Synthesis and Structure of the Niobium(III) Phosphido Complex $(C_5H_5)_2Nb(CO)(P^iPrPh)$: Efficient "Gauche Effect" and Low Inversion Barrier in Bent-Metallocene Chemistry

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Summary: **Reaction of $Cp_2Nb(CO)H$ with $P^iPrPhCl$ afforded the ionic product $[Cp_2Nb(CO)(P^iPrPhH)]Cl$, which upon treatment with NaOH gives the neutral niobium phosphido complex $Cp_2Nb(CO)(P^iPrPh)$ (1). 1 crystallizes in the monoclinic space group $P2_1/c$, with $a = 16.899$ (3) Å, $b = 15.409$ (2) Å, $c = 13.717$ (3) Å, $\beta = 90.94$ (2)°, $V = 3571.2$ Å^3, $Z = 8$, and $R = 0.038$, with two independent chiral molecules in the asymmetric unit of the unit cell. One of them is related to the other by rough translation by a half of the lattice vector a. The torsion angles in both molecules involving the metal and the phosphorus lone pairs are close to 73°, thus indicating an efficient operation of the "gauche effect". The origin of the observed low inversion barrier at phosphorus is discussed.**

There is an increasing interest in transition-metal phosphido compounds as appropriate complexes for stereochemical and theoretical studies.[2] In addition, they appear to be promising ligands for the preparation of new bimetallic catalytic systems.[3] In the terminal phosphido transition-metal complexes, the geometry at the phosphorus atom is strongly dependent on the electronic environment of the metallic moiety. In the case where the metal fragment is electron-deficient, the phosphido ligand is able to donate three electrons and the phosphorus atom to adopt a trigonal-planar geometry;[4] a pyramidal one, with a free nonbonding lone pair, is usually encountered with electronically saturated metals.[5] The torsion angle between the phosphorus lone pair and the HOMO of the metal fragment has been recently discussed in terms of a "transition-metal gauche effect" by Gladysz et al. in some rhenium complexes;[6] this "gauche effect" is assumed to exert an influence on both chemical and configurational properties of the phosphido group, enhancing its nucleophilicity and reducing its inversion barrier. For these reasons, we have synthesized the terminal phosphido d^2 complex $Cp_2Nb(CO)P^iPrPh$ (1) with a well-defined metal-fragment HOMO and we report its properties herein.

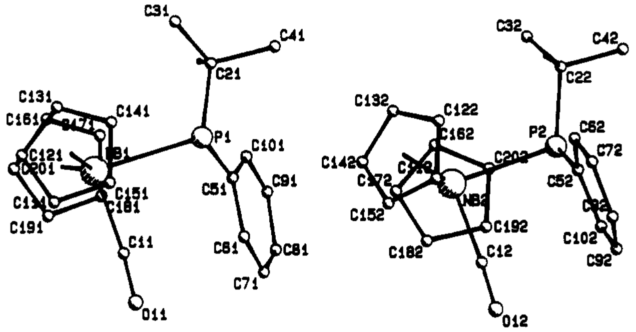
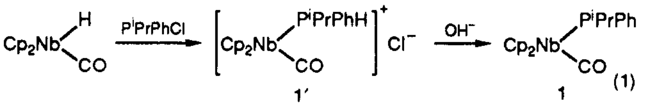


Figure 1. Two independent enantiomeric molecules of $Cp_2Nb(CO)P^iPrPh$ (1).

Results and Discussion

The niobiophosphine 1 was obtained by a two-step synthesis starting from the carbonyl monohydride $Cp_2Nb(CO)H$ and phenylisopropylchlorophosphine[7] (eq 1).



$$Cp_2Nb(H)(CO) \xrightarrow{P^iPrPhCl} \underset{1'}{[Cp_2Nb(P^iPrPhH)(CO)]^+} Cl^- \xrightarrow{OH^-} \underset{1}{Cp_2Nb(P^iPrPh)(CO)} \qquad (1)$$

The salt 1′ was formed in high yield and characterized by ^1H and ^{31}P NMR and IR spectroscopy. The ^1H NMR (D_2O) spectrum reveals the Cp nonequivalence (two doublets at 5.45 and 5.53 ppm, $^3J_{HP} = 2.2$ Hz) due to the asymmetric phosphorus center. Deprotonation of 1′ by sodium hydroxide led to the phosphido complex 1. The ^1H NMR ($(CD_3)_2CO$) spectrum of the neutral compound is temperature-dependent, in accordance with a dynamic process: at room temperature, a single Cp resonance is observed (δ 4.42 ppm, d, $^3J_{HP} = 1.3$ Hz), whereas two well-resolved signals appear at −70 °C (δ 5.31 ppm, d, $^3J_{HP} = 2$ Hz and δ 4.78 ppm, s). The coalescence temperature is found at −40 °C, giving an inversion barrier of 48 ± 2 kJ mol^{-1}. This value lies among the lowest inversion barriers at three-coordinate phosphorus, which were observed in the range of 48.1–60.2 kJ mol^{-1} in some rhenium,[6,8] iron,[9] and tungsten[10] phosphido complexes. In order

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Table I. Positional Parameters and Their Estimated Standard Deviations for $Cp_2Nb(CO)P^iPrPh$ (1)[a]

atom	x	y	z	B_{eq}, Å^2
Nb(1)	0.01025 (7)	0.13098 (5)	0.74392 (6)	2.31 (2)
Nb(2)	0.50659 (7)	0.16453 (5)	0.74970 (6)	2.50 (2)
P(1)	0.1594 (2)	0.0916 (2)	0.7846 (2)	2.53 (7)
P(2)	0.6542 (2)	0.1123 (1)	0.7579 (2)	2.44 (7)
CP(11)	−0.0122	0.0736	0.6096	
CP(21)	−0.0446	0.1532	0.8478	
CP(12)	0.4492	0.0945	0.6417	
CP(22)	0.4885	0.2123	0.8881	
O(11)	0.0638 (5)	0.3217 (4)	0.6799 (5)	5.1 (2)
O(12)	0.5668 (5)	0.3373 (4)	0.6451 (5)	4.3 (2)
C(11)	0.0483 (7)	0.2510 (5)	0.7045 (6)	3.2 (3)
C(12)	0.5477 (6)	0.2725 (6)	0.6811 (6)	2.7 (3)
C(21)	0.1712 (6)	−0.0075 (6)	0.8627 (6)	3.1 (2)*
C(31)	0.1270 (7)	−0.0847 (6)	0.8180 (7)	4.6 (2)*
C(41)	0.2608 (7)	−0.0296 (7)	0.8723 (8)	5.2 (3)*
C(51)	0.1929 (6)	0.1754 (5)	0.8708 (5)	2.2 (2)*
C(61)	0.2078 (6)	0.2585 (6)	0.8340 (6)	3.2 (2)*
C(71)	0.2288 (7)	0.3273 (6)	0.8928 (6)	3.9 (2)*
C(81)	0.2400 (7)	0.3155 (6)	0.9918 (6)	3.8 (2)*
C(91)	0.2289 (7)	0.2340 (6)	1.0299 (6)	3.5 (2)*
C(101)	0.2065 (6)	0.1650 (6)	0.9695 (6)	2.8 (2)*
C(22)	0.6644 (6)	−0.0074 (5)	0.7806 (6)	2.6 (2)*
C(32)	0.6125 (7)	−0.0378 (7)	0.8651 (7)	4.6 (2)*
C(42)	0.7507 (6)	−0.0280 (6)	0.8038 (6)	3.5 (2)*
C(52)	0.6915 (6)	0.1223 (5)	0.6335 (6)	2.5 (2)*
C(62)	0.6943 (6)	0.0573 (6)	0.5637 (6)	2.9 (2)*
C(72)	0.7237 (7)	0.0737 (6)	0.4705 (6)	3.6 (2)*
C(82)	0.7508 (7)	0.1543 (6)	0.4457 (7)	3.9 (2)*
C(92)	0.7495 (7)	0.2196 (7)	0.5154 (6)	4.0 (2)*
C(102)	0.7224 (6)	0.2048 (6)	0.6079 (6)	3.1 (2)*
C(111)	−0.0371 (7)	0.1420 (6)	0.5813 (6)	3.6 (2)*
C(121)	−0.0821 (7)	0.0776 (6)	0.6243 (6)	3.8 (2)*
C(131)	−0.0309 (7)	0.0081 (6)	0.6464 (6)	3.4 (2)*
C(141)	0.0463 (7)	0.0276 (6)	0.6179 (6)	3.6 (2)*
C(151)	0.0427 (7)	0.1129 (6)	0.5782 (6)	3.5 (2)*
C(161)	−0.0632 (7)	0.0787 (6)	0.8802 (6)	3.5 (2)*
C(171)	0.0076 (7)	0.1153 (6)	0.9187 (6)	3.8 (2)*
C(181)	0.0073 (7)	0.2045 (6)	0.8958 (6)	4.0 (2)*
C(191)	−0.0654 (7)	0.2222 (7)	0.8450 (7)	4.1 (2)*
C(201)	−0.1092 (7)	0.1453 (6)	0.8344 (6)	3.9 (2)*
C(112)	0.4971 (7)	0.1189 (6)	0.5842 (6)	3.2 (2)*
C(122)	0.5006 (7)	0.0418 (6)	0.6400 (6)	3.4 (2)*
C(132)	0.4332 (7)	0.0379 (6)	0.6975 (7)	4.1 (2)*
C(142)	0.3882 (7)	0.1125 (6)	0.6784 (7)	4.5 (2)*
C(152)	0.4267 (7)	0.1615 (6)	0.6086 (6)	3.8 (2)*
C(162)	0.4733 (7)	0.1417 (7)	0.9166 (7)	4.5 (2)*
C(172)	0.4187 (8)	0.2029 (7)	0.8752 (7)	5.1 (3)*
C(182)	0.4607 (7)	0.2754 (7)	0.8521 (7)	4.7 (3)*
C(192)	0.5422 (7)	0.2611 (7)	0.8776 (7)	4.8 (3)*
C(202)	0.5474 (7)	0.1805 (7)	0.9191 (7)	4.6 (2)*
HLP(1)	0.1980	0.0823	0.6957	
HLP(2)	0.6924	0.1604	0.8314	

[a] CP denotes the gravity centers of cyclopentadienyl rings. HLP denotes the dummy hydrogen atoms representing the phosphorus lone pairs. Starred values denote atoms refined isotropically.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Nb(CO)P^iPrPh$ (1)[a]

molecule 1		molecule 2	
Nb(1)–P(1)	2.644 (3)	Nb(2)–P(2)	2.622 (3)
Nb(1)–C(11)	2.034 (9)	Nb(2)–C(12)	2.039 (9)
Nb(1)–CP(11)	2.073	Nb(2)–CP(12)	2.062
Nb(1)–CP(21)	2.063	Nb(2)–CP(22)	2.064
C(11)–O(11)	1.18 (2)	C(12)–O(12)	1.16 (2)
P(1)–C(21)	1.874 (9)	P(2)–C(22)	1.879 (9)
P(1)–C(51)	1.834 (8)	P(2)–C(52)	1.834 (8)
P(1)–Nb(1)–C(11)	87.7 (3)	P(2)–Nb(2)–C(12)	86.5 (4)
P(1)–Nb(1)–CP(11)	104.5	P(2)–Nb(2)–CP(12)	107.8
P(1)–Nb(1)–CP(21)	107.2	P(2)–Nb(2)–CP(22)	103.0
C(11)–Nb(1)–CP(11)	101.9	C(12)–Nb(2)–CP(12)	104.8
C(11)–Nb(1)–CP(21)	103.2	C(12)–Nb(2)–CP(22)	101.0
CP(11)–Nb(1)–CP(21)	140.0	CP(12)–Nb(2)–CP(22)	140.6
Nb(1)–C(11)–O(11)	174.4 (9)	Nb(2)–C(12)–O(12)	175.1 (8)
Nb(1)–P(1)–C(21)	113.6 (4)	Nb(2)–P(2)–C(22)	113.1 (3)
Nb(1)–P(1)–C(51)	104.9 (3)	Nb(2)–P(2)–C(52)	106.0 (3)
C(21)–P(1)–C(51)	100.1 (4)	C(22)–P(2)–C(52)	101.8 (4)

[a] CP denotes the gravity centers of cyclopentadienyl rings.

to obtain precise geometrical information for 1, and in particular to ascertain the structural features of the niobium–phosphorus moiety, we undertook a single-crystal X-ray analysis.

Structure of $Cp_2Nb(CO)(P^iPrPh)$ (1). There are two enantiomeric molecules of 1 in the asymmetric unit (Figure 1) of the centrosymmetric $P2_1/c$ space group. It is worth noting that only one of these molecules per asymmetric unit could give rise to a racemic structure. An inspection of atomic coordinates (Table I) shows that the second molecule (isomer S' in Figure 1) is translated by half of the lattice vector **a** with respect to the first molecule (isomer R). In both molecules the arrangement of the $Cp_2Nb(CO)P^iPr$ fragments with respect to the lattice vectors is practically the same, so the overall structure may be regarded as an interpenetration of two sublattices: one of the isomers R and S of molecule 1 and the other of the isomers S' and R' of molecule 2. The sole difference between molecules 1 and 2 consists of the inversion of the lone pair and of the phenyl group at the phosphorus atom.

The cyclopentadienyl rings are eclipsed. The Nb–CP(centroid) distances of 2.062–2.073 Å (Table II) are slightly longer than those observed in other Nb^{III} bis(cyclopentadienyl) carbonyl complexes ($Cp_2Nb(CO)H$, 2.04 Å;[11] $Cp_2Nb(CO)SH$, 2.05 Å[12]). They are close to the values found in Cp_2NbH_3 (2.06 Å)[13] and $[Cp_2Nb^{III}(SiMe_3)(C_2H_4)]$ (2.086 Å)[14] but shorter than the corresponding distances in $Cp_2Nb^{IV}Cl_2$ (2.09 Å)[15] and in some Nb^V bis(cyclopentadienides) (2.10–2.13 Å).[14,16] The CP–Nb–CP angles (mean 140.3°) are among the largest observed in bis(cyclopentadienyl)niobium complexes (126–143°).[16] This suggests an electron-rich nature of the Cp_2Nb fragment and a covalent nature of the niobium–phosphorus bond and indicates that the phosphido ligand behaves as a good electron donor.[17]

The P–Nb–CP(centroid) angles involving the cyclopentadienyl rings lying, with respect to the bisecting OC–Nb–P plane, on the side of the phosphorus lone pair (CP11 and CP21, 104.5 and 103.0°) are smaller than the corresponding angles with the CP12 and CP22 rings lying on the side of the phenyl groups (107.2 and 107.8°). It is worth noting that in the structure of $Cp_2Mo(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$, in which the manganese atom is out of the bisecting H–Mo–P plane, both P–Mo–CP angles are exactly the same (107.8°).[18] The asymmetry of the P–Nb–CP angles of 1 may thus be due not only to the steric

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factors but also to the electronic effects of the phosphorus lone pair. The Nb–CO units are nearly linear with normal Nb^{III}–C bond lengths close to 2.03–2.04 Å.

There are few reports of niobium–phosphorus bond lengths in organometallic compounds. In monocyclopentadienyl complexes they were found in the range 2.445 (5)–2.734 (1) Å.[16] The longest bonds are observed in $CpNb^{IV}Cl_3(dppe)$ bearing a sterically demanding dppe ligand.[19] The mean niobium–phosphorus (phosphine) distance of 2.565 (15) Å in $CpNb^{III}(PPh_3)_2(CO)(H)_2$[20] is shorter than the Nb–P (phosphide) bond lengths found in our structure (2.644 (3) and 2.622 (3) Å). It has been observed in some other cases that the M–P bonds to pyramidal phosphide ligands are longer than those to phosphines.[6,21] This was attributed to repulsions[22] between the nonbonding electron pairs at the transition metal and at the phosphido ligand. Such an interaction consisting of avoided overlap between the adjacent metal- and ligand-donor orbitals is called a transition-metal "gauche effect". Its operation was established by Gladysz in some rhenium phosphido complexes.[6] The sum of the three bond angles about P1 and P2 are equal to 318.6 and 320.9°, respectively, and are close to the corresponding values observed in other pyramidal terminal phosphido complexes.[6,21,23] It has been suggested that the larger bond angles about phosphorus atoms in transition-metal phosphido complexes than in simple organophosphines (PMe_3, 95°; PPh_3, 103°[24]) are probably due to steric and electronic effects of the bulky electron-releasing metal substituents. However, in the structure of 1 there are electron-buffering Cp ligands, which are able to retain an excess electron density, and an electron-accepting carbonyl group on the metal; the bulky, electron-releasing substituent is the ^iPr group of the phosphide. Consequently, it seems possible that some interactions involving the phosphorus lone pair and an antibonding orbital of the $Cp_2Nb(CO)$ fragment occurs therein. This will be discussed below.

The "Gauche Effect". According to Hoffmann's model of bonding in bent metallocenes,[25] the metal lone pair in d^2 metal complexes (Nb^{III}, Mo^{IV}, ...) occupies an orbital ($1a_1$ in C_{2v} or 1a′ in C_s point groups, respectively) that is clearly localized in the plane bisecting the CP–M–CP angle. This nonbonding HOMO orbital may be stabilized by π-backbonding interactions with electron-withdrawing ligands such as CO but remains highest in energy. Thus, these d^2 bent bis(cyclopentadienides) seem to be a very likely class of compounds for conformational studies of the gauche effect. To measure its extent in 1, we needed the positions of the phosphorus lone pairs in both molecules. They were determined by locating the dummy hydrogen atoms (HLP, Table I) 1.4 Å away from P1 and P2 with the idealized geometries (HYDRO program of SDP[26]) for tetrahedral phosphorus. The torsion angles C(CO)–Nb–P–HLP, representative of the gauche effect, are equal to 72.9° (molecule 1) and 74.8° (molecule 2). These values are some 15° higher than those reported by Gladysz for rhenium terminal phosphides,[6] thus indicating that the gauche effect is efficiently operating in the structure discussed here and that the d^2 bent metallocenes are probably among the best adapted compounds for these kinds of stereochemical considerations. The maximal value of 90° for the torsion angles cannot be reached because of the steric hindrance induced by the presence of ^iPr and Ph groups at the phosphorus atoms. The operation of the gauche effect forbids the phosphorus lone pair to lie in the bisecting plane. Consequently, this position, assuring the weakest repulsions with the Cp rings, is occupied by the ^iPr group, which is bulkier than Ph.[27] The torsion angles C(CO)–Nb–P–C(^iPr) are equal to 14.5 and 18.4° for molecules 1 and 2, respectively.

Phosphorus Inversion. We have already mentioned that the phosphorus inversion barrier in 1 is observed in the lowest known range. The primary explanation of this low energy barrier may be approached by a supposition of the niobium–phosphorus bond breaking. At first sight this seems to be apparently supported by the long Nb–P bonds, suggesting some ionic nature ($Nb^{\delta+}$–$P^{\delta-}$) for these bonds. However, such a singular explanation is not likely, because the cyclopentadienyl protons are observed at high field in the ^1H NMR spectrum, which indicates a rather electron-rich Cp_2Nb fragment. Moreover, as discussed above, the long Nb–P bonds may result from the repulsions between the metal and the phosphorus lone pairs. Generally, inversion barriers are decreased by substituents that are good σ donors or good π acceptors. A carbonyl ligand in 1 is formally able to accept some electron density from a phosphorus lone pair. One of its antibonding π* orbitals (a′ in the bisecting plane) is already involved in the interactions with the HOMO (metal lone pair), but the second π* one (a″) remains free. If there could be some overlap of this orbital with a phosphorus lone pair, the infrared stretching frequency ν_{CO} should be shifted to lower energies with respect to any other structurally analogous system without a potential π-donor ligand. However, in an example of such a system, $Cp_2Nb(CO)H$, the ν_{CO} vibration was observed at 1902 cm^{-1},[28] 20 cm^{-1} lower than in 1 (1922 cm^{-1}).

Consequently, we looked for an alternative origin of the low inversion barrier in 1 by considering the electronic structure of the metallocene Cp_2Nb fragment. We have already noted in the discussion of the gauche effect that in the presence of a carbonyl ligand the HOMO is stabilized by the *in-plane* a′ π* CO orbital. Interestingly, some mixing of the a″ π* CO orbital with the a″ antibonding Cp_2M orbitals occurs, leading also to stabilization of this unoccupied a″ (Cp_2M) orbital. Hoffmann suggested that the molecular orbital resulting from this interaction is occupied in the 20-electron nitrosyl complexes of molybdenum $Cp_2Mo(NO)R$.[25,29] Given the formal electronic analogy between the 10-electron [Mo(NO)R] fragment and $[Nb(CO)PR_2]$ in 1, we conclude that the phosphorus lone pair may interact with the Cp_2Nb a″ antibonding orbital, thus allowing an easier transient planarization of phosphorus. A gauche effect assures the best overlap between the phosphorus lone pair, which is roughly perpendicular to the bisecting plane, and the symmetry-adapted Cp_2Nb

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Table III. Crystallographic Data for $Cp_2Nb(CO)P^iPrPh$ (1)

mol formula	$C_{20}H_{22}NbOP$
fw, g	402.28
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
cell dimens	
a, Å	16.899 (3)
b, Å	15.409 (2)
c, Å	13.717 (3)
β, deg	90.94 (2)
V, Å^3	3571.2
Z	8
ρ_{calc}, g cm^{-3}	1.496
linear abs coeff, μ, cm^{-1}	7.346
$F(000)$	1648
radiation, Å	λ(Mo Kα) = 0.71073
scan type	ω–2θ
scan speed, deg min^{-1}	1.5–8.3
scan width, deg	$\Delta\omega = 1.2 + 0.347 \tan\theta$
rflns measd	$\pm h,k,l$
θ range, deg	2–22
no. of rflns meads	4411
temp, K	296 (1)
decay, %	−3.6, cor
cutoff for obsd data	$I \geq 3\sigma(I)$
no. of unique obsd data (NO)	1920
no. of variables (NV)	225
transmissn coeff (DIFABS)	0.9107, 1.1340
$R(F)$	0.038
$R_w(F)$	0.039
weighting scheme	$w^{-1} = [\sigma^2(I) + (0.04I)^2]^{1/2}$
GOF	2.780

antibonding orbital. This may contribute to an explanation of asymmetry observed for the P–Nb–CP angles in the structure of 1.

Finally, the low inversion barrier due to an easy antibonding-orbital-assisted planarization of the phosphorus atom may be responsible for the particularity observed in the crystal structure of 1 consisting of the presence of two enantiomers in the asymmetric unit of the unit cell.

Experimental Section

Syntheses were performed under an argon atmosphere by using standard Schlenk-tube techniques. ^{1}H and ^{31}P NMR spectra were recorded on JEOL FX100 and Bruker WM400 spectrometers; chemical shifts are given relative to TMS and H_3PO_4. IR spectra were obtained on a Perkin-Elmer 580B spectrophotometer. $Cp_2Nb(CO)H$ was prepared according to the literature procedure.[28]

$[Cp_2Nb(CO)P^iPrPhH]^+Cl^-$ (1′). To a toluene solution (20 mL) of $Cp_2Nb(CO)H$ (0.3 g, 1.19 mmol) was added dropwise a toluene solution (2 mL) of $P^iPrPhCl$ (0.27 g, 1.22 mmol). An orange precipitate was gradually formed which, after the system was stirred for 30 min, was collected, washed with heptane, and dried under vacuum (0.41 g, yield 78%). Anal. Calcd for $C_{20}H_{23}OPClNb$: C, 54.73; H, 5.21. Found: C, 54.3; H, 5.4. NMR (δ, ppm): ^{1}H (D_2O) 7.61–7.54 (m, Ph), 5.45 (d, J = 2.2 Hz, Cp), 5.53 (d, J = 2.2 Hz, Cp), 2.31 (m, CH), 1.22 (m, CH_3), 5.54 (dd, J = 7.7, 349 Hz, PH); ^{31}P (D_2O) +36. IR (ν_{CO}, CH_2Cl_2): 1960 cm^{-1}.

$Cp_2Nb(CO)P^iPrPh$ (1). A 1 M aqueous solution of NaOH (15 mL) was added to a suspension of 1′ (0.4 g, 0.91 mmol) in 15 mL of toluene, and the mixture was stirred for 15 min. The organic layer was separated and evaporated, yielding a maroon product, which was washed with heptane and dried (0.26 g, yield 72%). Anal. Calcd for $C_{20}H_{22}OPNb$: C, 52.86; H, 4.85. Found: C, 51.7, H 4.3. NMR (δ, ppm): ^{1}H (C_6D_6) 7.61–6.89 (m, Ph), 4.42 (d, J = 1.3 Hz, Cp), 1.85 (m, CH), 1.20 (dd, J = 6.6, 13 Hz, CH_3); ^{31}P (C_6D_6) −13.7. IR (ν_{CO}, toluene): 1922 cm^{-1}.

Crystallographic Studies. An orange irregularly shaped crystal grown from acetone solution (approximate dimensions 0.25 × 0.15 × 0.12 mm) was mounted on an Enraf-Nonius CAD4 diffractometer. The crystal data and data collection parameters are summarized in Table III. The unit cell was determined and refined from 25 randomly selected reflections obtained by use of the CAD4 automatic routines. Intensities were corrected for Lorentz and polarization effects. All calculations were carried out by use of the Enraf-Nonius SDP package[26] with neutral-atom scattering factors. The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. The empirical absorption correction DIFABS[30] was applied. The Nb, P, O, and C (carbonyl) atoms were refined with anisotropic temperature factors and all other carbon atoms with isotropic factors. The positions of all the hydrogen atoms were calculated by the HYDRO program of SDP, and these atoms were placed riding on the carbon atoms bearing them and included in the final calculations with B_{iso} fixed at 5.0 Å^2.

Registry No. 1, 137966-97-3; 1′, 137966-98-4; $Cp_2Nb(CO)H$, 11105-68-3; $P^iPrPhCl$, 54006-34-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, complete bond distances and angles, and least-squares planes (7 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Convenient One-Pot Synthesis of *tert*-Butyldimethylantimony

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Summary: *tert*-Butyldimethylantimony, (t-Bu)Me_2Sb, was prepared by a one-pot reaction of $SbCl_3$ with 1 equiv of (t-Bu)MgCl at −50 °C followed by 2 equiv of MeMgBr at 0 °C in diethyl ether. (t-Bu)Me_2Sb was isolated in 64% yield (based on $SbCl_3$) after fractional vacuum distillation (63 °C at 30 Torr) and can be used as a precursor in the chemical vapor deposition of antimony-containing semiconductor materials.

The III/V antimony-containing semiconductor materials are useful in infrared detection, high-speed devices, and optical fiber communication systems. A variety of binary, ternary, and quaternary III/V semiconductor systems containing antimony have been investigated for use in infrared detectors operating in the 3–5- and 8–12-μm spectral ranges.[1] These wavelength ranges are important since they are natural windows in the atmosphere for IR transmission.

The ternary alloy $InAs_{1-x}Sb_x$ has the smallest band gap ($x = 0.6$, $E_g \approx 0.1$ eV at 300 K) of any of the III/V semiconductor materials, and this has attracted interest for

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