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Niobium(III) Monocyclopentadienyl Isocyanide, Acetylene, and Diene Complexes. X-ray Crystal Structures of $Nb(\eta^5\text{-}C_5Me_5)Cl_4(CN\text{-}2,6\text{-}Me_2C_6H_3)$ and $Nb(\eta^5\text{-}C_5Me_5)Cl_2(CN\text{-}2,6\text{-}Me_2C_6H_3)_3\cdot{}^1/_2MeC_6H_5$

María Isabel Alcalde, Javier de la Mata, Manuel Gómez, and Pascual Royo*

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain

Maria Angela Pellinghelli and Antonio Tiripicchio

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy

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$NbCp^*Cl_4$ ($Cp^* = \eta^5\text{-}C_5Me_5$) reacts with isocyanides to give the pseudooctahedral adducts $NbCp^*Cl_4(CNR)$ (R = ^{t}Bu, **1**; R = 2,6-$Me_2C_6H_3$, **2**). Reduction of these adducts or alternatively $NbCp^*Cl_4$ with 2 equiv of Na/Hg in the presence of stoichiometric amounts of isocyanides gives the diamagnetic pseudooctahedral niobium(III) complexes $NbCp^*Cl_2(CNR)_3$ (R = ^{t}Bu, **3**; R = 2,6-$Me_2C_6H_3$, **4**). A similar reduction of $NbCp^*Cl_4$ in the presence of acetylenes and dienes leads to the isolation of new niobium(III) derivatives $NbCp^*Cl_2(R'C{\equiv}CR'')$ (R′ = R″ = Me, **5**; R′ = R″ = $SiMe_3$, **6**; R′ = Me, R″ = Et, **7**; R′ = Ph, R″ = $SiMe_3$, **8**) and $NbCp^*Cl_2$(diene) (diene = isoprene, **9**; diene = methyl methacrylate, **10**. Complexes **5**–**8** can also be prepared by reactions with acetylenes of the niobium(III) phosphine complexes $NbCp^*Cl_2L_2$ (L = PMe_3, PMe_2Ph) and by addition of acetylenes to the dichloroniobium(III) dimer $[NbCp^*Cl_2]_2$. All the complexes were characterized by mass spectrometry and IR and NMR spectroscopy, and the molecular structures of **2** and **4** were confirmed by X-ray diffraction methods. Crystals of **2** are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions a = 8.274(4) Å, b = 33.313(10) Å, c = 8.656(3) Å, and β = 116.71(2)°. Crystals of the toluene solvate of **4** are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions a = 17.130(8) Å, b = 15.781(7) Å, c = 14.922(5) Å, and β = 108.43(2)°. Both structures were solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1509 (**2**) and 4164 ($\mathbf{4}\cdot{}^1/_2MeC_6H_5$) observed reflections to R and R_w values of 0.0365 and 0.0432 (**2**) and 0.0435 and 0.0602 ($\mathbf{4}\cdot{}^1/_2MeC_6H_5$), respectively.

Introduction

We have reported[1] recently the reduction of $NbCp^*Cl_4$ with sodium amalgam in the presence of carbon monoxide or phosphine ligands as a method to prepare mononuclear niobium(III) complexes. We were particularly interested in studying the isolation of similar low-valent niobium(III) complexes containing isocyanide ligands and also in exploring the reactivity of these and other niobium(III) complexes with different unsaturated organic ligands, such as acetylenes and dienes. The organo-transition-metal chemistry of isocyanide complexes has been a fertile field of research during the last few years,[2] the insertion of isocyanides into metal–alkyl bonds being a very well-known process,[3] although not many group 5 metallocene isocyanides[4] and even fewer monocyclopentadienyl derivatives have been reported.[5] Isocyanides can be easily inserted into metal–alkyl bonds of high-oxidation-state group 5 metal complexes, such as $TaCp^*Cl_nMe_{4-n}$,[6] leading to iminoacyl derivatives with a very versatile reactivity. On the other hand, early-transition-metal alkyne and diene chemistry has been extensively developed, basically due to the numerous important catalytic applications known for these compounds in relation to alkyne oligomerization and polymerization processes and their use in regioselective reactions with unsaturated organic substrates.[7] Most half-sandwich acetylene complexes of the heavier group 5 elements[8] have been prepared by two-electron reduction of d^0 metal derivatives, and some have been reported[9] by substitution of other labile ligands. Related diene complexes have been prepared[7u,10] by reaction of $MCpCl_4$ with (diene)magnesium.

We report here the reduction of $NbCp^*Cl_4$ with sodium amalgam in the presence of isocyanides, acetylenes, and dienes, the characterization of the resulting products by IR and NMR spectroscopy, and the molecular structures of $[NbCp^*Cl_4(CN\text{-}2,6\text{-}Me_2C_6H_3)]$ and $[NbCp^*Cl_2(CN\text{-}2,6\text{-}Me_2C_6H_3)_3]$ determined by X-ray diffraction methods.

Results and Discussion

$NbCp^*Cl_4$ easily coordinates isocyanides when they are added to its toluene solution, leading to the pseudoocta-

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[1] de la Mata, J.; Galakhov, M. V.; Gómez, M.; Royo, P. *Organometallics* **1993**, *12*, 1189.

[2] Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1984**, *22*, 209.

[3] (a) Crociani, B.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1973**, *127*. (b) Wilkins, J. D. *J. Organomet. Chem.* **1974**, *67*, 269.

[4] Serrano, R.; Royo, P. *J. Organomet. Chem.* **1983**, *247*, 33.

[5] Aspinall, H. C.; Roberts, M. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263.

[6] Galakhov, M. V.; Gómez, M.; Jimenez, G.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics*, submitted for publication.

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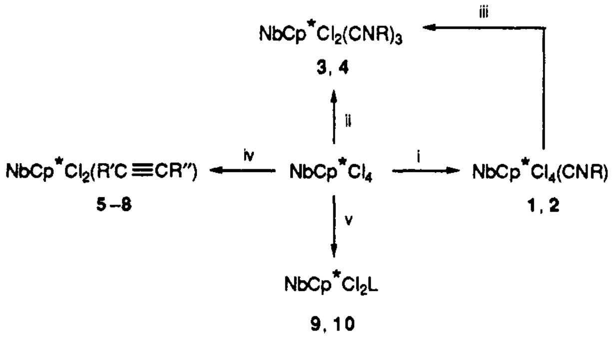
Scheme 1[a]



[a] Reagents and conditions: (i) 1 equiv of CNR, toluene, room temperature, 12 h; (ii) 3 equiv of CNR, 2 equiv of Na/Hg, toluene, room temperature, 12 h; (iii) 2 equiv of CNR, 2 equiv of Na/Hg, toluene, room temperature, 12 h; (iv) 1 equiv of R'C≡CR", 2 equiv of Na/Hg, toluene, room temperature, 12 h; (v) 1 equiv of isoprene or methyl methacrylate, 2 equiv of Na/Hg, toluene, room temperature, 12 h. Definitions for compounds: **1**, **3**, R = ^{t}Bu; **2**, **4**, R = 2,6-Me$_2$C$_6$H$_3$; **5**, R' = R" = Me; **6**, R' = R" = SiMe$_3$; **7**, R' = Me, R" = Et; **8**, R' = Ph, R" = SiMe$_3$; **9**, L = isoprene; **10**, L = methyl methacrylate.

hedral adducts NbCp*Cl$_4$(CNR) (R = ^{t}Bu; **1**; R = 2,6-Me$_2$C$_6$H$_3$, **2**) as shown in Scheme 1. The advantage of lower solubility of these adducts improves and facilitates the isolation of the niobium complex,[11] when the isocyanide is present in the reaction solution of NbCl$_5$ with Si(η^1-C$_5$Me$_5$)Me$_3$. Reduction of toluene solutions of NbCp*Cl$_4$, or of the previously isolated complexes **1** and **2**, with 2 equiv of 10% sodium amalgam, or KC$_8$[12] in the presence of appropriate amounts of the isocyanide leads to the diamagnetic, pseudooctahedral, 18-electron niobium(III) complexes NbCp*Cl$_2$(CNR)$_3$ (R = ^{t}Bu, **3**; R = 2,6-Me$_2$C$_6$H$_3$, **4**). Complexes **1**–**4** are isolated as air- and moisture-sensitive crystalline solids, soluble in chloroform and aromatic hydrocarbons but insoluble in aliphatic solvents.

Along with the absorptions expected for the permethylated ligand and ν(Nb—Cl) stretching vibrations, complexes **1** and **2** show one absorption at 2237 and 2217 cm^{-1}, respectively, whereas complexes **3** and **4** show two absorptions at 2101–2130 and 2021–2100 cm^{-1}, respectively, due to ν(C≡N) stretching frequencies. The ^{1}H NMR spectra of complexes **1** and **2** show the expected one singlet for the methyl protons of the alkyl isocyanide substituent, whereas two singlets with an intensity ratio 2:1 are observed for complexes **3** and **4**, thus revealing that two of the isocyanide groups are equivalent and different from a third one. This behavior is in agreement with the expected disposition locating one of the isocyanides trans to Cl and the other two occupying mutually trans equatorial positions, as proved by the X-ray molecular structure of **4** in the solid (see Figure 2). The 2,6-dimethyl protons of each equatorial phenyl isocyanide group are equivalent, even at low temperatures (−90 °C in toluene-d_6), indicating a free rotation around the Nb–C–N axis, and an analogous behavior can also be assumed for the *tert*-butyl derivative. The ^{13}C NMR spectrum for complex **4** is in agreement with this structure, rather broad signals being observed probably due to a high ^{93}Nb quadrupolar moment.[13]

The same reduction of NbCp*Cl$_4$ with 2 equiv of 10% sodium amalgam in the presence of 1 equiv of different acetylenes, R'C≡CR", leads to the isolation in high yields of the (acetylene)niobium(III) complexes NbCp*Cl$_2$(R'C≡CR") (R' = R" = Me, **5**; R' = R" = SiMe$_3$, **6**; R' = Me, R" = Et, **7**; R' = Ph, R" = SiMe$_3$, **8**). The time required for the reaction increases in the order[8c] Me < Et < Ph < SiMe$_3$. The same compounds can alternatively be prepared, although in lower yield, by substitution of phosphine ligands, when acetylenes are added to toluene solutions of (phosphine)niobium(III) derivatives,[1] and also by addition of acetylenes or isocyanides to the dichloroniobium(III) dimer [NbCp*Cl$_2$]$_2$.[8c] Facile substitution of phosphine ligands also takes place easily on addition of isocyanides and is therefore an alternative way to isolate complexes **3** and **4**.

The same reduction of NbCp*Cl$_4$ with 10% sodium amalgam in the presence of isoprene and methyl methacrylate allows the isolation of the niobium(III) complexes NbCp*Cl$_2$(isoprene) (**9**)[11a] and NbCp*Cl$_2$(methyl methacrylate) (**10**).

All the (acetylene)- and (diene)niobium(III) complexes are soluble in the usual organic solvents and stable under an inert atmosphere, but they are very air and moisture sensitive, reacting to give a mixture of the (μ-oxo)-hydroxoniobium dimer and the oxoniobium trimer previously reported.[11b] All complexes **5**–**10** must be formulated as monomeric species according to the parent peaks observed in their mass spectra. The IR and NMR behavior is in agreement with a pseudo-square-pyramidal geometry with the acetylenic carbons or the terminal atoms of the diene occupying two basal positions, as found for similar tantalum derivatives.[8b,d] Only one singlet is observed for methyl protons of equivalent R' and R" substituents in the ^{1}H NMR spectra for complexes **5** and **6**. The ^{1}H NMR spectrum of complex **7** shows the expected triplet for the methyl protons of the ethyl group, but only one quadruplet

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(7) (a) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, T. *J. Am. Chem. Soc.* **1983**, *105*, 7473. (b) Masuda, T.; Niki, A.; Isobe, E.; Higashimura, *Macromolecules* **1985**, *18*, 2109. (c) Katz, T. J.; Hacker, S. M.; Kendrick, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 2182. (d) Clarke, T. C.; Yannoni, C. S.; Katz, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 7787. (e) Cotton, F. A.; Hall, W. T.; Conn, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233. (f) Cotton, F. A.; Roth, W. J. *Inorg. Chim. Acta* **1984**, *85*, 17. (g) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094. (h) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604. (i) Grubbs, R. H. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1982; Vol. 8, pp 499–552. (j) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (k) Taqui Kahn, M. M.; Martel, A. E. *Homogeneous Catalysis by Metal Complexes*; Academic Press: New York, 1974; Vol. II. (l) Bleukers, J.; Hessen, B.; von Bolhuis, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459. (m) Chen, J.; Kai, Y.; Kasai, N.; Yamamoto, H.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1987**, 1547. (n) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (o) Yasuda, H.; Tatsuni, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (p) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (q) Datta, S.; Fischer, H. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353. (r) Yasuda, H.; Kajihara, Y.; Mashima, K.; Lee, K.; Nakamura, A. *Chem. Lett.* **1981**, 519. (s) Krüger, C.; Müller, G.; Erker, G.; Dorf, V.; Engel, K. *Organometallics* **1985**, *4*, 215. (t) Yasuda, H.; Kajihara, Y.; Nagasuna, K.; Mashima, K.; Nakamura, A. *Chem. Lett.* **1981**, 719; **1981**, 671. (u) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanahisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008. (v) Kwon, D.; Curtis, M. D. *Organometallics* **1990**, *9*, 1.

(8) (a) Passynskii, A. A. *J. Organomet. Chem.* **1979**, *165*, 39. (b) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387. (c) Belmonte, P. A.; Cloke, F. G. N.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 2365. (d) Curtis, M. D.; Real, J. *Organometallics* **1985**, *4*, 490. (e) Curtis, M. D.; Real, J.; Kwon, D. *Organometallics* **1989**, *8*, 1644.

(9) Hartrung, J. B., Jr.; Pedersen, S. F. *Organometallics* **1990**, *9*, 1414.

(10) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

(11) (a) Yasuda, H.; Okamoto, T.; Nakamura, A. *Organomet. Synth.* **1988**, *4*, 20–40. (b) de la Mata, J.; Fandos, R.; Gómez, M.; Gómez-Sal, P.; Martinez-Carrera, S.; Royo, P. *Organometallics* **1990**, *9*, 2846.

(12) Savoia, D.; Trombini, C.; Umani-Ronchi, A. *Pure Appl. Chem.* **1985**, *57*, 1887.

(13) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670; 1988, *4*, 20.

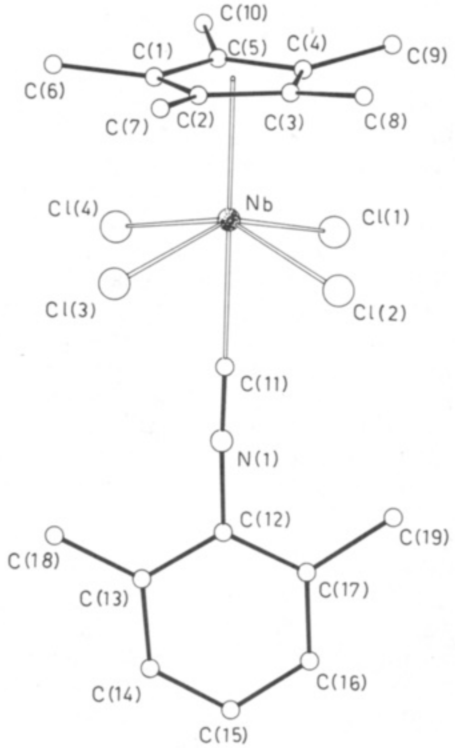

Figure 1. View of the molecular structure of Nb(η^5-C_5Me_5)Cl_4(CN-2,6-$Me_2C_6H_3$) (**2**) with the atom-numbering scheme.

for the ethyl methylene protons and one singlet for the protons of the methyl substituent are observed, with no coupling between them, indicating a change of hybridization of the acetylenic carbon atoms with loss of linearity of both R′ and R″ groups. This behavior is also in agreement with the observed absorption at 1600 cm^{-1}, due to the olefinic ν(C═C) stretching vibration. Chemical shifts observed for the acetylenic carbon atoms in the ^{13}C NMR spectra are in the region of δ 200, comparable to other reported complexes[14] containing four-electron-donor alkyne ligands and close to values described for analogous niobium and tantalum derivatives.[8b,15] The ^1H NMR spectrum for niobium diene complex **9** confirms a σ^2-π-1-metallacyclo-3-pentene[10] structure, and a similar 3-methoxy-1-tantala-2-oxacyclo-3-pentene[7v] structure is in agreement with the two high-field doublets observed for complex **10** at δ 1.47 (H_{syn}) and δ 0.61 (H_{anti}) due to the methylene protons, with a coupling constant $^2J_{H-H}$ = 6.35 Hz. The ^{13}C NMR spectra are also in agreement with the proposed structures.

Description of the Crystal Structures of Nb(η^5-C_5Me_5)Cl_4(CN-2,6-$Me_2C_6H_3$) (2) and Nb(η^5-C_5Me_5)Cl_2(CN-2,6-$Me_2C_6H_3$)$_3$·$^1/_2$$MeC_6H_5$ (4·$^1/_2$$MeC_6H_5$). A view of the complex Nb(η^5-C_5Me_5)Cl_4(CN-2,6-$Me_2C_6H_3$) (**2**) is shown in Figure 1 together with the atom-numbering scheme. Selected bond distances and angles are given in Table 1. The pentamethylcyclopentadienyl ring is bound to the Nb atom in a nearly symmetric η^5 fashion (with Nb–C distances ranging from 2.424(10) to 2.508(13) Å), with the distance between the metal and the centroid of the ring, (Nb–CE) being 2.169(11) Å. The isocyanide ligand is linearly bound to the Nb atom, the values of the Nb–C(11) bond distance and of the Nb–C(11)–N(1) and C(11)–N(1)–C(12) angles being 2.245(10) Å and 179.1(8) and 176.7(10)°, respectively, and the value of the N(1)–C(11) bond length (1.136(13) Å) is in agreement with a triple bond. The coordination around the Nb atom is completed by four Cl atoms with Nb–Cl bond distances ranging from 2.396(3) to 2.435(3) Å. The complex is of pseudooctahedral type if the centroid of the cyclopentadienyl ring is considered as occupying a coordination site, even if the Nb atom is displaced by 0.603(1) Å from the mean equatorial plane passing through the four Cl atoms, toward the cyclopentadienyl ring.

Table 1. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for Compound 2

Nb–Cl(1)	2.409(2)	Nb–C(11)	2.245(10)
Nb–Cl(2)	2.396(3)	Nb–CE[a]	2.169(11)
Nb–Cl(3)	2.412(3)	N(1)–C(11)	1.136(13)
Nb–Cl(4)	2.435(3)	N(1)–C(12)	1.392(13)
CE–Nb–Cl(1)	104.9(3)	Cl(1)–Nb–Cl(2)	88.2(1)
CE–Nb–Cl(2)	104.0(3)	Cl(1)–Nb–Cl(3)	150.9(1)
CE–Nb–Cl(3)	104.0(3)	Cl(1)–Nb–Cl(4)	84.3(1)
CE–Nb–Cl(4)	104.9(3)	Cl(2)–Nb–Cl(3)	88.1(1)
CE–Nb–C(11)	179.6(3)	Cl(2)–Nb–Cl(4)	151.0(1)
Cl(1)–Nb–C(11)	75.4(2)	Cl(3)–Nb–Cl(4)	85.1(1)
Cl(2)–Nb–C(11)	75.7(3)	Nb–C(11)–N(1)	179.1(8)
Cl(3)–Nb–C(11)	75.7(3)	C(11)–N(1)–C(12)	176.7(10)
Cl(4)–Nb–C(11)	75.4(3)		

[a] CE is the centroid of the C(1)···C(5) ring.

Crystals of Nb(η^5-C_5Me_5)Cl_2(CN-2,6-$Me_2C_6H_3$)$_3$ (**4**·$^1/_2$$MeC_6H_5$) contain also toluene molecules of solvation. A view of the complex **4** is shown in Figure 2 together with the atom-numbering scheme. Selected bond distances and angles are given in Table 2. The pentamethylcyclopentadienyl ring is bound to the Nb atom in a nearly symmetric η^5 fashion (with Nb–C distances ranging from 2.356(6) to 2.496(5) Å), with the distance between the metal and the centroid of the ring (Nb–CE) being 2.099(5) Å. Three isocyanide ligands are coordinated to the Nb atom: two are linearly bound, and one is rather bent. The bending for this isocyanide trans to Cl determines an increasing bond order of the M–C bond and a decreasing bond order of the C–N bond, which is the expected effect due to the presence of a weaker π-acceptor substituent located in the trans position. As expected, the Nb–C(20) and Nb–C(29) bond distances (2.195(5) and 2.188(5) Å) are longer than the Nb–C(11) distance 2.113(6) Å), the C(20)–N(2) and C(29)–N(3) bond distances (1.163(6) and 1.162(7) Å) are shorter than the C(11)–N(1) distance (1.186(8) Å), and the C(20)–N(2)–C(21) and C(29)–N(3)–C(30) angles are close to 180° (177.8(5) and 172.5(5)°), whereas the C(11)–N(1)–C(12) angle is much narrower (159.4(6)°). The coordination around the Nb atom is completed by two Cl atoms with Nb–Cl bond distances of 2.575(2) and 2.546(2) Å. Also, this complex can be considered pseudooctahedral if the centroid of the cyclopentadienyl ring is designated as occupying a coordination site, the Nb atom being displaced by 0.511(1) Å from the mean equatorial plane passing through the four Cl atoms, toward the cyclopentadienyl ring. The values of the Nb–Cl and Nb–C bond distances in **4** are comparable with those found in the cationic Nb(III) complex [Nb(η^5-C_5H_5)Cl(CN^{t}Bu)$_4$]$^+$, having an imposed C_s symmetry. In the latter complex, which is the only other structurally characterized niobium mononuclear cyclopentadienyl isocyanide complex,[16] the value for the Nb–Cl bond length is 2.505(4) Å and those

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[14] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

[15] (a) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311. (b) Bianconi, P. A.; Vrtis, R. N.; Rao, C. P.; Williams, I. D.; Engel, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968. (c) McGeary, M. J.; Gamble, A. S.; Templeton, J. L. *Organometallics* **1988**, *7*, 271.

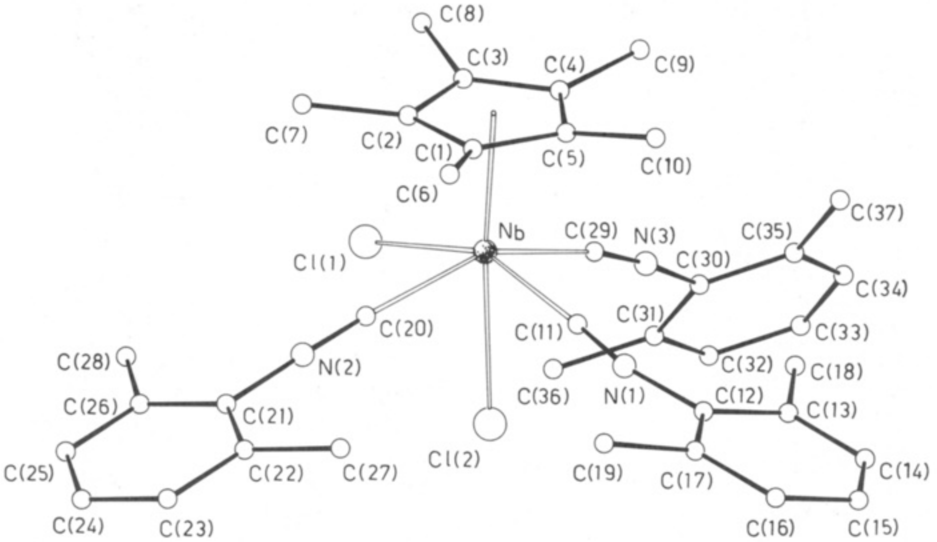

Figure 2. View of the molecular structure of $Nb(\eta^5\text{-}C_5Me_5)Cl_2(CN\text{-}2,6\text{-}Me_2C_6H_3)_3$ (4) with the atom-numbering scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for Compound $4\cdot{}^1/_2MeC_6H_5$

Nb–Cl(1)	2.575(2)	N(1)–C(11)	1.186(8)
Nb–Cl(2)	2.546(2)	N(1)–C(12)	1.404(9)
Nb–C(11)	2.113(6)	N(2)–C(20)	1.163(6)
Nb–C(20)	2.195(5)	N(2)–C(21)	1.411(7)
Nb–C(29)	2.188(5)	N(3)–C(29)	1.162(7)
Nb–CE[a]	2.099(5)	N(3)–C(30)	1.415(7)
CE–Nb–Cl(1)	106.0(2)	Cl(1)–Nb–Cl(2)	80.3(1)
CE–Nb–Cl(2)	173.6(2)	C(11)–Nb–C(29)	90.9(2)
CE–Nb–C(11)	99.7(2)	C(11)–Nb–C(20)	88.4(2)
CE–Nb–C(20)	104.1(2)	C(20)–Nb–C(29)	152.6(2)
CE–Nb–C(29)	103.0(2)	Nb–C(11)–N(1)	176.6(5)
Cl(1)–Nb–C(11)	154.2(2)	Nb–C(20)–N(2)	176.0(5)
Cl(2)–Nb–C(11)	74.1(2)	Nb–C(29)–N(3)	170.4(4)
Cl(1)–Nb–C(20)	83.2(2)	C(11)–N(1)–C(12)	159.4(6)
Cl(2)–Nb–C(20)	77.3(1)	C(20)–N(2)–C(21)	177.8(5)
Cl(1)–Nb–C(29)	85.7(1)	C(29)–N(3)–C(30)	172.5(5)
Cl(2)–Nb–C(29)	76.2(1)		

[a] CE is the centroid of the C(1)···C(5) ring.

for the Nb–C bonds are 2.210(10) and 2.203(9) Å, with all four isocyanide ligands linearly bound to the Nb atom.

Experimental Section

All reactions were conducted under an argon atmosphere by use of Schlenk techniques and solids handled in a Vacuum Atmospheres glovebox equipped with an HE-63-P Dri-Train. Solvents were dried over appropriate reagents and distilled under argon before use by employing the drying agents in parentheses: *n*-hexane (sodium–potassium alloy) and toluene (sodium). Reagent-grade chemicals purchased from commercial sources and used without further purification were as follows: carbon (Aldrich), mercury (Panreac), sodium (Panreac), potassium (Fluka), *tert*-butyl isocyanide (Fluka), acetylenes R′C≡CR″ (Aldrich), isoprene (Aldrich), and methyl methacrylate (Aldrich). $NbCp^*Cl_2(PR_3)_2$,[1] $NbCp^*Cl_4$,[11b] and $2,6\text{-}Me_2C_6H_3NC$[17] were prepared as described previously.

Infrared spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000–200 cm^{-1}) as Nujol mulls between CsI pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 Unity instrument, and chemical shifts are reported in δ units (positive chemical shifts to a higher frequency) relative to a TMS standard. Mass spectra were recorded on a HP 5988 Å instrument. C, H, and N analyses were performed with a Perkin-Elmer 240C microanalyzer.

Preparation of $NbCp^*Cl_4(CNR)$ (R = ^{t}Bu, 1; R = $2,6\text{-}Me_2C_6H_3$, 2). CNR (1.35 mmol) was added to a toluene (50 mL) suspension of $NbCp^*Cl_4$ (0.50 g, 1.35 mmol), and the mixture was vigorously stirred for 30 min at room temperature. The red solution was filtered and concentrated to ca. 25 mL, and *n*-hexane (10 mL) was carefully added. This mixture was then cooled to −20 °C to give **1** or **2** as orange-red crystals. The data for **1** are as follows: yield 0.46 g (75%); IR (Nujol mull; ν, cm^{-1}) 2237 (vs), 1013 (m), 322 (s); ^1H NMR (δ, ppm; in $CDCl_3$) 2.30 (s, 15H, C_5Me_5), 1.62 (s, 9H, ^{t}Bu); MS (EI, 70 eV; *m/e* (relative intensity)) 333 ($M^{\bullet+} - Cl(CNR)$, 20.7), 297 (6.5), 261 (12.1), 135 (100). Anal. Calcd for $C_{15}H_{24}Cl_4NNb$: C, 39.70; H, 5.31; N, 3.12. Found: C, 39.59; H, 5.40; N, 2.88. The data for **2** are as follows: yield 0.54 g (80%); IR (Nujol mull; ν, cm^{-1}) 2217 (vs), 1015 (m), 324 (s); ^1H NMR (δ, ppm; in C_6D_6) 6.60 (t, 1H, $2,6\text{-}Me_2C_6H_3$), 6.40 (d, 2H, $2,6\text{-}Me_2C_6H_3$), 2.31 (s, 6H, $2,6\text{-}Me_2C_6H_3$), 2.06 (s, 15H, C_5Me_5); MS (EI, 70 eV; *m/e* (relative intensity)) 369 ($M^{\bullet+}$ − CNR, 1.5), 333 (93.1), 297 (15.1), 261 (23.2), 135 (98.1). Anal. Calcd for $C_{19}H_{24}Cl_4NNb$: C, 45.52; H, 4.79; N, 2.79. Found: C, 45.70; H, 4.85; N, 2.66.

Preparation of $NbCp^*Cl_2(CNR)_3$ (R = ^{t}Bu, 3; R = $2,6\text{-}Me_2C_6H_3$, 4). A toluene solution (60 mL) of RNC (5.4 mmol) was added to a mixture of $NbCp^*Cl_4$ (0.69 g, 1.80 mol) and 10% sodium amalgam (0.086 g, 3.7 mmol of Na). The mixture was stirred for 12 h at room temperature. The resulting red suspension was filtered with Celite, the filtrate was concentrated to ca. 15 mL, n-hexane (10 mL) was slowly added, the mixture was cooled to −40 °C to give **3** or $4\cdot{}^1/_2MeC_6H_5$ as red crystals. The data for **3** are as follows: IR (Nujol mull; ν, cm^{-1}) 2130 (vs), 2100 (br), 1196 (m), 1025 (m), 723 (s), 440 (w), 310 (w); ^1H NMR (δ, ppm; in C_6D_6) 1.96 (s, 15H, C_5Me_5), 1.27 (s, 9H, ^{t}Bu), 1.08 (s, 18H, ^{t}Bu). Anal. Calcd for $C_{25}H_{42}Cl_2N_3Nb$: C, 54.75; H, 7.72; N, 7.66. Found: C, 54.62; H, 7.70; N, 7.54. The data for **4** are as follows: yield 0.77 g (60%); IR (Nujol mull; ν, cm^{-1}) 2101 (vs), 2021 (vs), 1586 (w), 1028 (m), 783 (m), 724 (s), 488 (m), 318 (w); ^1H NMR (δ, ppm; in C_6D_6) 6.76 (m, 2H, $2,6\text{-}Me_2C_6H_3$), 6.66 (m, 1H, $2,6\text{-}Me_2C_6H_3$), 2.53 (s, 12H, $2,6\text{-}Me_2C_6H_3$), 2.44 (s, 6H, $2,6\text{-}Me_2C_6H_3$), 2.0 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR (δ, ppm; in C_6D_6) 206 (s, br, −NC), 184 (s, −NC), 135.37 (s, C_{ipso}, $2,6\text{-}Me_2C_6H_3$), 134.49 (s, C_{ipso}, $2,6\text{-}Me_2C_6H_3$), 130.32 s, 129.2 s, 125.6 s (several signals for $2,6\text{-}Me_2C_6H_3$), 105.4 (s, C_5Me_5), 19.54 (s, $2,6\text{-}Me_2C_6H_3$), 19.51 (s, $2,6\text{-}Me_2C_6H_3$), 13.16 (s, C_5Me_5); MS (EI, 70 eV; *m/e* (relative intensity)) 561 ($M^{\bullet+}$, 1), 417 (26), 298 (8), 258 (15). Anal. Calcd for $C_{40.5}H_{46}Cl_2N_3Nb$: C, 65.86; H, 6.28; N, 5.69. Found: C, 66.03; H, 6.39; N, 5.56.

Preparation of $NbCp^*Cl_2(R'C{\equiv}CR'')$ (R′ = R″ = Me, 5; R′ = R″ = $SiMe_3$, 6; R′ = Me, R″ = Et, 7; R′ = Ph, R″ = $SiMe_3$, 8). A solution of 1.90 mmol of acetylene R′C≡CR″ in 70 mL of

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[16] Aspinall, H. C.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1984**, *23*, 1782.

[17] Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

Table 3. Experimental Data for the X-ray Diffraction Studies

	2	**$4\cdot{}^1/_2MeC_6H_5$**
mol formula	$C_{19}H_{24}Cl_4NNb$	$C_{37}H_{42}Cl_2N_3Nb\cdot{}^1/_2MeC_6H_5$
mol wt	501.12	738.64
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
radiatn	Nb-filtered Mo Kα ($\bar{\lambda}$ = 0.710 73 Å)	Ni-filtered Cu Kα ($\bar{\lambda}$ = 1.541 84 Å)
a, Å	8.274(4)	17.130(8)
b, Å	33.313(10)	15.781(7)
c, Å	8.656(3)	14.922(5)
β, deg	116.71(2)	108.43(2)
V, Å^3	2131(1)	3827(3)
Z	4	4
D_{calcd}, g cm^{-3}	1.562	1.282
F(000)	1016	1540
cryst dimens, mm	0.22 × 0.27 × 0.35	0.18 × 0.23 × 0.30
μ(Mo Kα), cm^{-1}	10.50	41.55
diffractometer	Siemens AED	Siemens AED
2θ range, deg	6–48	6–130
no. of rflns measd	$h,k,\pm l$	$\pm h,k,l$
no. of unique total data	3369	6549
no. of unique obsd data	1509 [$I > 2\sigma(I)$]	4164 [$I > 2\sigma(I)$]
R	0.0365	0.0435
R_w	0.0432	0.0602

Table 4. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of 2

	x/a	y/b	z/c	U[a]
Nb	3141(1)	3562(1)	2513(1)	321(3)
Cl(1)	387(3)	3522(1)	−151(3)	611(11)
Cl(2)	2066(4)	4182(1)	3105(3)	602(14)
Cl(3)	6181(3)	3808(1)	4176(3)	576(12)
Cl(4)	4427(4)	3173(1)	953(3)	591(14)
N(1)	3739(10)	4233(2)	−117(9)	417(36)
C(1)	4162(12)	2986(3)	4428(13)	512(49)
C(2)	3983(14)	3284(3)	5459(11)	477(48)
C(3)	2150(14)	3384(3)	4772(12)	484(48)
C(4)	1186(12)	3135(3)	3338(11)	415(43)
C(5)	2440(14)	2881(2)	3133(11)	447(50)
C(6)	5916(15)	2764(4)	4813(17)	1078(83)
C(7)	5374(16)	3457(4)	7083(12)	1056(72)
C(8)	1288(17)	3652(4)	5592(15)	932(81)
C(9)	−848(12)	3102(4)	2422(13)	865(63)
C(10)	1930(18)	2547(3)	1894(15)	981(83)
C(11)	3522(11)	4007(3)	758(11)	404(42)
C(12)	3910(12)	4519(3)	−1204(11)	390(42)
C(13)	5577(13)	4556(3)	−1238(11)	428(45)
C(14)	5617(15)	4846(3)	−2347(12)	600(57)
C(15)	4194(18)	5088(3)	−3298(12)	644(62)
C(16)	2574(15)	5042(3)	−3205(12)	577(51)
C(17)	2422(11)	4761(3)	−2158(11)	408(44)
C(18)	7158(14)	4305(3)	−173(14)	711(59)
C(19)	643(13)	4708(4)	−2043(13)	733(58)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of $4\cdot{}^1/_2MeC_6H_5$

	x/a	y/b	z/c	U
Nb	2359(1)	583(1)	1526(1)	411(1)[a]
Cl(1)	1406(1)	−518(1)	1917(1)	679(6)[a]
Cl(2)	3299(1)	−707(1)	1822(1)	631(5)[a]
N(1)	4132(3)	1255(3)	1364(4)	672(20)[a]
N(2)	3255(3)	567(3)	3878(3)	596(17)[a]
N(3)	1925(3)	−465(3)	−516(3)	524(16)[a]
C(1)	2252(4)	2037(3)	1848(4)	583(21)[a]
C(2)	1556(4)	1608(3)	1977(4)	582(21)[a]
C(3)	1043(3)	1344(3)	1071(4)	575(21)[a]
C(4)	1414(3)	1581(3)	392(4)	557(20)[a]
C(5)	2147(3)	2008(3)	859(4)	554(21)[a]
C(6)	2860(4)	2576(4)	2545(5)	861(30)[a]
C(7)	1311(5)	1564(5)	2864(5)	925(35)[a]
C(8)	186(4)	992(5)	887(6)	881(32)[a]
C(9)	1006(4)	1500(4)	−662(4)	800(28)[a]
C(10)	2635(4)	2530(4)	372(5)	864(32)[a]
C(11)	3485(3)	1011(3)	1391(4)	520(19)[a]
C(12)	4787(3)	1414(4)	1011(5)	645(24)[a]
C(13)	4706(4)	1156(4)	82(5)	736(27)[a]
C(14)	5364(5)	1311(5)	−239(6)	952(39)[a]
C(15)	6058(5)	1713(6)	323(8)	1113(47)[a]
C(16)	6120(4)	1955(5)	1219(7)	990(37)[a]
C(17)	5470(4)	1828(4)	1589(5)	777(28)[a]
C(18)	3928(5)	724(5)	−541(6)	997(36)[a]
C(19)	5516(4)	2132(5)	2574(5)	967(35)[a]
C(20)	2937(3)	605(3)	3065(4)	516(18)[a]
C(21)	3651(4)	490(3)	4859(4)	586(20)[a]
C(22)	4421(4)	895(4)	5229(4)	663(23)[a]
C(23)	4802(5)	804(5)	6203(5)	878(31)[a]
C(24)	4440(6)	369(6)	6747(5)	1007(38)[a]
C(25)	3681(5)	2(5)	6368(5)	922(36)[a]
C(26)	3276(4)	44(5)	5396(4)	730(26)[a]
C(27)	4807(5)	1363(5)	4606(5)	933(34)[a]
C(28)	2468(6)	−401(7)	4954(7)	1263(48)[a]
C(29)	2042(3)	−36(3)	146(4)	473(17)[a]
C(30)	1782(3)	−1077(3)	−1244(4)	507(19)[a]
C(31)	1715(3)	−1911(3)	−992(4)	563(20)[a]
C(32)	1567(4)	−2511(4)	−1731(4)	706(26)[a]
C(33)	1497(5)	−2275(4)	−2632(5)	826(31)[a]
C(34)	1573(4)	−1436(4)	−2854(4)	783(29)[a]
C(35)	1720(4)	−809(4)	−2167(4)	640(23)[a]
C(36)	1794(4)	−2176(4)	2(4)	680(25)[a]
C(37)	1824(5)	105(4)	−2384(5)	918(35)[a]
C(1S)	91(19)	390(13)	5060(19)	1684(101)
C(2S)	−257(14)	−269(13)	5474(15)	1021(56)
C(3S)	−382(12)	−1040(12)	5156(14)	1192(65)
C(4S)	−212(24)	−1265(16)	4217(23)	1546(135)
C(5S)	182(17)	−625(17)	3877(16)	1602(89)
C(6S)	251(20)	134(18)	4202(19)	1582(128)
C(7S)	161(30)	1261(20)	5430(29)	1973(174)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

toluene was added to a mixture of $NbCp^*Cl_4$ (0.70 g, 1.90 mmol) and 10% sodium amalgam (0.087 g, 3.80 mmol of Na) and stirred at room temperature overnight to give a reddish suspension. This was filtered with Celite, the solvent was removed completely, and the residue was extracted with *n*-hexane (3 × 15 mL). The solution was concentrated to ca. 20 mL and cooled to −40 °C to give **5**–**8** as red-orange microcrystalline solids. The data for **5** are as follows: yield 0.47 g (70%); IR (Nujol mull; ν, cm^{-1}) 1510 (m), 1023 (m), 802 (w), 726 (w), 410 (m), 347 (s); ^1H NMR (δ, ppm; in C_6D_6) 2.47 (s, 6H, $MeC\equiv CMe$), 1.62 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ (δ, ppm; in C_6D_6) 214.0 (s, $MeC\equiv CMe$), 120.68 (s, C_5Me_5), 18.59 (s, $MeC\equiv CMe$), 11.58 (s, C_5Me_5); MS (EI, 70 eV; m/e (relative intensity)) 354 ($M^{\bullet+}$, 5.10), 298 (100), 262 (41). Anal. Calcd for $C_{14}H_{21}Cl_2Nb$: C, 47.62; H, 5.99. Found: C, 47.54; H, 5.8. The data for **6** are as follows: yield 0.53 g (60%); IR (Nujol mull; ν, cm^{-1}) 1567 (m), 1245 (s), 1025 (m), 885 (m), 833 (s), 481 (m), 378 (m); ^1H NMR (δ, ppm; in C_6D_6) 1.48 (s, 15H, C_5Me_5), 0.50 (s, 18H, $Me_3SiC\equiv CSiMe_3$); $^{13}C\{^1H\}$ (δ, ppm; in C_6D_6) 198.36 (s, $Me_3SiC\equiv CSiMe_3$), 110.03 (s, C_5Me_5), 12.52 (s, C_5Me_5), 2.64 (s, $Me_3SiC\equiv CSiMe_3$); MS (EI, 70 eV; m/e (relative intensity)) 468 ($M^{\bullet+}$, 1), 433 (40), 298 (29), 261 (100). Anal. Calcd for $C_{18}H_{33}Cl_2NbSi_2$: C, 46.05; H, 7.08. Found: C, 45.63; H, 6.74. The data for **7** are as follows: yield 0.49 g (70%); IR (Nujol mull; ν, cm^{-1}) 1520 (s), 1022 (m), 425 (m), 358 (m); ^1H NMR (δ, ppm; in C_6D_6) 2.87 (q, 2H, $CH_3\mathit{CH}_2C\equiv CMe$), 2.57 (s, 3H, $CH_3CH_2C\equiv C\mathit{Me}$), 1.64 (s, 15H, C_5Me_5), 1.11 (t, 3H, $\mathit{CH}_3CH_2C\equiv CMe$); $^{13}C\{^1H\}$ NMR (δ, ppm; in C_6D_6) 217 (s, $CH_3CH_2\mathit{C}\equiv CMe$), 214 (s, $CH_3CH_2C\equiv\mathit{C}Me$), 120.4 (s, C_5Me_5), 28.76 (s, $CH_3CH_2C\equiv C\mathit{Me}$), 19.38 (s, $CH_3\mathit{CH}_2C\equiv CMe$), 13.76 (s, $\mathit{CH}_3CH_2C\equiv CMe$), 11.60 (s, C_5Me_5); MS (EI, 70 eV; m/e (relative intensity)) 366 ($M^{\bullet+}$, 5), 298 (100), 262 (57). Anal. Calcd for $C_{15}H_{23}Cl_2Nb$: C, 49.07; H, 6.31. Found: C, 49.02; H, 6.25. The data for **8** are as follows: yield 0.54 g (60%); IR (Nujol mull; ν, cm^{-1}) 1642 (m), 1600 (w), 1246 (m), 1023 (m), 841 (s), 690 (m), 343 (w); ^1H NMR (δ, ppm; in

C$_6$D$_6$) 7.87 (d, 2H, *Ph*C≡CSiMe$_3$), 7.22 (t, 2H, *Ph*C≡CSiMe$_3$), 7.06 (t, 1H, *Ph*C≡CSiMe$_3$), 1.65 (s, 15H, C$_5$Me$_5$), 0.36 (s, 9H, PhC≡C*SiMe*$_3$); ^{13}C{^{1}H} NMR (δ, ppm; in C$_6$D$_6$) 213.53 (s, PhC≡*C*SiMe$_3$), 180.39 (s, Ph*C*≡CSiMe$_3$), 131.44 (s, C$_{ipso}$, *Ph*C≡CSiMe$_3$), 129.9 s, 129.35 s, 128.62 s (several signals, *Ph*C≡CSiMe$_3$), 122 (s, C$_5$Me$_5$), 12.31 (s, C$_5$Me$_5$), 1.16 (s, PhC≡C*SiMe*$_3$); MS (EI, 70 eV; *m*/*e* (relative intensity)) 472 (M$^{\bullet+}$, 4.2), 437 (4.6), 298 (100), 262 (33.2). Anal. Calcd for C$_{21}$H$_{29}$Cl$_2$NbSi: C, 53.28; H, 6.17. Found: C, 53.16; H, 6.08.

Preparation of NbCp*Cl$_2$(isoprene) (9) and NbCp*Cl$_2$(methyl methacrylate) (10). A toluene (60 mL) solution of isoprene or methyl methacrylate (2.10 mmol) was added to a mixture of NbCp*Cl$_4$ (0.78 g, 2.10 mmol) and 10% sodium amalgam (0.097 g, 4.20 mmol of Na). The resulting mixture was stirred overnight at room temperature, filtered with Celite, concentrated to ca. 25 mL, and cooled to −40 °C to give **9** or **10** as green microcrystals. The data for **9** are coincidental with those previously reported by Yasuda et al.[11] The data for **10** are as follows: yield 0.63 g (75%); IR (Nujol mull; ν, cm^{-1}) 1731 (m), 1525 (s), 1260 (s), 1186 (m), 1016 (m), 803 (m), 719 (s), 443 (w), 394 (w), 328 (w), 278 (w); ^{1}H NMR (δ, ppm; in C$_6$D$_6$) 3.38 (s, 3H, CH$_2$C(Me)=COO*Me*), 2.4 (s, 3H, CH$_2$C(*Me*)= COOMe), 1.84 (s, 15H, C$_5$Me$_5$), 1.47 (d, 1H, C*H*$_2$C(Me)=COOMe, $^2J_{H-H}$ = 6.35 Hz), 0.61 (d, 1H, C*H*$_2$C(Me)=COOMe, $^2J_{H-H}$ = 6.35 Hz); ^{13}C{^{1}H} NMR (δ, ppm; i n C$_6$D$_6$) 160.4 (s, CH$_2$C(Me) = *C*OOMe), 127.06 (s, C$_5$Me$_5$), 86.88 (s, CH$_2$*C*(Me)=COOMe), 73.58 (s, br, *C*H$_2$C(Me)=COOMe), 53.71 (s, CH$_2$C(Me)=COO*Me*), 15.68 (s, CH$_2$C(*Me*)=COOMe), 11.49 (s, C$_5$Me$_5$); MS (EI, 70 eV; *m*/*e* (relative intensity)) 398 (M$^{\bullet+}$, 2.76), 363 (19.8), 272 (4.46), 101 (100). Anal. Calcd for C$_{15}$H$_{23}$Cl$_2$NbO$_2$: C, 45.14; H, 5.81. Found: C, 45.26; H, 6.11.

Substitution Reactions of Phosphine Complexes. To a toluene solution (50 mL) of NbCp*Cl$_2$(PR$_3$)$_2$ (2.00 mmol) was added ligand L (L = RNC, R′C≡CR″, isoprene, methyl methacrylate) in a stoichiometric amount. The mixture was stirred for 24 h at room temperature. The solution was filtered, concentrated to ca. 20 mL, and cooled to −40 °C to give NbCp*Cl$_2$L$_x$ complexes **3**–**10** (x = 3, L = RNC; x = 1, L = R′C≡CR″, isoprene, methyl methacrylate).

X-ray Data Collection, Structure Determination, and Refinement for Compounds 2 and 4·$^1/_2$MeC$_6$H$_5$. Crystals suitable for the X-ray analyses were obtained by recrystallization from toluene solutions. The crystallographic data for both compounds are summarized in Table 3. Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the niobium-filtered Mo Kα (**2**) and the nickel-filtered Cu Kα (4·$^1/_2$MeC$_6$H$_5$) radiation and the $\theta/2\theta$ scan type. The reflections for both **2** and **4**·$^1/_2$MeC$_6$H$_5$ were collected with a variable scan speed of 3–12° min^{-1} and a scan width (deg) of 1.20 + 0.346 tan θ for **2** and of 1.20 + 0.142 tan θ for **4**·$^1/_2$MeC$_6$H$_5$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following the method of Lehmann and Larsen.[18] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied only to **4**·$^1/_2$MeC$_6$H$_5$ (maximum and minimum values for the transmission factors were 1.132 and 0.870).[19] Only the observed reflections were used in the structure solutions and refinements.

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic and thermal parameters and then with anisotropic thermal parameters for the non-hydrogen atoms, except for the carbons of the solvent for **4**·$^1/_2$MeC$_6$H$_5$ (the toluene has been found to be disordered and distributed to two positions, of equal occupancy factor, close to a center of symmetry). All hydrogen atoms, except those of the toluene in **4**·$^1/_2$MeC$_6$H$_5$, were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms, with isotropic thermal parameters. The final cycles of refinement were carried out on the basis of 236 (**2**) and 436 (**4**·$^1/_2$MeC$_6$H$_5$) variables; after the last cycles, no parameters shifted by more than 0.16 (**2**) and 0.25 (**4**·$^1/_2$MeC$_6$H$_5$) esd. The highest remaining peak in the final difference map was equivalent to about 0.36 (**2**) and 0.60 e/Å^3 (**4**·$^1/_2$MeC$_6$H$_5$). In the final cycles of refinement the weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 0.667 and 0.0026 (**2**) and 0.652 and 0.0083 (**4**·$^1/_2$MeC$_6$H$_5$), respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 20. All calculations were carried out on the Gould Powernode 6040 and Encore 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" of the CNR, Parma, Italy, using the SHELX-76 and SHELX-86 systems of crystallographic computer programs.[21] The final atomic coordinates for the non-hydrogen atoms are given in Table 4 (**2**) and Table 5 (**4**·$^1/_2$MeC$_6$H$_5$). The atomic coordinates of the hydrogen atoms are given in Tables SI (**2**) and SII (**4**·$^1/_2$MeC$_6$H$_5$) and the thermal parameters in Tables SIII (**2**) and SIV (**4**·$^1/_2$MeC$_6$H$_5$).

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Supplementary Material Available: Tables of hydrogen atom coordinates (Tables SI and SII), thermal parameters (Tables SIII and SIV), and complete bond distances and angles (Tables SV and SVI) for **2** and **4**·$^1/_2$MeC$_6$H$_5$ (8 pages). Ordering information is given on any current masthead page.

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(18) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.

(19) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158. Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

(20) *International Tables for X-Ray Crystallograhy*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(21) Sheldrick, G. M. SHELX-76 Program for Crystal Structure Determination; University of Cambridge, Cambridge, U.K., 1976. SHELX-86 Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1986.