(2) or 1.780(2) Å and the Nb−N−C bond angle of 171.9(2) or 170.9(2)° are in agreement with a linear Nb−N triple bond[31] and indicate that the imido ligand is acting as a four-electron donor. A deviation from linearity of 12−15° is also observed in other imido niobocene complexes (Table 2).[31] Thus, the total number of valence electrons for this compound is 20,[30,31,32] with two electrons being localized in a nonbonding orbital, similar to the case for [Mo(N^{t}Bu)(η^5-C$_5$H$_5$)$_2$].[30]

Experimental Section

General Details. All operations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The reagents and solvents were purified by standard procedures. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on an

---

[25] Baudler, M.; Hahn, J.; Dietsch, H.; Fürstenberg, G. *Z. Naturforsch. B* **1976**, *31*, 1305−1310.

[26] Both diastereomers are observed in the ^{31}P NMR spectrum of a solution of these crystals; thus, a racemic mixture of crystals is present in the solid.

[27] Bonnet, G.; Kubicki, M. M.; Moïse, C.; Lazzaromi, R.; Savadori, P.; Vitulli, G. *Organometallics* **1992**, *11*, 964−967.

[28] Nikonov, G. I.; Lemenowskij, D. A.; Dorogov, K. Y.; Churakov, A. V. *Polyhedron* **1999**, *18*, 1159−1162.

[29] Humphries, M. J.; Douthwaite, R. E.; Green, M. L. H. *Dalton Trans.* **2000**, 2952−2959.

[30] Chernega, A. N.; Green, M. L. H.; Suarez, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3031−3034.

[31] Antiñolo, A.; Fajardo, M.; Otero, A.; Prashar, S. *Eur. J. Inorg. Chem.* **2003**, 17−28.

[32] Bailey, N. J.; Cooper, J. A.; Galius, H.; Green, M. L. H.; James, J. T.; Leech, M. A. *J. Chem. Soc., Dalton Trans.* **1997**, 3579−3584.

Table 2. Comparison of Selected Structural Data of 1 and Related Niobocene Complexes

complex	CE−Nb−CE (deg)[a]	Nb−N−C (deg)	Nb−N (Å)	Nb−P (Å)[c]	Nb−P−C (deg)[d]	ref
1[b]	128.6	171.9(2)	1.779(2)	2.6242(9)	115.8(1)	this work
	128.9	170.9(2)	1.780(2)	2.6240(9)		
[NbCl{Me$_2$C(η^5-C$_5$H$_4$)$_2$}(N^{t}Bu)]	113.3	178.4(3)	1.762(3)			32
[NbBr{Me$_2$C(η^5-C$_5$H$_4$)$_2$}(N^{t}Bu)]	113.4	178.3(4)	1.765(2)			32
[Nb{Me$_2$C(η^5-C$_5$H$_4$)$_2$}(N^{t}Bu)I]	114.2	171.8(2)	1.770(2)			32
[NbCl(η^5-C$_5$H$_5$)$_2$(N^{t}Bu)]	122.7	173.6(4)	1.789(4)			30
[Nb(η^5-C$_5$H$_5$)$_2$(PPh$_2$)(PHPh$_2$)]	138.2			2.610(2)	113.2(2)	28
[Nb(η^5-C$_5$H$_5$)$_2$(P^{i}PrPh)(CO)]	140.0			2.644(3)	104.9(3)	27

[a] CE refers to the center of the C_5H_4 fragment for *ansa*-metallocene complexes and C_5H_5 for metallocene complexes. [b] Two independent molecules in the asymmetric unit. [c] Nb−P of niobium−phosphanido group. [d] Ipso C of the phenyl group.

AVANCE DRX 400 spectrometer (Bruker): ^{1}H NMR (400.13 MHz), internal standard TMS; ^{13}C NMR (100.6 MHz), internal standard TMS; ^{31}P NMR (161.9 MHz), external standard 85% H_3PO_4. The IR spectra were recorded on a Perkin-Elmer System 2000 FTIR spectrometer (KBr) in the range 350−4000 cm^{-1}. EI-MS: MAT 212 (Varian). FAB: ZAB-HSQ-VG Analytical Manchester. The melting points were determined in sealed capillaries under nitrogen and are uncorrected (Boetius). The crystal data were measured on a Siemens SMART CCD diffractometer. Li[(C$_5$H$_4$)CMe$_2$PHPh][10] and [Nb(N^{t}Bu)Cl$_3$(py)$_2$][24] were prepared by literature procedures.

(Phenylphosphanidodimethylmethylcyclopentadienyl)(phenylphosphinodimethylmethylcyclopentadienyl)(*tert*-butylimido)niobium(V), [Nb(N^{t}Bu){(η^5-C$_5$H$_4$)CMe$_2$P^{t}Bu-κP}{(η^5-C$_5$H$_4$)CMe$_2$PH^{t}Bu}] (1). A solution of Li[(C$_5$H$_4$)CMe$_2$PHPh] (1.0 g, 4.50 mmol) in THF (20 mL) was added at −78 °C to a solution of [Nb(N^{t}Bu)Cl$_3$(py)$_2$] (0.9 g, 2.25 mmol) in THF (30 mL). The solution turned green-brown and was brown after the addition was complete. The reaction mixture was warmed to room temperature and stirred for 12 h. Afterward the solvent was removed in vacuo, and the slimy brown residue was dissolved in hexane (50 mL). LiCl was removed by filtration and the solvent removed in vacuo to give a brown oil. Recrystallization from petroleum ether at −20 °C gave yellow single crystals suitable for X-ray analysis. Yield: 0.69 g (49%). Mp: 152 °C.

^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.85 (m, 4H, *m*-C*H* in Ph), 7.16 (m, 16H, *o*-, *m*-, and *p*-C*H* in Ph), 6.02 (m, 4H, C*H* in C$_5$H$_4$), 5.47 (m, 4H, C*H* in C$_5$H$_4$), 5.28 (m, 2H, C*H* in C$_5$H$_4$), 5.16 (s, 2H, C*H* in C$_5$H$_4$), 4.87 (s, 2H, C*H* in C$_5$H$_4$), 4.55 (m, 2H, C*H* in C$_5$H$_4$), 4.26 and 4.23 (each d, $\sum$2H, P*H*, $^1J_{PH}$ = 182.0 Hz, P*H*, $^1J_{PH}$ = 182.0 Hz), 1.87 and 1.85 (each d, $\sum$6H, CH_3 in CMe$_2$, $^3J_{PH}$ = 16.0 Hz, CH_3 in CMe$_2$, $^3J_{PH}$ = 16.0 Hz), 1.63, 1.59, and 1.56 (each d, $\sum$12H, CH_3 in CMe$_2$, $^3J_{PH}$ = 14.5 Hz, CH_3 in CMe$_2$, $^3J_{PH}$ = 16.1 Hz, CH_3 in CMe$_2$, $^3J_{PH}$ = 14.4 Hz), 1.32 (s, 6H, CH_3 in CMe$_2$), 0.88 and 0.87 (each s, $\sum$18H, CH_3 in N^{t}Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 143.82 (d, $^1J_{PC}$ = 57.1 Hz, ipso *C* in Ph), 143.76 (d, $^1J_{PC}$ = 56.7 Hz, ipso *C* in Ph), 136.30 (d, J_{PC} = 15.8 Hz, *C*H in Ph), 136.08 (d, J_{PC} = 15.4 Hz, *C*H in Ph), 134.74 (s, J_{PC} = 16.2, ipso *C* in Ph or C$_5$H$_4$), 134.58 (s, J_{PC} = 16.6 Hz, ipso *C* in Ph or C$_5$H$_4$), 127.12 (s, *C*H in Ph), 126.70 (d, J_{PC} = 5.0 Hz, *C*H in Ph), 126.28 (s, *C*H in Ph), 126.16 (d, J_{PC} = 8.5 Hz, *C*H in Ph), 114.24 (s, *C*H in C$_5$H$_4$), 114.17 (s, *C*H in C$_5$H$_4$), 112.94 (d, J_{PC} = 6.0 Hz, *C*H in C$_5$H$_4$), 112.16 (d, J_{PC} = 2.0 Hz, *C*H in C$_5$H$_4$), 111.45 (d, J_{PC} = 12.7 Hz, *C*H in C$_5$H$_4$), 110.84 (d, J_{PC} = 12.7 Hz, *C*H in C$_5$H$_4$), 110.44 (d, J_{PC} = 2.3 Hz, *C*H in C$_5$H$_4$), 110.33 (d, J_{PC} = 2.3 Hz, *C*H in C$_5$H$_4$), 103.48 (s, *C*H in C$_5$H$_4$), 103.44 (s, *C*H in C$_5$H$_4$), 102.49 (d, J_{PC} not determinable, *C*H in C$_5$H$_4$), 102.46 (d, J_{PC} not determinable, *C*H in C$_5$H$_4$), 102.43 (s, *C*H in C$_5$H$_4$), 101.48 (d, J_{PC} = 6.6 Hz, *C*H in C$_5$H$_4$), 94.29 (s, *C*H in C$_5$H$_4$), 94.24 (s, *C*H in C$_5$H$_4$), 67.70 (s, *C*(CH$_3$)$_3$), 36.74 (d, $^2J_{PC}$ = 33.4 Hz, C−*C*H$_3$), 36.71 (d, $^2J_{PC}$ = 32.3 Hz, C−*C*H$_3$), 34.55 (d, $^1J_{PC}$ = 13.6 Hz, *C*−CH$_3$), 34.49 (d, $^1J_{PC}$ = 13.6 Hz, *C*−CH$_3$), 31.89 (s, C(*C*H$_3$)$_3$), 31.87 (s, C(*C*H$_3$)$_3$), 29.74 (d, $^1J_{PC}$ = 25.8 Hz, *C*−CH$_3$), 29.70 (d, $^1J_{PC}$ = 25.7 Hz, *C*−CH$_3$), 29.47 (d, $^2J_{PC}$ = 11.9 Hz, C−*C*H$_3$), 29.16 (d, $^2J_{PC}$ = 17.4 Hz, C−*C*H$_3$), 29.10 (d, $^2J_{PC}$ = 17.7 Hz, C−*C*H$_3$), 28.59 (d, $^2J_{PC}$ = 16.4 Hz, C−*C*H$_3$), 24.45 (s, C−*C*H$_3$); signals of aromatic C atoms are partially obscured by signals of deuterated benzene. ^{31}P NMR (CDCl$_3$, 25 °C): δ 10.1 (d, $^1J_{PH}$ = 182.8 Hz), 9.6 (d, $^1J_{PH}$ = 181.6 Hz), −66.0 (br, s). IR (KBr pellet; $\tilde{\nu}$ (cm^{-1})): 3045 w (ν(CH)), 2963 and 2891 m (ν(CH$_3$)), 2288 w (ν(PH)), 1611 br, w (ν(C=C)), 1463 and 1433 m (δ(CH$_3$)). Anal. Calcd for $C_{32}H_{40}NNbP_2$ (593.5): C, 64.8; H, 6.8; N, 2.4. Found: C, 65.0; H, 6.8; N, 2.4.

Data Collection and Structural Refinement Details of 1: $C_{32}H_{40}NNbP_2$, M_r = 593.50, triclinic, space group $P\bar{1}$, a = 8.6803(2) Å, b = 14.365(3) Å, c = 23.879(5) Å, α = 96.213(3)°, β = 92.010(3)°, γ = 93.761(3)°, V = 2951.1(10) Å^3, Z = 4, d_{calcd} = 1.336 g cm^{-3}, μ = 0.537 mm^{-1}, θ_{max} = 29.33°. R ($I > 2\sigma(I)$): R1 = 0.0498, wR2 = 0.0972. R (all data): R1 = 0.0726, wR2 = 0.1041, 24 351 measured reflections, 14 076 independent reflections, 658 refined parameters, minimum/maximum residual electron density −0.475/0.500 e Å^{-3}. Data were collected with a Siemens CCD (SMART) diffractometer (λ(Mo Kα) = 0.710 73 Å, T = 220(2) K). Empirical absorption correction was carried out with SADABS.[33] The structures were solved by direct methods.[34] Nb, C, P, and N atoms were refined anisotropically; H atoms were located by difference maps and refined isotropically. CCDC 259706 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; email deposit@ccdc.cam.ac.uk).

Acknowledgment. We gratefully acknowledge financial support from the EU Marie-Curie Training Site (Grant No. HPMT-CT-2000-00110, S.G.R.) and the Universidad Rey Juan Carlos (Grant No. GVC-2004-12). We would also like to thank H. C. Starck GmbH & Co. KG for a generous donation of NbCl$_5$.

Supporting Information Available: Tables giving X-ray crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0500319

---

(33) Sheldrick, G. M. SADABS-A Program for Empirical Absorption Correction, University of Göttingen, Göttingen, Germany, 1998.

(34) SHELXTL PLUS, Siemens Analytical X-ray Instruments Inc., 1990 (XS, Program for Crystal Structure Solution; XL, Program for Crystal Structure Determination; XP, Interactive Molecular Graphics).