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Isolation and X-ray Molecular Structure of the First Oxo- and Phosphanido-Bridged Diniobium(III) Complex with a Short Double Nb═Nb Bond. Oxidation of the Dichloro(pentamethylcyclopentadienyl)niobium(III) Dimer

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The reaction of $[NbCp^*Cl_2]_2$, $Cp^* = \eta^5\text{-}C_5Me_5$, with 4 equiv of $LiP(C_6H_5)_2$ in the presence of water gives $[(NbCp^*)_2(\mu\text{-}PPh_2)_2(\mu\text{-}O)]$ (**1**). The niobium(III) dimer is transformed in the air and reacts with oxygen to give the already reported oxo complexes $[NbCp^*Cl_2(OH)]_2(\mu\text{-}O)$ and $(NbCp^*)_3Cl_4O_4$, respectively. An analogous reaction with azobenzene does not allow one to isolate either any hydrazido(2–) or amido derivatives, but in the presence of water the same oxo trimer is formed with elimination of 1,2-diphenylhydrazine. A similar reaction with azobiphenylene gives $NbCp^*Cl_2$(azobiphenylene) (**2**), which was characterized by mass spectrometry and IR and ^1H and ^{13}C NMR spectroscopy. The molecular structure of complex **1** was determined by X-ray diffraction methods. Complex **1** crystallizes in the monoclinic space group $C2/c$, with unit cell dimensions of $a = 19.327(8)$ Å, $b = 11.198(2)$ Å, $c = 22.248(9)$ Å, $\beta = 122.98(2)°$, and $V = 4039(4)$ Å^3, with $Z = 4$ and $\rho_{calcd} = 1.412$ g cm^{-3}. The compound shows a very short double bond Nb═Nb distance of 2.625(5) Å.

Introduction

In the last few years, a large number of new niobium and tantalum complexes containing metal–metal multiple bonds have been prepared, and in particular, complexes with doubly bonded niobium(III) and tantalum(III) represent a remarkable type of compounds.[1] Their reactions in aqueous solutions leading to oxo compounds[2] and with nitrogen containing unsaturated organic molecules such as azo compounds, isocyanides and nitriles, leading respectively to double bond metathesis or C–C reductive coupling with simultaneous oxidation of the metal atoms, have been intensively investigated.[3] However, very few similar doubly metal–metal-bonded cyclopentadienyl derivatives have been reported,[4] and studies of their reactivity are scarce. We have recently published[5] the use of $[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$, first reported by Schrock,[6] as an alternative method to prepare different types of phosphino- and carbonylniobium(III) complexes. Here, we describe the isolation of a new phosphanidoniobium(III) complex containing a double niobium–niobium bond and the reactions of a dichloroniobium(III) dimer with oxygen, azobenzene, and azobiphenylene.

Results and Discussion

Substitution Reactions. Attempts to replace chloride by alkyl groups by reacting $[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$ with alkylating agents such as MgClMe, $LiCH_2SiMe_3$, or $Mg(CH_2Ph)_2\cdot 2THF$ only led to untractable decomposition products, due to the very low stability of the electron-deficient alkyl bridges formed by these substituents unable to preserve the double metal–metal bond. However, when a phosphanido ligand, able to form stable bridges, is used in reactions of the niobium(III) dimer with 4 equiv of $LiPPh_2$, the metal–metal bond remains unaltered. The expected complex, with a 4-fold bridging phosphanido ligand, could not be isolated as its solutions are extremely sensitive to air, moisture, and chlorinated solvents probably due to the steric requirements of four phosphorus bridging atoms. Nevertheless, it is very easily hydrolyzed by the presence of traces of water or addition of the stoichiometric amount of water to produce the substitution of two phosphanido groups, which are eliminated as $PHPh_2$ and replaced by one oxygen bridge, leading to the formation of complex **1** (see Scheme I). The presence of free $PHPh_2$ in the residual solutions can be checked by ^1H and ^{31}P NMR spectroscopy.

The IR spectrum of complex **1** shows one absorption band at 508 cm^{-1} corresponding to $\nu(Nb\text{–}P_{bridge})$[7] and a strong absorption at 737 cm^{-1}, due to the $\nu(Nb\text{–}O\text{–}Nb)$ stretching frequency, probably overlaped with that due to phenyl δ(C–H) absorption. The $^{31}P\{^1H\}$ NMR spectrum shows one broad singlet at δ 168.78

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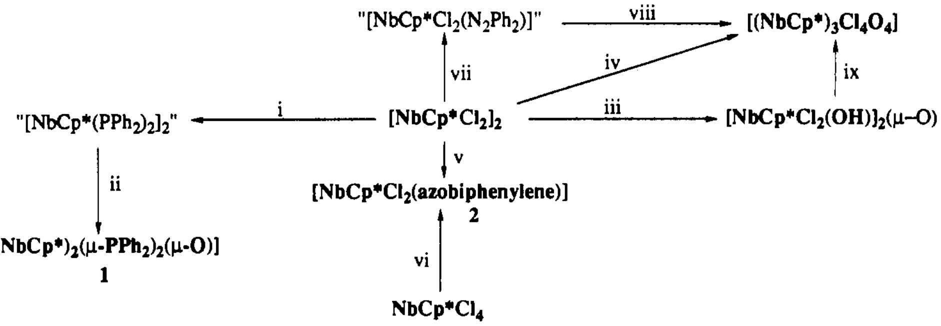
Scheme I



Reagents and conditions:

i) 4 equiv $LiPPh_2$, n-hexane/THF, -78°C, 30 min,. r.t.
ii) H_2O
iii) Air
iv) dry O_2
v) 2 equiv azobiphenylene, toluene, r.t., 6 h
vi) 2 equiv Na/Hg, 2 equiv azobiphenylene, toluene, r.t., 12 h
vii) 2 equiv. azobenzene, benzene-d_6, NMR tube sealed
viii) H_2O
ix) 170°C, in vacuum, 6 h

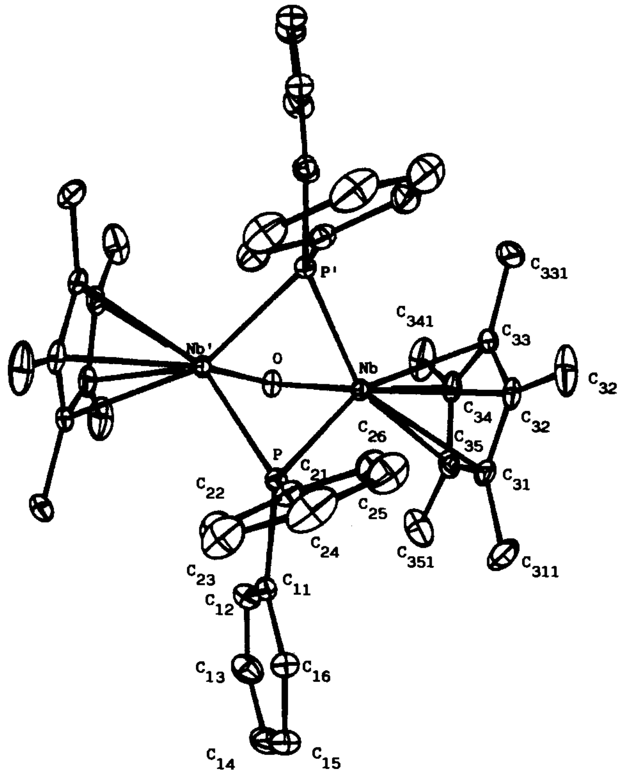


Figure 1. ORTEP view of molecular structure of complex 1.

that confirms the equivalency of both bridging phosphorus atoms.[8] Two pairs of equivalent phenyl groups, each one involving one phenyl group from each phosphanido ligand, are present, as shown by the two doublets observed in the $^{13}C\{^1H\}$ NMR spectrum at δ 140.20 and 147.90 ($^1J_{C-P}$ = 20 Hz) due to the C_{ipso} atoms of the phenyl groups (see Experimental Section).

X-ray Crystal Structure of 1. The crystal structure of 1 is shown in Figure 1 together with the atomic labeling scheme. Final atomic coordinates and equivalent isotropic thermal parameters for non hydrogen atoms are displayed in Table I. Selected bond distances and bond angles are given in Table II. The molecular structure of this compound consists of symmetrically equivalent halves, related by one symmetry axis passing through the oxygen atom bridging the two niobium atoms. Each half of the structure is essentially formed by one niobium atom exhibiting a three-legged piano stool configuration, where the legs are formed by the oxygen and the phosphorus atoms of two bridging diphenylphosphanido groups. The coordination around each niobium atom could be considered as pseudotetrahedral if the centroid of each C_5Me_5 ring is considered as a unique coordination site or alternatively pseudooctahedral if the ring is assumed to occupy three coordination positions. In this case, the structure could be described as a confacial bioctahedral diniobium complex, similar to those reviewed by Messerle[9] and Cotton.[1w] The most relevant aspect of this structure is the very strong metal–metal interaction defined by the short Nb–Nb distance of 2.625(5) Å. This distance which is clearly much shorter than those found in complexes containing a single Nb–Nb bond,[10] is

Table I. Positional Parameters and their Estimated Standard Deviations for the Non-Hydrogen Atoms of 1

atom	x	y	z	B,[a] Å^2
Nb1	0.51472(1)	0.00863(2)	0.69906(1)	2.363(4)
P1	0.39745(4)	0.12130(7)	0.68743(3)	2.73(1)
O1	0.500	–0.1200(3)	0.750	3.21(6)
C11	0.2915(2)	0.0660(3)	0.6292(1)	3.16(6)
C12	0.2798(2)	–0.0561(3)	0.6153(2)	4.33(9)
C13	0.2023(2)	–0.1063(4)	0.5786(2)	5.7(1)
C14	0.1342(2)	–0.0361(4)	0.5545(2)	6.0(1)
C15	0.1436(2)	0.0849(4)	0.5660(2)	5.5(1)
C16	0.2216(2)	0.1359(4)	0.6030(2)	4.28(8)
C21	0.3844(2)	0.2833(3)	0.6800(1)	3.39(6)
C22	0.3567(2)	0.3418(3)	0.6156(2)	4.83(8)
C23	0.3513(2)	0.4653(4)	0.6123(2)	6.7(1)
C24	0.3716(2)	0.5305(4)	0.6719(2)	7.3(1)
C25	0.3983(2)	–0.4741(4)	0.7354(2)	6.4(1)
C26	0.4052(2)	0.3502(3)	0.7399(2)	4.54(8)
C31	0.6040(2)	0.0237(4)	0.6528(1)	4.04(7)
C32	0.5267(2)	0.0701(3)	0.5989(1)	3.98(6)
C33	0.4685(2)	–0.0242(4)	0.5750(1)	4.12(7)
C34	0.5106(2)	–0.1284(3)	0.6133(1)	4.15(7)
C35	0.5934(2)	–0.088(3)	0.6612(1)	4.09(7)
C311	0.6850(2)	0.0895(5)	0.6893(2)	7.7(1)
C321	0.5108(3)	0.1935(4)	0.5680(2)	8.0(1)
C331	0.3795(2)	–0.0157(6)	0.5133(2)	8.0(1)
C341	0.4740(3)	–0.2501(4)	0.6057(2)	7.9(1)
C351	0.6609(3)	–0.1832(5)	0.7113(2)	8.2(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\,[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)\,B(1,2) + ac(\cos\beta)\,B(1,3) + bc(\cos\alpha)\,B(2,3)]$.

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Table II. Selected Bond Distances (Å) and Bond Angles (deg) for **1**

Bond Distances			
Nb–Nb	2.625(5)	Nb–P	2.4814(8)
Nb–Cp*	2.118	Nb–O	1.947(2)
Nb–C(31)	2.449(4)	C(22)–C(23)	1.386(6)
Nb–C(32)	2.461(3)	C(23)–C(24)	1.371(7)
Nb–C(33)	2.423(3)	C(24)–C(25)	1.366(7)
Nb–C(34)	2.416(3)	C(25)–C(26)	1.391(5)
Nb–C(35)	2.421(4)	C(31)–C(32)	1.410(3)
P–C(11)	1.834(2)	C(31)–C(35)	1.414(5)
P–C(21)	1.826(3)	C(31)–C(311)	1.507(5)
C(11)–C(12)	1.393(5)	C(32)–C(33)	1.419(5)
C(11)–C(16)	1.386(4)	C(32)–C(321)	1.499(6)
C(12)–C(13)	1.377(5)	C(33)–C(34)	1.412(5)
C(13)–C(14)	1.368(6)	C(33)–C(331)	1.510(4)
C(14)–C(15)	1.372(7)	C(34)–C(35)	1.396(4)
C(15)–C(16)	1.387(5)	C(34)–C(341)	1.502(6)
C(21)–C(22)	1.391(5)	C(35)–C(351)	1.502(5)
C(21)–C(26)	1.384(5)		
Bond Angles			
Nb–O–Nb′	84.6(2)	Nb–P–Nb′	63.7(1)
P–Nb–O	91.3(1)	P–Nb–P′	85.9(2)
Nb–Nb′–P	58.1(1)	Nb–Nb′–Cp′*	167.7
P–Nb–Cp*	129.5	O–Nb–Cp*	120.0
Nb–Nb′–O	47.7(2)	Nb–P–C(11)	120.4(1)
Nb–P–C(21)	126.0(1)	C(11)–P–C(21)	103.0(1)
P–C(11)–C(12)	118.2(2)	P–C(21)–C(22)	121.2(3)

[a] Cp* is the centroid of the C_5Me_5 ring. [b] Symmetry related positions are denoted by a prime.

actually in the range of distances assigned to triply bonded Nb≡Nb systems;[11] so, the distance determined is clearly the shortest distance observed for a double Nb=Nb bond, assigned on the basis of electron-counting criteria. This very strong metal–metal interaction forces the rest of the geometry of the compound. As a matter of fact, the Nb–P–Nb′ [63.7(1)°] and Nb–O–Nb′ [84.6(2)°] angles are acute, whereas the P–Nb–P′ [85.9(2)°] and P–Nb–O [91.3(1)°] angles are close to 90° and are therefore more open than most of the reported[9] values for confacial bioctahedral structures. The two niobium and two phosphorus atoms altogether display a butterfly disposition with a NbPNb′–NbP′Nb′ dihedral angle of 106.58(8)° bisected by the Nb–O–Nb′ plane. The two phenyl rings on each phosphorus are mutually almost perpendicular. The Cp*(centroid)–Nb–P and Cp*(centroid)–Nb–O angles of 129.5(3) and 120.0(2)°, respectively, show a great deviation from a tetrahedral environment. Bond lengths and angles in the Cp* and phenyl rings are normal with C–Nb distances in the usual range. The observed Nb–O distance [1.947(2) Å] is similar to that found in $[Nb_3(\eta^5\text{-}C_5Me_5)_3Cl_4O_4]$.[12] X-ray structures for similar phosphanido-bridging niobium or tantalum derivatives are not known, but the Nb–P distances are in the same range found for Mo–P distance in $[(PPh_3)Pd(\mu\text{-}PPh_2)Mo(CO)_4]$.[13]

Oxidation Reactions. As shown in Scheme I, the complex $[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$ is quantitatively transformed into $[Nb(\eta^5\text{-}C_5Me_5)Cl_2(OH)]_2(\mu\text{-}O)$[12] in the presence of air, but its reaction with dry oxygen leads to the trimer $[Nb(\eta^5\text{-}C_5Me_5)]_3Cl_4O_4$,[12] which can only be obtained by thermal decomposition of the μ-oxo–hydroxo dimer. Therefore, the formation of the trimer can only be explained by assuming a different pathway that could involve the intermediate formation of a peroxo compound of the type "$[Nb(\eta^5\text{-}C_5Me_5)Cl_2(O\text{-}O)]$". In order to obtain additional information, we studied the reaction with azobenzene. Unfortunately we were not able to isolate the expected η^2-hydrazido(2–) derivative, whose formation must be accepted to explain the presence of 1,2-diphenylhydrazine, detected by ^1H NMR spectroscopy in the resulting solution. From this solution we recovered in high yield the above mentioned oxo trimer as the unique reaction product, which undoubtedly results from hydrolysis by water introduced during manipulation of the intermediate hydrazido(2–) compound. When the reaction was monitored by ^1H NMR spectroscopy into a sealed NMR tube, we observed the presence in solution of a compound[14] that could be formulated as the intermediate derivative containing terminal or bridging imido groups but could not be isolated. Addition of a small amount of water to this solution led to the formation of the trimer.

In order to prove the formation of the intermediate hydrazido(2–) compound, we carried out the reaction of the niobium(III) dimer with azobiphenylene, where the presence of an additional rigid bond between the two phenyl rings helps to avoid the transformation into the imido derivative. This reaction led to the isolation of complex **2**. Compound **2** can also be easily prepared by reduction with sodium amalgam of a toluene solution of $Nb(\eta^5\text{-}C_5Me_5)Cl_4$ in the presence of azobiphenylene. Complex **2** is readily soluble in aromatic hydrocarbons, and its solutions are unstable in the presence of air, being transformed into the μ-oxo–hydroxo complex with elimination of biphenylenehydrazine. According to the parent peak observed in the mass spectrum at $m/e = 478$, **2** can be formulated as a monomer with a four-legged piano stool structure, although a dimeric structure with two bridging η^2-biphenylenehydrazido(2–) groups cannot be excluded. Its IR spectrum reveals one strong absorption at 634 cm^{-1} due to the ν(Nb–N) stretching frequency. The ^1H and ^{13}C NMR spectra show the characteristic behavior expected for the ligand (see Experimental Section) along with resonances due to the permethylated ring in agreement with the proposed structure.

Experimental Section

Reactions were carried out under an argon atmosphere by use of Schlenk techniques and solids handled in a Vacuum Atmospheres glovebox equipped with a HE-63-P Dri-Train. Organic solvents were dried over appropriate reagents and distilled under argon prior use: *n*-hexane (calcium hydride), tetrahydrofurane (sodium–benzophenone), and toluene (sodium). Reagent-grade chemicals were used as purchased without further purification: sodium and mercury (Panreac), oxygen (SEO), azobenzene (C.Erba), and azobiphenylene (Aldrich). $NbCp^*Cl_4$,[12] $[NbCp^*Cl_2]_2$,[5] and $LiPPh_2$[15] 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, ^{13}C, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 Unity instrument. Chemical shifts are reported in δ units (positive chemical shifts to a higher frequency), relative to TMS standard and phosphoric acid. Mass spectra were recorded on a HP 5988A instrument. C, H, and N analyses were performed with a Perkin-Elmer 240C microanalyzer.

Preparation of $[(NbCp^*)_2)(\mu\text{-}PPh_2)_2(\mu\text{-}O)]$ (1). A *n*-hexane (25 mL) suspension of $LiPPh_2$ (0.36 g, 1.87 mmol) was cooled to –78 °C, and then a THF solution of $[NbCp^*Cl_2]_2$ (0.28 g, 0.47 mmol) was added. After 30 min of stirring, H_2O (8.4 μL, 0.47 mmol) was added, and the suspension was permitted to warm to room temperature. A gradual color change from green to blue-green occurred. The suspension was concentrated to dryness and residue extracted with toluene (3 × 10 mL). The solution was concentrated to ca. 15 mL and *n*-hexane (15 mL) added carefully. Slow *n*-hexane diffusion in toluene to –20 °C yielded **1** as green crystals in 55% yield. The residual solution, which contains $PHPh_2$, can be recrystallized from toluene/hexane to give a further crop of **1**. Yield: 0.30 g (75%). IR (Nujol mull; ν, cm^{-1}): 1579 (m), 1023 (m), 737 (s),

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(14) ^1H NMR (δ, ppm, in C_6D_6): 8.07, 7.22, 6.88 (m, *Ph*), 1.74 (s, C_5*Me_5*). ^{13}C NMR (δ, ppm, in C_6D_6): 153.24 (s, C_{ipso}), *Ph*), 131.06 (s, $C_{3,5}$, *Ph*), 129.24 (s, $C_{2,6}$, *Ph*), 125.25 (s, C_4, *Ph*), 123.28 (s, C_5Me_5), 11.59 (s, C_5*Me_5*).

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Table III. Crystallographic Data for Complex 1

chem formula	$C_{44}H_{50}P_2ONb_2$
a, Å	19.327(8)
b, Å	11.198(2)
c, Å	22.248(9)
β, deg	122.98(2)
V, Å^3	4039(4)
Z	4
MW	842.64
symmetry; space group	monoclinic; C2/c (No. 15)
T, °C	22
λ, Å	0.7107
ρ_{calcd}, g cm^{-3}	1.412
μ, cm^{-1}	6.54
R^a	0.028
$R_w{}^b$	0.030^c

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w\{|F_o| - |F_c|\}^2/\sum w|F_o|^2]^{1/2}$. ^{c} $w = 4F_o{}^2[\sigma(F_o)^2]^2$.

694 (s), 377 (m). ^{1}H NMR (δ, ppm, in C_6D_6): 7.03, 6.84, 6.64 (m, 20H, Ph), 2.01 (s, 30H, C_5Me_5). $^{13}C\{^1H\}$ NMR (δ, ppm, in C_6D_6): 147.9 (s, C_{ipso}, $^1J_{C-P}$ = 20 Hz, Ph), 140.2 (s, C_{ipso}, $^1J_{C-P}$ = 20 Hz, Ph), 136–132 (several signals for Ph), 114.9 (s, C_5Me_5), 11.9 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (δ, ppm, in C_6D_6): 168.78 (br, PPh_2).

Reaction of $[NbCp^*Cl_2]_2$ with O_2. A 100-mL Schlenk flask was charged with $[NbCp^*Cl_2]_2$ (0.40 g, 0.67 mmol) and 30 mL of toluene. An atmosphere of dry oxygen was immediately established, and the solution was vigorously stirred for 30 min. The green color of the solution quickly changed to yellow. Solvent was removed in vacuo and the residue washed twice with n-hexane (2 × 20 mL) to yield a yellow solid identified as $Nb_3Cp^*{}_3Cl_4O_4$[12].

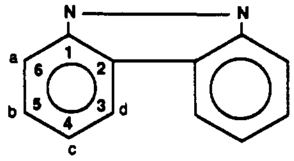
Reaction of $[NbCp^*Cl_2]_2$ with Azobenzene. A 5-mL NMR tube was charged with $[NbCp^*Cl_2]_2$ (0.10 g, 0.17 mmol), azobenzene (0.06 g, 0.34 mmol), and benzene-d_6 (0.5 mL) and then sealed. The resulting reddish solution was monitored by NMR spectroscopy (^{1}H and ^{13}C) until a unique niobium complex was observed. Then, the solution was filtered under argon, the stoichiometric amount of water (3 μL, 0.17 mmol) added, and solvent removed by evaporation. The resulting yellow solid was washed with n-hexane (2 mL), dried, and identified as the trimer complex $(NbCp^*)_3Cl_4O_4$.[12]

An analogous result was obtained by using standard Schlenk techniques.

Preparation of $NbCp^*Cl_2$(azobiphenylene) (2). Method A. Azobiphenylene (0.30 g, 1.68 mmol) was added to a solution of $[NbCp^*Cl_2]_2$ (0.50 g, 0.84 mmol) in toluene (50 mL), and the mixture was stirred for 6 h at room temperature. Then, the red solution was concentrated to ca. 20 mL and cooled to −40 °C overnight to give **2** as red needles. Yield: 0.68 g (85%).

Method B. A solution of azobiphenylene (0.28 g, 1.60 mmol) in toluene (50 mL) was added to a mixture of $NbCp^*Cl_4$ (0.58 g, 1.60 mmol) and 10% sodium amalgam (0.072 g, 3.20 mmol of Na). The reaction mixture was vigorously stirred for 12 h and then decanted and filtered through Celite. The resulting red dark solution was handled as described for method A to yield red needles of **2**. Yield: 0.53 g (70%).

IR (Nujol mull; ν, cm^{-1}): 1600 (m), 1023 (m), 761 (s), 726 (s), 634 (s), 567 (s), 329 (s). ^{1}H NMR (δ, ppm, in C_6D_6): 8.10 (dd, 1H, $^3J_{H-H}$ = 8.30 Hz, $^4J_{H-H}$ = 1.22 Hz, H_a), 7.52 (dd, 1H, $^3J_{H-H}$ = 8.30 Hz, $^4J_{H-H}$ = 1.22 Hz, H_d), 7.12 (td, 1H, $^3J_{H-H}$ = 8.30 Hz, $^4J_{H-H}$ = 1.22 Hz, H_b or H_c), 6.87 (td, 1H, $^3J_{H-H}$ = 8.30 Hz, $^4J_{H-H}$ = 1.22 Hz, H_c or H_b), 1.97 (s, 15H, C_5Me_5). ^{1}H NMR (δ, ppm, in $CDCl_3$): 7.82 (dd, 1H, $^3J_{H-H}$ = 8.06 Hz, $^4J_{H-H}$ = 1.10 Hz, H_a), 7.69 (dd, 1H, $^3J_{H-H}$ = 8.06 Hz, $^4J_{H-H}$ = 1.10 Hz, H_d), 7.16 (m, 1H, H_b or H_c), 7.07 (td, 1H, $^3J_{H-H}$ = 1.10 Hz, H_c or H_b), 2.16 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (δ, ppm, in $CDCl_3$): 145.6 (s, C_1, *azobiphenylene*), 131.6 (s, C_5Me_5), 127.7 and 125.4 (s, C_3 and C_5, *azobiphenylene*), 124.2 (s, C_6, *azobiphenylene*), 121.7 (s, C_4, *azobiphenylene*), 121.0 (s, C_2, *azobiphenylene*), 12.6 (s, C_5Me_5). ^{13}C NMR (δ, ppm, in $CDCl_3$): 145.5 (m, C_1, *azobiphenylene*), 131.6 (s, C_5Me_5), 127.8 and 125.5 (dd, $^1J_{C-H}$ = 160 Hz, $^3J_{C-H}$ = 7–8 Hz, C_3 and C_5, *azobiphenylene*), 124.2 (m, C_6, *azobiphenylene*), 121.7 (dd, $^1J_{C-H}$ = 160 Hz, $^3J_{C-H}$ = 7–8 Hz, C_4, *azobiphenylene*), 121.0 (dd, $^1J_{C-H}$ = 160 Hz, $^3J_{C-H}$ = 7–8 Hz, C_2, *azobiphenylene*), 12.7 (q, $^1J_{C-H}$ = 128.21 Hz, C_5Me_5). MS (EI, 70 eV): m/e 478 ($[M]^{+\bullet}$, 6), 443 (35.5), 298 (56.2), 262 (49.1), 181 (12.8), 135 (19.3). Anal. Calcd for $NbCl_2C_{22}H_{23}N_2$: C, 55.13; H, 4.83: N, 5.84. Found: C, 55.23; H, 5.24; N, 5.57. Azobiphenylene ligand:



Crystallography. Single crystals of **1** suitable for X-ray analysis were grown from a mixture of n-hexane/toluene upon slow evaporation. Crystallographic and experimental details of X-ray structure determination are reported in Table III, while other details related to data collection and refinement procedure have been deposited as supplementary material.

Data were collected at room temperature with the crystal sealed in a Lindeman glass capillary under dry argon. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made.

The structure was solved by a combination of direct methods and Fourier synthesis and refined (on F) by full-matrix least-squares calculations.

All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms for phenyl groups were found in the difference synthesis map and refined isotropically in two cycles. The ones of the methyl groups were regulated and included in the last refinement in fixed position and thermal parameters equivalent to those of the carbon atom to which they are attached.

Final values of R = 0.028 and R_w = 0.030 with $R_w = [\sum w\{|F_o| - |F_c|\}^2/\sum w|F_o|^2]^{1/2}$ and $w = 4F_o{}^2/[\sigma(F_o)^2]^2$ were obtained.

Anomalous dispersion corrections and atomic scattering factors were taken from ref 16. Calculations were performed with the SDP package[17] and the programs MULTAN[18] and DIRDIF[19] on a MICROVAX II computer.

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Supplementary Material Available: Tables of crystallographic data, least-squares planes, coordinates of hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles (11 pages). Ordering information is given on any current masthead page.

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