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Simple Synthesis and Structure Characterization of a Stable Niobium(V) Phosphoniomethylidyne Complex

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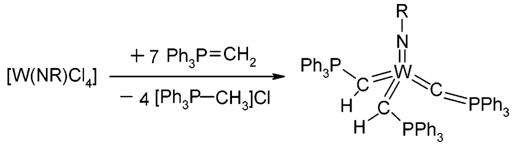
*Summary: The half-sandwich high-valent niobium(V) phosphoniomethylidyne complex [CpNb{CPPh$_3$}Cl$_2$] (**4**) was obtained by the transylidation reaction of CpNbCl$_4$ with 3 equiv of Ph$_3$P=CH$_2$. The X-ray structure shows a three-legged piano-stool geometry. The mechanism of formation is discussed.*

The first compounds with a formal metal−carbon triple bond ((X)(CO)$_4$M(≡CR): X = Cl, Br, I; M = Cr, Mo, W; R = Ph) were reported by Fischer and coworkers in 1973.[1] Since that time, the field of transition-metal carbyne complexes has developed tremendously. Only a few complexes with a terminal [M≡CPR$_3$] function have been discovered thus far.[2−5] Their syntheses were effected by reaction of a phosphine with a tungsten chlorocarbyne functionality[2] or by insertion of a tungsten(II) complex fragment into the C=C bond of Ph$_3$P=C=C=O.[4] Until now there have been very few examples of phosphoniomethylidyne complexes with a d^0 electron configuration. The first such complex, [Cl$_2$Ti(μ-CP(NEt$_2$)$_3$)$_2$TiCl$_2$], containing the ligand [R$_3$PC]$^{2-}$ in a bridging coordination mode, was reported by Schmidbaur in 1986.[6] It was found to have interesting applications in C−C coupling reactions as a synthon for [C].[4−7]

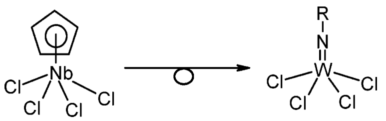
Phosphorus ylides have been used as precursors for the formation of transition-metal carbyne complexes in few cases. Recently we found that transylidation reactions of [W(NR)Cl$_4$] (R = 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl) with 7 equiv of triphenylmethylenephosphorane afforded the first d^0 tungsten phosphoniomethylidyne complexes (Scheme 1).[8]

Scheme 1. Synthesis of Tungsten Phosphoniomethylidyne Complexes

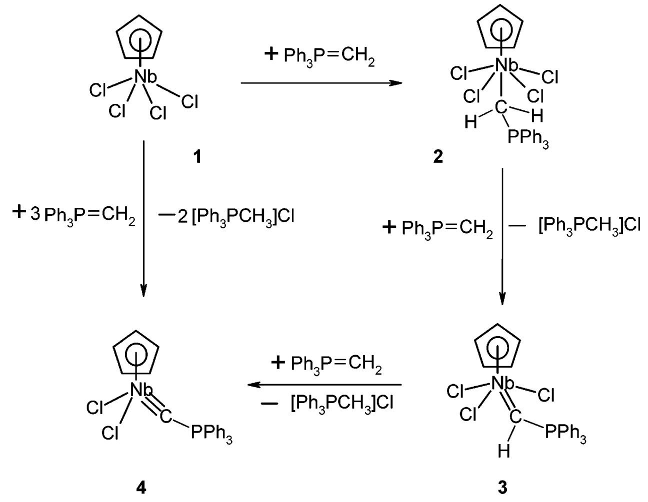


R = 2, 6-diisopropylphenyl **1**
R = 2, 4, 6-trimethylphenyl **2**

Scheme 2. Isolobal Relationship



Scheme 3. Synthesis and Proposed Mechanism for the Formation of Complex 4



CpNbCl$_4$ is isolobal with W(NR)Cl$_4$ (Scheme 2), and therefore the two complexes should have similar reactivities toward triphenylmethylenephosphorane. We have found that the transylidation reaction of CpNbCl$_4$ (**1**) with 3 equiv of triphenylmethylenephosphorane gave orange crystals of [CpNb{CPPh$_3$}Cl$_2$] (**4**) (Scheme 3). To our knowledge this is the first example of a stable niobium complex with a terminal [M≡CPR$_3$] function.

Compound **4** was characterized analytically and spectroscopically. The ^{1}H NMR spectrum shows a singlet at 6.03 ppm for the cyclopentadienyl ligand. The ^{31}P NMR spectrum shows a singlet at −30.5 ppm for the [Nb≡CPPh$_3$] function. This signal is shifted to higher

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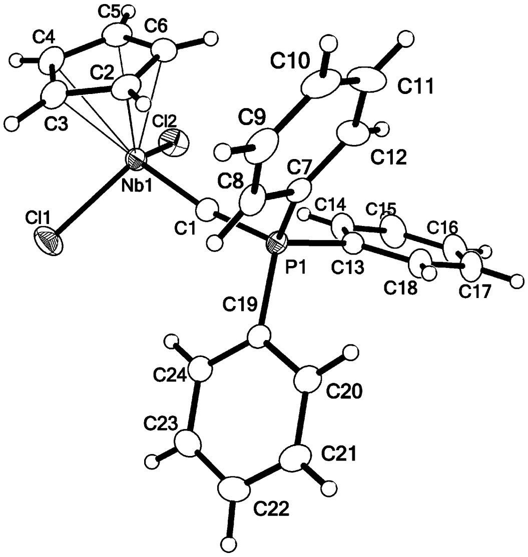


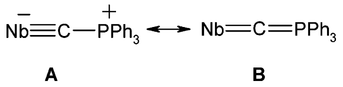
Figure 1. ORTEP diagram of **4**. Selected bond distances (Å) and angles (deg): Nb1−C1, 1.8287(18); Nb1−C2, 2.405(2); Nb1−C3, 2.462(2); Nb1−C4, 2.519(2); Nb1−C5, 2.465(2); Nb1−C6, 2.379(2); Nb1−Cl1, 2.3766(6); Nb1−Cl2, 2.3850(6); P1−C1, 1.7160(18); P1−C7, 1.8022(18); P1−C13, 1.7996(18); P1−C19, 1.8087(18); C2−C3, 1.400(3); C3−C4, 1.402(4); C4−C5, 1.395(4); C5−C6, 1.408(4); C2−C6, 1.403(3); Nb−C1−P1, 164.64(12); Cl−Nb−Cl1, 102.45(6); Cl−Nb−Cl2, 102.28(6); Cl1−Nb−Cl2, 105.00(2). Displacement ellipsoids are drawn at the 50% probability level.

field in comparison to signals for other high-valent but more π-bond-loaded complexes such as W(NDip)($CPPh_3$)($CHPPh_3$)$_2$ (Dip = 2,6-diisopropylphenyl; δ_P −13.0),[8] W(NMes)($CPPh_3$)($CHPPh_3$)$_2$ (Mes = 2,4,6-trimethylphenyl; δ_P −11.1),[8] Re(N^tBu)$_2$($CPPh_3$)(O^tBu) (δ_P 6.8),[9] and [Re(N^tBu)$_2$($CPPh_3$)(SR)] (R = adamantyl; δ_P 10.8 ppm).[10]

Recrystallization from pentane at 4 °C gave single crystals of **4** as orange plates suitable for X-ray diffraction analysis. A view of the molecular geometry is shown in Figure 1 with selected bond distances and angles. The niobium atom possesses a slightly distorted pseudotetrahedral three-legged piano-stool geometry. This structure is related to that of [CpNb(imido)Cl_2][11] by formal replacement of the two isoelectronic ligands [NCR_3] and [CPR_3]. The Nb−C distance of 1.829(2) Å lies within the range expected for a metal−carbon triple bond[12] and compares perfectly with the bond length of the structurally and electronically related d^0 phosphoniomethylidyne complexes noted above (Re1−C1 = 1.758(6) Å in Re(N^tBu)($CP(NEt_2)_3$)Cl_3,[13] W−C = 1.813(6) Å in W(NDip)($CHPPh_3$)$_2$($CPPh_3$)[8]).

The ylidic C_{yl}−P distance C1−P1 = 1.716(2) Å is substantially shorter than other C_{ar}−P distances of the PPh_3 group in the complexes noted above (1.800−1.809 Å). This shortening reflects a considerable contribution of the resonance form **B** (Scheme 4).

Scheme 4. Polarizable π-Bonds in 4



$$\overset{-}{Nb}\equiv C-\overset{+}{P}Ph_3 \longleftrightarrow Nb=C=PPh_3$$

A B

The phosphoniomethylidyne unit is quasi-linear, the Nb−C1−P angle being 164.64(12)°. This slight deviation from linearity is due to the bending of the PPh_3 group on the carbyne carbon atom toward the C_5H_5 ring. As a result of the trans influence of the phosphoniomethylidyne unit, the distances Nb−C3 = 2.462(2) Å, Nb−C4 = 2.519(2) Å, and Nb−C5 = 2.465(2) Å of the C_5H_5 ring in trans positions are considerably longer than the other two Nb−C bonds in cis positions. The Nb atom has a ring slip in the direction of C2−C6. The distance between the perpendicular projection of Nb(1) on the least-squares plane and the ring centroid is 0.142 Å. The distance of Nb(1) to the C_5H_5 ring is 2.1316(2) Å, and that to the centroid of the ring is 2.136(1) Å.

The reaction mechanism is proposed in Scheme 3. The reaction proceeds via the hexacoordinate classical ylide adduct **2**,[14] which was isolated in good yield when the parent compound **1** was treated with 1 equiv of $Ph_3P{=}CH_2$ in toluene. **2** is stable as the solid. In solution it is deprotonated by 2 equiv of $Ph_3P{=}CH_2$ to provide the title complex **4** and phosphonium chloride **5**. We were not able to isolate the phosphoniomethylidene complex **3** when a reaction of complex **2** with 1 equiv of $Ph_3P{=}CH_2$ was carried out. However, [Ph_3PCH_3]Cl as a white solid could be identified.

Complex **4** is formally a 16-electron species with a polar niobium−carbon triple bond. It is very reactive toward different reagents (CO, CH_3NC, $Ph_2C{=}C{=}O$, etc.). We will report the results of these studies and the possible application of **4** as a catalyst for olefin polymerization in the near future.

Experimental Section

General Procedures and Materials. All procedures were carried out under an argon atmosphere in freshly distilled anhydrous solvents. [$CpNbCl_4$][15] and $Ph_3P{=}CH_2$[16] were prepared by published procedures. NMR spectra were recorded on a Bruker AMX 400 spectrometer (^1H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz). Elemental analyses were obtained on a Heraeus CHN-Rapid instrument. Single-crystal structures were determined on a Stoe IPDS diffractometer.

Synthesis of 2. To 0.86 g (2.86 mmol) of $CpNbCl_4$ (**1**) in 60 mL of toluene was added 0.79 g (2.86 mmol) of $Ph_3P{=}CH_2$ in 10 mL of toluene at 0°C. After 10 h of stirring at ambient temperature the resulting red suspension was filtered, reduced in volume, layered with pentane, and stored at 4 °C. The product precipitated as a purple-red powder. Yield: 0.86 g (52%). Anal. Calcd for $C_{24}H_{22}Cl_4PNb$ (**2**): C, 50.03; H, 3.85. Found: C, 50.15; H, 3.88. ^1H NMR (400.1 MHz, C_6D_6, 300 K): δ 4.20 (d, ^2J(PH) = 13.2 Hz, 2H, NbCH_2PPh$_3$), 6.41 (s, 5H, C_5H_5), 6.90−7.70 (m, 15H, P(C_6H_5)$_3$) ppm. ^{31}P NMR (162.0 MHz, C_6D_6, 300 K) δ 33.0 (s, PPh_3) ppm.

Synthesis of 4. Method a. To 0.86 g (2.86 mmol) of $CpNbCl_4$ (**1**) in 50 mL of toluene was added 2.37 g (8.57 mmol) of $Ph_3P{=}CH_2$ in toluene (50 mL), dropwise with stirring at 0 °C. The reaction mixture was warmed to ambient temperature

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and then was stirred for 16 h. During this period, the reaction mixture turned orange. After removal of the solvent at reduced pressure the solid residue was extracted with pentane (80 mL) and diethyl ether (2 × 80 mL), respectively, which upon cooling to −30 °C gave an orange powder: the yield of raw material of **4** was ca. 40%, and ^{31}P NMR indicated that the purity of **4** is above 50%. Repeated recrystallization from pentane at 4 °C yielded orange single crystals suitable for X-ray structure analysis: yield 150 mg (10.4%). Anal. Calcd for $C_{24}H_{20}Cl_2NbP$: C, 57.29; H, 4.01; Cl, 14.11. Found: C, 57.12; H, 4.05; Cl, 14.21. ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 6.03 (s, 5H, C_5H_5), 7.08 (m, 10 H, $P(C_6H_5)_3$), 7.78 (m, 5H, $P(C_6H_5)_3$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ 109.2 (s, C_5H_5), 129.0, 129.1, 130.0, 130.2, 132.1, 132.2, 133.1, 133.2, 134.0 ppm. ^{31}P NMR (162.0 MHz, C_6D_6, 300 K): δ −30.5 (s, NbCP) ppm.

Method b. In a procedure similar to that of method a, starting from 0.60 g of **2** (1.04 mmol) in 30 mL of toluene and 0.57 g of $Ph_3P{=}CH_2$ (2.08 mmol) in 30 mL of toluene, 42 mg of **4** (8% yield) was obtained.

Crystallographic data for **4**: $C_{24}H_{20}Cl_2NbP$, $M_r = 503.18$, crystal dimensions 0.30 × 0.25 × 0.05 mm, monoclinic, space group $P2_1/n$, $a = 9.9053(8)$, $b = 13.4053(9)$, $c = 16.8249(15)$ Å, $\beta = 94.180(7)°$, $V = 2228.1(3)$ Å^3, $T = 223(2)$ K, $Z = 4$, $D_c = 1.500$ g cm^{-3}, $\mu = 0.859$ mm^{-1}. A total of 30 377 reflections was collected, of which 4470 were unique ($R_{int} = 0.0502$): $\theta_{max} = 26.22°$, semiempirical absorption correction. R1 = 0.0234 (for 3833 reflections with $I > 2\sigma(I)$), wR2 = 0.0629 (all data). The structure was solved by direct methods and refined with full-matrix least squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic. Cambridge database files: CCDC-226534(4).

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Supporting Information Available: Tables containing full X-ray crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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