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Reduction of Half-Sandwich Niobium Compounds: Tertiary Phosphine and Carbonyl Derivatives of (Pentamethylcyclopentadienyl)niobium(III)

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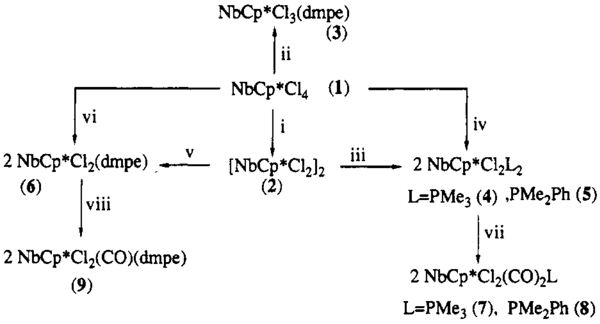
The reduction of $[Nb(\eta^5\text{-}C_5Me_5)Cl_4]$, (1), with sodium amalgam permitted the isolation of the trivalent niobium chloride $[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (2) in high yield. The reduction of 1 in the presence of $Me_2PCH_2CH_2PMe_2$ (dmpe) with 1 equiv of sodium amalgam led to the paramagnetic niobium(IV) derivative $[Nb(\eta^5\text{-}C_5Me_5)Cl_3(dmpe)]$ (3), whereas monomeric and paramagnetic niobium(III) complexes of the type $[Nb(\eta^5\text{-}C_5Me_5)Cl_2L_2]$ were obtained by using 2 equiv of the reducing agent in the presence of different phosphine ligands, PMe_3 (4), PMe_2Ph (5), and $Me_2PCH_2CH_2PMe_2$ (6), or by addition of the ligands to toluene solutions of 2. These niobium(III) complexes reacted with carbon monoxide to give pseudo-octahedral diamagnetic species $[Nb(\eta^5\text{-}C_5Me_5)Cl_2(CO)_2L]$, where L = PMe_3 (7), PMe_2Ph (8), and $[Nb(\eta^5\text{-}C_5Me_5)Cl_2(CO)(dmpe)]$ (9). Complexes 3–5 were characterized by ^1H NMR, EPR, and magnetic measurements at room temperature. The ^1H, ^{13}C, and ^{31}P NMR studies of complex 9 indicated a pseudo-octahedral arrangement with both phosphorus atoms occupying one equatorial position trans to chlorine and one axial position trans to the cyclopentadienyl ring.

Introduction

The chemistry of pentamethylcyclopentadienyl half-sandwich complexes of the heavier group 5d elements niobium and tantalum is receiving growing attention[1] after the tetrahalides were made readily accessible in high yields.[1b,2] Reduction of the tantalum complex to different tertiary phosphine, carbonyl, butadiene, and acetylene derivatives[3] in oxidation states I–IV and also the isolation of the first trimethylphosphine and carbonylniobium(III) complexes have recently been reported.[4] Here, we describe the synthesis and characterization of new (pentamethylcyclopentadienyl)niobium(III) derivatives containing carbon monoxide and trimethylphosphine, dimethylphenylphosphine, and 1,2-bis(dimethylphosphino)ethane and the niobium(IV) derivative of this bidentate phosphine.

Scheme I[a]



[a] **Reagents and conditions**: (i) 2 mol Na/Hg, rt, 12 h; (ii) 1 mol Na/Hg, toluene, rt, 12 h; (iii) 4 mol L, toluene; (iv) 2 mol Na/Hg, 2 mol L, toluene, rt, 12 h; (v) 2 mol dmpe, toluene; (vi) 2 mol Na/Hg, 1 mol dmpe, toluene, rt, 12 h; (vii) CO, 1 atm, toluene, 24 h; (viii) CO, 1 atm, toluene, 24 h.

Results and Discussion

$[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$ and some of its reactions have been reported,[5] the green crystalline dimer being isolated from the reaction of $[Nb(\eta^5\text{-}C_5Me_5)Cl_2Me_2]$ with hydrogen. We have also obtained the same compound in an attempt to isolate $[Nb(\eta^5\text{-}C_5Me_5)Cl_3(SiMe_3)]$ following the same reaction of 1 (Scheme I) with $Al(SiMe_3)_3$ reported for the analogous tantalum complex.[6] This reaction takes place but with simultaneous elimination of $SiClMe_3$ leading to the niobium(III) complex 2. However, the best method to isolate pure 2 in high yield is by the reduction of toluene solutions of 1 with 2 equiv of 10% sodium amalgam. The previously reported[5] formulation as a dimer is in agreement with its diamagnetic behavior, the cryoscopic determination of molecular weight in benzene, and the mass spectrum, which shows the parent peak at 596. The existence of the expected Nb═Nb double bond is supported by the low field observed in the ^1H NMR spectrum for the methyl protons of the cyclopentadienyl ring due to the magnetic anisotropy associated with the double bond.[7] The ν(Nb–Cl) absorption appears in the IR spectrum at 331 cm^{-1} (see Experimental Section). All these data suggest a structure with the two 18-electron niobium atoms having four chlorine bridges with a linear disposition

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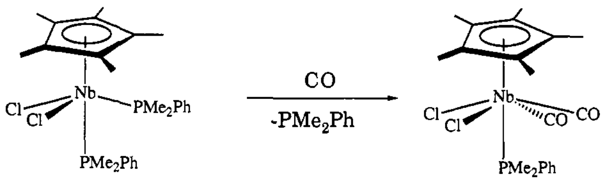
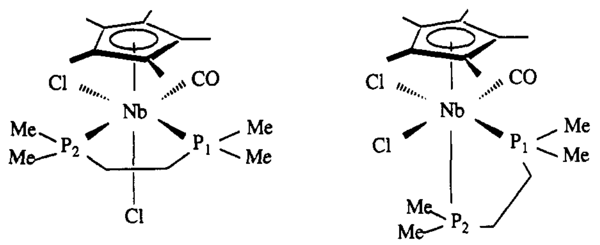
Scheme II



(5) (8)

Scheme III



A B

of both cyclopentadienyl rings, similar to that described for the analogous bromotantalum derivative.[7]

Compound **2** is air sensitive in solution and also in the solid and is easily transformed by simultaneous oxidation and hydrolysis.[8]

The reduction of toluene solutions of **1** with 1 equiv of 10% sodium amalgam in the presence of 1,2-bis(dimethylphosphino)ethane leads to the paramagnetic niobium(IV) complex **3**. When the same reduction is done in the presence of different mono or bidentate tertiary phosphines by using 2 equiv of the reducing agent, the mononuclear paramagnetic niobium(III) complexes [Nb(η^5-C_5Me_5)Cl_2L_2] [L_2 = 2PMe_3[4] (**4**), 2PMe_2Ph (**5**), dmpe (**6**)] are obtained. The formation of pseudo-octahedral species of the type described for $TaCpCl_2L_3$[3a,9] was not observed when an excess of ligand was used. The same compounds can also be prepared by addition of the ligands to toluene solutions of **2**, but this always gives lower yields.

One of the phosphine ligands is easily substituted when toluene solutions of **4** and **5** are stirred under a CO atmosphere and the coordination number is increased to give diamagnetic pseudo-octahedral complexes [Nb(η^5-C_5Me_5)$Cl_2(CO)_2L$] [L = PMe_3[4] (**7**), PMe_2Ph (**8**)] (Scheme II). However, the reduction of toluene solutions of **1** with sodium amalgam in the presence of dmpe, under CO, gives the monocarbonyl pseudo-octahedral diamagnetic complex [Nb(η^5-C_5Me_5)Cl_2(CO)(dmpe)] (**9**).

All the new niobium(III) compounds are air sensitive and soluble in aromatic hydrocarbons and partially soluble in alkanes. Their formulation is in agreement with the elemental analyses and their monomeric nature is supported by their magnetic behavior and mass spectra. All the complexes were characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Magnetic susceptibility measurements at room temperature give magnetic moments (μ_{eff}) of 2.45 μ_B for complex **5** and 1.84 μ_B for complex **3**. The ESR spectrum of a toluene solution of **3** shows 10 doublets [$\langle g\rangle = 1.975$; $\langle a\rangle_{iso} = 13.5$ mT (^{93}Nb, $I = {}^9/_2$) and $\langle a\rangle_{iso} = 1.8$ mT (^{31}P, $I = {}^1/_2$)], indicating that both phosphorus atoms are magnetically nonequivalent, in agreement with a pseudo-octahedral structure with the chelating dmpe occupying one equatorial and one axial position trans to the Cp* ring, an arrangement similar to that known for Nb(η^5-C_5H_5)Cl_3(dppe),[10] and in contrast to the observed 10 triplets for Nb(η^5-C_5H_5)Cl_3(dmpe),[11] which suggests the equivalency of both of the assumed to be equatorial phosphorus atoms. The ^{1}H NMR spectrum of **3** shows two broad signals at δ 11.6 ($\Delta\nu \approx 2$ kHz, 15 H) and δ −7.7 ($\Delta\nu \approx 2.4$ kHz, 16 H), which were assigned to the pentamethylcyclopentadienyl and phosphine methyl and methylene protons, respectively.

The structural behavior of complexes **4** and **7** is coincidental with data reported by Gibson.[4] The IR spectra of complexes **5**, **6**, **8**, and **9** show the expected characteristic absorptions due to the phosphine ligands,[12] and strong ν(CO) absorptions are observed for **8** (2004, 1910 cm^{-1}) and **9** (1861 cm^{-1}). The ^{1}H NMR resonances observed for **5** were assigned according to their relative intensities. The spectral behavior can be explained in terms of "contact and pseudocontact shifts",[13] assuming that the unpaired electron is essentially localized on the niobium–Cp* system, causing a very high shift down field, as observed for the ring methyl protons. The behavior observed for the methyl phosphine protons means that both PMe_2Ph are not equivalent, suggesting an axial–equatorial disposition of the two ligands. This would explain the monomeric structure and paramagnetic behavior of these complexes and the formation of the carbonyl compound.

The easy decomposition of complex **6** in solution meant that NMR and ESR studies could not be carried out.

The ^{1}H NMR spectrum of **8** shows one singlet due to the ring methyl protons at δ 1.57, one doublet for the methylphosphine protons at δ 1.81 with a coupling constant $^2J_{P-H} = 10.2$ Hz, and signals for phenyl phosphine protons (7.03, *m*- and *p*-H; 7.54, *o*-H).

A detailed NMR study was carried out for complex **9** from which a definitive structural assignment could be concluded. The ^{1}H NMR spectrum of **9** in $CDCl_3$ shows one singlet at δ 1.82 due to the methyl ring protons, four doublets at δ 1.27, ($^2J_{H-P} = 6.35$ Hz), 1.34 ($^2J_{H-P} = 7.32$ Hz), 1.64 ($^2J_{H-P} = 10.5$ Hz), and 1.78 ($^2J_{H-P} = 9.5$ Hz) due to the four nonequivalent phosphine methyl protons, and a complex ABCD spin system multiplet for the methylene protons. The $^{13}C\{^1H\}$ spectrum also shows four doublets for the phosphine methyl groups and two doublets of doublets for the methylene carbon atoms. The $^{31}P\{^1H\}$ NMR spectrum shows two broad resonances with an intensity ratio of 1:1, due to both phosphorus atoms, not only showing different chemical shifts but also different widths. The width of these signals must be due to the quadrupole moment interaction with the ^{93}Nb nucleus, whereas the resonances observed for the same tantalum derivative[3b] show normal widths. Therefore, the molecule can adopt only two different isomeric configurations, with phosphorus atoms occupying two equatorial positions (**A**) or one equatorial position trans to chlorine and one axial position (**B**). (See Scheme III.) Structure **B** would be

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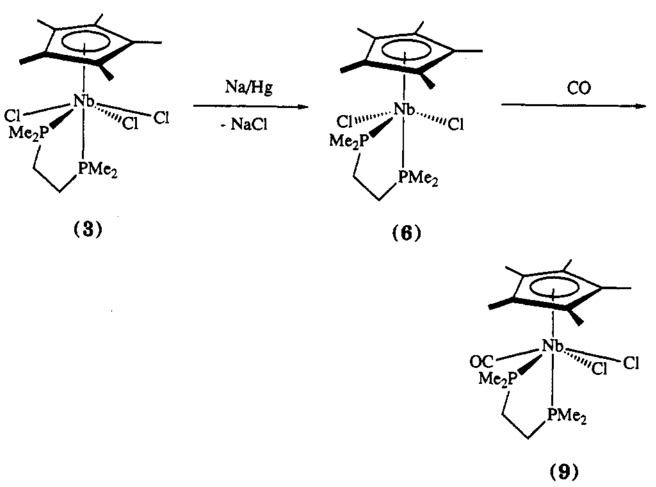
Scheme IV



similar to that found by X-ray diffraction for the analogous tantalum derivative $TaCp^{*}Cl_2(CO)(dmpe)$,[3b] whereas structure **A** would be in agreement with that proposed for $NbCpCl_2(CO)(dmpe)$.[11]

This behavior can be explained by taking into account that the theoretically estimated positive charge on both equatorial phosphorus atoms in **A** is not very different, whereas in **B** the equatorial phosphorus P_1 supports a clearly higher positive charge than the axial phosphorus P_2 and therefore the two Nb–P distances must be different. Due to the negative sign[14] of the direct coupling constant for ^{13}C–^{31}P, the bigger values (smaller absolute values) should correspond to the coupling with the participation of P_1. So, the two ^{13}C signals with higher $^1J_{C-P}$ at δ 14.74 (−18.5 Hz) and 10.20 (−17.5 Hz) must be assigned to P_1, whereas the two with lower $^1J_{C-P}$ at δ 13.51 (−27.5 Hz) and 13.06 (−30.0 Hz) must correspond to P_2. This is in agreement with the difference in chemical shifts of the two ^{13}C NMR signals observed for the methyl groups bound to P_1 ($\Delta\delta = 2.5$), in comparison with the smaller difference between the other two, due to methyl groups bound to P_2 ($\Delta\delta = 0.45$). The broadest lower field ^{31}P signal at δ 25.7 ($\Delta\nu = 270$ Hz) has to be assigned to P_1. Therefore, we must conclude that **9** has to be formulated with the structure shown for isomer **B**.

Complex **9** can also be obtained by reduction of **3** (see Scheme IV) in the presence of CO through a pseudo-pentacoordinate intermediate species, without modification of the structural configuration of the niobium atom.

Concluding Remarks

Pseudo-pentacoordinate paramagnetic mono(pentamethyl cyclopentadienyl)niobium(III) complexes can be isolated when only phosphines are used as ligands. These compounds are easily transformed into diamagnetic pseudo-octahedral derivatives by incorporation of carbon monoxide. The structural study and chemical behaviour observed for the pseudopentacoordinate compounds is in agreement with an arrangement in which both phosphorus donor atoms are located in one equatorial and one axial position trans to the cyclopentadienyl ring. One additional equatorial position is occupied by carbon monoxide to give the pseudo-octahedral complex, without any modification of the remaining substituents, as proved by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy, when a bidentate phosphine, dmpe, is present. A further substitution of phosphine takes place for complexes containing monodentate phosphines, and a second molecule of carbon monoxide is always coordinated in one of the equatorial positions trans to chlorine.

Experimental Section

All operations were performed under an atmosphere of argon by using Schlenk techniques, vacuum-line, or a Vacuum Atmospheres glovebox equipped with a HE-63-P Dri-Train. The following solvents were dried and distilled under argon before use by employing the drying agents in parentheses: *n*-hexane (calcium hydride), tetrahydrofuran (sodium–potassium alloy), and toluene (sodium). $NbCp^{*}Cl_4$ was prepared as described.[1b] Reagents purchased from commercial sources and used without further purification were as follows: sodium (Panreac), potassium (Fluka), mercury (Panreac), 1,2-bis(dimethylphosphine)ethane (98%, Strem), dimethylphenylphosphine (Janssen Chimica), 1 M trimethylphosphine in toluene (Aldrich), and carbon monoxide (>99%, SEO). Infrared spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000–200 cm^{-1}) as Nujol mulls between CsI pellets. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ 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 a TMS standard and phosphoric acid. Mass spectra were recorded on an HP 5988A instrument. Magnetic susceptibilities were measured by the Faraday method using a Bruker B-E 15 magnetic balance with a temperature control unit. C and H analyses were performed with a Perkin-Elmer 240C microanalyzer.

$[NbCp^{*}Cl_2]_2$ (2). Toluene (70 mL) was added to a mixture of **1** (0.67 g, 1.81 mmol) and 10% sodium (0.083 g, 3.62 mmol) amalgam. The mixture was vigorously stirred for 12 h at room temperature and then the resultant green suspension decanted and filtered through Celite. The solvent was removed in vacuum and the green residue extracted twice with THF (2 × 15 mL). After concentration to ca. 15 mL, the solution was cooled to −40 °C to give green crystalline **2**. Yield: 0.41 g (75%). IR (Nujol mull, cm^{-1}): 1023 (m), 839 (m), 393 (w), 331 (w). ^1H NMR (δ, ppm, in benzene-d_6): 2.16 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (δ, ppm, in benzene-d_6): 120.58 (s, C_5Me_5), 13.38 (s, C_5Me_5). MS (EI, 70 eV): *m/e* 596 (M^+, 13.06), 298 (59.08), 258 (100). Anal. Calcd for $C_{10}H_{15}Cl_2Nb$: C, 40.16; H, 5.06. Found: C, 39.98; H, 4.96.

$[NbCp^{*}Cl_3(dmpe)]$ (3). A toluene solution (50 mL) of dmpe (0.43 mL, 2.60 mmol) was added to a mixture of 10% sodium (0.060 g, 2.60 mmol) amalgam and **1** (0.96 g, 2.60 mmol). The mixture was vigorously stirred for 12 h at room temperature, filtered, concentrated to ca. 20 mL, and cooled to −20 °C to give purple crystals of **3**. Yield: 0.51 g (65%). IR (Nujol mull, cm^{-1}): 1280 (m), 1022 (m), 941 (s), 896 (m), 741 (m), 727 (m), 364 (m), 312 (s), 288 (s). ^1H NMR (δ, ppm, in benzene-d_6, 20 °C): 11.6 (s, 15 H, C_5Me_5), −7.7 (s, 16 H, dmpe). MS (EI, 70 eV): *m/e* 483 ($M^{+\bullet}$, 9.7), 333 (81.8), 297 (29.7), 261 (52.7). $\mu_{eff} = 1.84$ (μ_B) at 295 K. Anal. Calcd for $C_{16}H_{31}Cl_3NbP_2$: C, 39.65; H, 6.45. Found: C, 39.78; H, 6.29.

$[NbCp^{*}Cl_2L_2]$ [L = PMe_3 (4), PMe_2Ph (5)]. A toluene solution (70 mL) of L (4.32 mmol) was added to a mixture of **1** (0.80 g, 2.16 mmol) and 10% sodium (0.10 g, 4.32 mmol) amalgam. The mixture was stirred for 12 h at room temperature. The dark red suspension was filtered through Celite. The solvent was removed in vacuum and the residue extracted with *n*-hexane (3 × 15 mL). The solution was concentrated to ca. 15 mL and cooled to −40 °C overnight to give **4** or **5** as red crystals. The data for **4** follow. Yield: 0.68 g (70%). IR (Nujol mull, cm^{-1}): 1297 (m), 1276 (m), 1023 (m), 953 (s), 728 (s), 468 (m), 364 (m), 310 (m). ^1H NMR (δ, ppm, in benzene-d_6):[4] 72.6 (s, C_5Me_5), 14.9 (s, PMe_3). MS (EI, 70 eV): *m/e* 298 ($M^{+\bullet} - 2PMe_3$, 96.9), 258 (100), 135 (9.0), 119 (18.6), 77 (17.1). Anal. Calcd for $C_{16}H_{33}Cl_2NbP_2$: C, 42.59; H, 7.37. Found: C, 42.47; H, 7.44. The data for **5** follow.

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Yield: 0.87 g (70%). IR (Nujol mull, cm^{-1}): 1586 (w), 1298 (w), 1022 (m), 956 (m), 912 (m), 738 (s), 692 (s), 489 (m), 359 (m), 310 (s), 284 (s). ^{1}H NMR (*δ*, ppm, in benzene-*d*$_6$): 68.9 (br, 15 H, C$_5$Me$_5$), 13.7 (br, 4 H, PMe$_2$*Ph*), 11.9 (br, 4 H, PMe$_2$*Ph*), 10.5 (br, 2 H, PMe$_2$*Ph*), 5.3 (br, 6 H, P*Me*$_2$Ph), −0.65 (br, 6 H, P*Me*$_2$Ph). MS (EI, 70 eV): *m/e* 558 (M$^{+\bullet}$ − CH$_3$, 74.1), 298 (61.6), 263 (89.6). μ_{eff} = 2.45 (μ_B) at 295 K. Anal. Calcd for $C_{26}H_{37}Cl_2NbP_2$: C, 54.28; H, 6.48. Found: C, 54.03; H, 6.35.

[NbCp*Cl$_2$(dmpe)] (6). A toluene solution (50 mL) of dmpe (0.27 mL, 1.62 mmol) was added to a mixture of **1** (0.60 g, 1.62 mmol) and 10% sodium (0.074 g, 3.22 mmol) amalgam. The mixture was stirred for 12 h at room temperature. The resultant orange suspension was decanted and filtered through Celite, and then the solution was concentrated to ca. 25 mL and cooled to −40 °C overnight to give **6** as orange crystals. Yield: 0.55 g (75%). IR (Nujol mull, cm^{-1}): 1280 (m), 1023 (m), 941 (s), 896 (m), 721 (m), 367 (w), 313 (w). MS (EI, 70 eV): *m/e* 449 (M$^{+\bullet}$, 4.3), 297 (18.4), 262 (24.9). Anal. Calcd for $C_{16}H_{31}Cl_2NbP_2$: C, 42.78; H, 6.96. Found: C, 42.49; H, 6.53.

[NbCp*Cl$_2$(CO)$_x$L] [*x* = 2, L = PMe$_3$ (7), PMe$_2$Ph (8); *x* = 1, L = dmpe, (9)]. A Schlenk tube containing a solution of **4**, **5**, or **6** (1 mmol) in toluene (30 mL) was sealed under 1 atm of CO. The solution was stirred for 24 h at room temperature, filtered, and concentrated to ca. 10 mL. Crystalline carbonyl derivatives **7** (purple), **8** (purple), or **9** (green) were obtained by cooling to −40 °C overnight. The data for **7** follow. Yield: 0.40 g (95%). IR (Nujol mull, cm^{-1}): 2000 (s), 1913 (s), 1295 (m), 1019 (m), 967 (s), 726 (s), 476 (m), 367 (m), 313 (s). ^{1}H NMR (*δ*, ppm, in benzene-*d*$_6$):[4] 1.63 (s, 15 H, C$_5$Me$_5$), 1.24 (d, 9 H, $^2J_{H-P}$ = 9.8 Hz, PMe$_3$). MS (EI, 70 eV): *m/e*, 297 (M$^+$ − PMe$_3$ − 2CO, 33.2), 261 (88.1). Anal. Calcd for $C_{15}H_{24}Cl_2NbO_2P$: C, 41.79; H, 5.61. Found: C, 41.83; H, 5.60. The data for **8** follow. Yield: 0.47 g (95%). IR (Nujol mull, cm^{-1}): 2004 (s), 1910 (s), 1024 (m), 954 (m), 741 (m), 486 (m), 402 (w), 281 (w). ^{1}H NMR (*δ*, ppm, in benzene-*d*$_6$): 7.54 (m, 2 H, PMe$_2$*Ph*), 7.03 (m, 3 H, PMe$_2$*Ph*), 1.81 (d, 6 H, $^2J_{H-P}$ = 10.2 Hz, P*Me*$_2$Ph), 1.57 (s, 15 H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (*δ*, ppm, in benzene-*d*$_6$): 237.4 (s, CO), 137 (d, $^1J_{C-P}$ = 25 Hz, C$_{ipso}$), 130.43 (d, $^2J_{C-P}$ = 7.3 Hz, C$_{ortho}$), 129.8 (s, C$_{para}$), 128.2 (s, C$_{meta}$), 107.64 (s, *C*$_5$Me$_5$), 14.37 (d, $^1J_{C-P}$ = 27 Hz, P*Me*$_2$Ph), 11.67 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (*δ*, ppm, in benzene-*d*$_6$): −10.58 (s). Anal. Calcd for $C_{20}H_{26}Cl_2NbO_2P$: C, 48.7; H, 5.31. Found: C, 48.65; H, 5.14. The data for **9** follow. Yield: 0.29 g (60%). IR (Nujol mull, cm^{-1}): 1861 (s), 1281 (m), 1023 (m), 937 (s), 898 (m), 722 (m), 364 (w), 313 (w). ^{1}H NMR (*δ*, ppm, in chloroform-*d*$_1$): 1.82 (s, 15 H, C$_5$Me$_5$), 1.78 (d, 3 H, $^2J_{H-P}$ = 9.5 Hz, dmpe), 1.64 (d, 3 H, $^2J_{H-P}$ = 10.5 Hz, dmpe), 1.34 (d, 3 H, $^2J_{H-P}$ = 7.32 Hz, dmpe), 1.27 (d, 3 H, $^2J_{H-P}$ = 6.35 Hz, dmpe). ^{13}C{^{1}H} NMR (*δ*, ppm, in chloroform-*d*$_1$): 270.29 (s, CO), 105.87 (s, C$_5$Me$_5$), 31.55 [dd, $^1J_{C-P}$ = −28 Hz, $^2J_{C-P}$ = 16.0 Hz, CH$_2$(P$_2$)], 24.06 [dd, $^1J_{C-P}$ = −20.0 Hz, $^2J_{C-P}$ = 9.0 Hz, CH$_2$(P$_1$)], 14.74 [d, $^1J_{C-P}$ = −18.5 Hz, CH$_3$(P$_1$)], 13.51 [d, $^1J_{C-P}$ = −27.5 Hz, CH$_3$(P$_2$)], 13.06 [d, $^1J_{C-P}$ = −30 Hz, CH$_3$(P$_2$)], 11.35 (s, C$_5$Me$_5$), 10.20 [d, $^1J_{C-P}$ = −17.5 Hz, CH$_3$(P$_1$)]. ^{31}P{^{1}H} NMR (*δ*, ppm, in chloroform-*d*$_1$): 25.7 (br, $\Delta\nu \approx 270$ Hz, P$_1$), 14.1 (br, $\Delta\nu \approx 90$ Hz, P$_2$). Anal. Calcd for $C_{17}H_{31}Cl_2NbOP_2$: C, 42.79; H, 6.55. Found: C, 42.60; H, 6.38.

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Supplementary Material Available: ^{1}H, ^{13}C, and ^{31}P NMR spectra and assignments for complex **9** (3 pages). Ordering information is given on any current masthead page.

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