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Notes

The First Arsenido-Substituted Niobocene Derivative

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Organometallic complexes of the main group elements are of interest both from the viewpoint of elucidating the bonding between transition metals and main group elements and for searching for new reactive species.[1−5] However, synthetic approaches to the main group element substituted complexes are often restricted since they either demand preparation of difficult starting materials or face severe reaction conditions as in the case of widespread transmetalation reactions, usually occurring under strong reducing conditions.[6] We have recently developed a convenient entry into phosphorus-substituted niobocene chemistry (Scheme 1), based on direct insertion of monohalophosphines into the Nb−H bond under very mild conditions.[7] This approach is also promising for the synthesis of other group 15 derivatives, and we now report our results on the preparation of the first arsenic-substituted niobocenes, which reveals new interesting reactivity patterns in comparison with the related phosphorus chemistry.

Results and Discussion

Similarly to the case of phosphorus, diethylarsenic bromide smoothly inserts into the Nb−H bond of Cp_2NbH_3, affording an ionic complex $[Cp_2NbH_2(HAsEt_2)]Br$ (**6**) in high yield (~83%). Complex **6** precipitates in form of pale-beige flakes after mixing toluene solutions of $BrAsEt_2$ and Cp_2NbH_3 at room temperature. This compound was established by ^1H and ^{13}C NMR and IR spectroscopy.[8] The ^1H NMR spectrum of **6** is in general similar to that of **1**. The As−H resonance was not found, however, either because of quadrupolar broadness due to the ^{75}As nucleus or because of rapid proton/deuterium exchange in MeOD, analogous to the case of its phosphorus analogue **1**.[7] However, deprotonation of **6** results in a product quite different from that formed in the case of **1**: the monoarsenido complex $Cp_2NbH_2AsEt_2$ (**7**) is produced in 93% yield (eq 1) rather than the hydride arsine compound $Cp_2Nb(HAsEt_2)H$.

$$Cp_2NbH_3 + BrAsEt_2 \xrightarrow[-10\text{ to }-20\ ^\circ C]{\text{toluene}} \underset{\mathbf{6}}{(Cp_2NbH_2(HAsEt_2))Br\downarrow} \xrightarrow[Et_2O]{NaN(SiMe_3)_2} \underset{\mathbf{7}}{Cp_2NbH_2AsEt_2} \quad (1)$$

For **1** the situation was reverse; i.e., phosphine complex **3** was the only detectable product while the formation of intermediate phosphido complex **2** was established only indirectly.[7] Formation of **7** suggests a delicate balance between a trisubstituted d^0 structure and the d^1 $Cp_2Nb(HER_2)H$ isomer depending on the nature of the main group element E. In our opinion, the preference of a trisubstituted structure for **7** is driven by the decreasing energy of the As−H bond in comparison with the P−H bond. Formation of **7** also further confirms our earlier deduction that deprotonation of $Cp_2NbH_2(ER_2H)X$ initially affords a trisubstituted complex $Cp_2NbH_2ER_2$.[7] Complex **7** was obtained as air-sensitive pale crystals after recrystallization from ether. The formulation of **7** as an arsenido complex was supported by the NMR and IR spectra[8] and X-ray diffraction study (Figure 1).

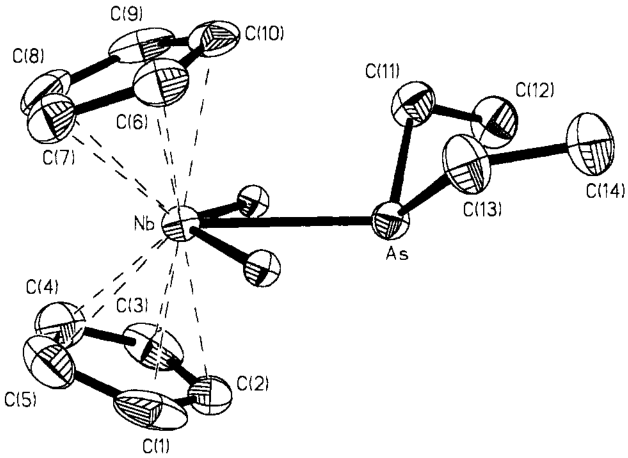

Figure 1. Molecular structure of **7**.

Selected bond distances and angles in **7** are given in Table 1. The molecular structure determination of **7** revealed it to be a trisubstituted d^0 niobocene with the central position of the arsenido group at an Nb−As distance 2.720(1) Å, which is in perfect agreement with the calculated distance of 2.73 Å obtained by subtracting the carbon radius (0.77 Å[9]) from the Nb−C (Et) bond length (2.316(8) Å) in $Cp_2Nb(C_2H_4)Et$[10] and combining the resulting niobocene radius (1.55 Å) with the As radius of 1.18 Å.[9] Two hydrides were also located (but not refined) at distances 1.752 and 1.745 Å, close to those found for Cp_2NbH_3 (average 1.69(4) Å).[11] The geometry around arsenic can be described as tetrahedral, taking into account the

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(6) For examples of transmetalation see: (a) Dick, D. G.; Stephan, D. W. *Organometallics* **1991**, *10*, 2811. (b) Cassidy, J. M.; Whitmire, K. *Inorg. Chem.* **1991**, *30*, 2788.

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(8) These data have been deposited as supplementary material.

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(12) (a) For the structure of $Cp_2TaH_2SiMe_2Ph$ see: Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701. (b) For the structure of $Cp_2Ta(SiMe_2H)_2$ see: Jiang, Q.; Carrol, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648. (c) For the structure of $Cp_2TaH_2(SnMeCl_2)$ see: Arkhireeva, T. M.; Bulychev, B. M.; Protsky, A. N.; Soloveichik, G. L.; Bel'sky, V. K. *J. Organomet. Chem.* **1986**, *317*, 33.

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Scheme 1

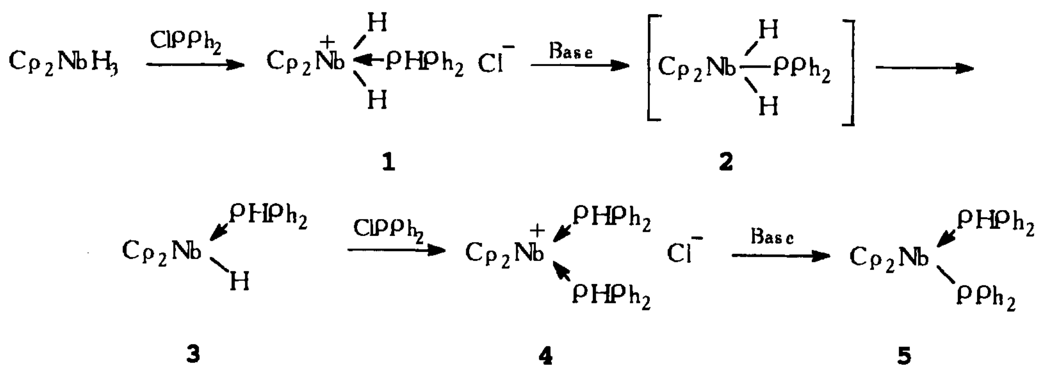

Table 1. Selected Bond Distances (Å) and Angles (deg) for $Cp_2NbH_2AsEt_2$

	Bonds		
Nb−As	2.720(1)	H(15)−Nb	1.752
H(16)−Nb	1.745	Nb−X(1)[a]	2.082
Nb−X(2)	2.060	As−C(13)	1.981(9)
As−C(11)	1.996(6)		
	Angles		
As−Nb−H(15)	51.1	As−Nb−H(16)	61.5
H(15)−Nb−H(16)	112.1	C(11)−As−C(13)	97.6(0.3)
Nb−As−C(11)	106.9(0.2)	Nb−As−C(13)	106.0(0.2)
As−C(11)−C(12)	112.8(0.4)	As−C(13)−C(14)	114.6(0.6)
Cp(1)−Cp(2)[b]	137.7		

[a] X(1) and X(2) are the gravity centers of the cyclopentadienyl rings. [b] Cp(1)−Cp(2) denotes the angle between the normals to the cyclopentadienyl rings.

stereoactive arsenic lone pair. The latter is fairly well directed toward one of the Cp rings to minimize repulsion from the Nb−H bonds. Complex **7** is the second example of a structurally characterized trisubstituted niobocene, the first being Cp_2NbH_3.[11] Structures of some related group 4 element/hydride substituted tantalocenes are also known.[12]

Complex **7** has two nucleophilic centers: the Nb−H bond, amenable to the insertion process, and the arsenic lone pair. However, repeated action of $BrAsEt_2$ on **7** in toluene resulted exclusively in the formation of a cationic complex $[Cp_2NbH_2(AsEt_2AsEt_2)]Br$ (**8**), a product of nucleophilic substitution at the chloroarsine by the arsenido lone pair of **7**. No products of the insertion into the Nb−H bond of **7** were found, which is consistent with the higher availability of the arsenido lone pair. The high nucleophilicity of terminally coordinated arsenido ligands was earlier exhibited by their propensity to form bridged arsenido complexes and in their reactions with alkyl halides.[13] The formulation of **8** as a diarsine hydride complex is derived from the following spectroscopic data: (1) in the ^1H NMR spectrum of **7**, the ratio of Cp ring signal to hydride signal is 10:2, (2) only the Nb−H stretching frequency (1624 cm^{-1}) is observed in the IR spectrum, and (3) the ^{13}C NMR spectrum exhibits two different $AsEt_2$ groups; moreover, the signals of coordinated $AsEt_2$ in **8** are close to those of **6** (20.75 and 10.11 versus 19.58 and 11.24 ppm), while the signal of uncoordinated $AsEt_2$ are close to the signal of free $(AsEt_2)_2$ (17.22 and 12.24 versus 14.70 and 12.73 ppm). ^{13}C NMR does not conform to the insertion structure $[Cp_2Nb(AsEt_2H)_2]Br$ (**9a**), while another insertion structure $[Cp_2Nb(AsEt_2H)(AsEt_2)H]Br$ (**9b**) can be rejected on the basis of ^1H NMR and IR. **9a** and **9b** could be precursors to $Cp_2Nb(AsEt_2)_2H$ (**10a**) and $Cp_2Nb(HAsEt_2)AsEt_2$ (**10b**), and it would be of interest to establish which structure, **10a** or **10b**, is more preferable. Since the reaction between **7** and $BrAsEt_2$ does not lead to **9a** or **9b**, alternative synthetic routes are desirable. This problem is currently being explored.

Table 2. Positional Parameters and Their Estimated Standard Deviations for $Cp_2NbH_2AsEt_2$

atom	*x*	*y*	*z*	*U*(iso)/*U*(eq),[a] Å^2
Nb	0.1715(1)	0.2348(1)	0.1960(1)	0.021(1)
As	0.0302(1)	0.3958(1)	0.2141(1)	0.026(1)
C(1)	0.4718(9)	0.2611(7)	0.2999(7)	0.055(3)
C(2)	0.4194(9)	0.3276(5)	0.2138(9)	0.048(3)
C(3)	0.3813(10)	0.2875(6)	0.1103(8)	0.050(3)
C(4)	0.4054(9)	0.1975(6)	0.1262(8)	0.047(3)
C(5)	0.4630(9)	0.1794(5)	0.2402(8)	0.047(3)
C(6)	0.0011(9)	0.1458(5)	0.2830(7)	0.035(3)
C(7)	0.1089(10)	0.0894(4)	0.2435(7)	0.038(3)
C(8)	0.0566(11)	0.0949(5)	0.1200(8)	0.047(3)
C(9)	−0.0842(9)	0.1554(5)	0.0856(7)	0.044(3)
C(10)	−0.1164(8)	0.1877(4)	0.1861(7)	0.034(3)
C(11)	−0.1943(9)	0.4039(4)	0.0856(7)	0.038(3)
C(12)	−0.2424(10)	0.4994(5)	0.0448(7)	0.049(3)
C(13)	−0.0697(10)	0.3844(5)	0.3416(7)	0.039(3)
C(14)	−0.1729(10)	0.4643(5)	0.3577(7)	0.047(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U**(*ij*) tensor.

Experimental Section

All manipulations were carried out *in vacuo* using conventional Schlenk techniques. Solvents were dried over sodium benzophenone ketyl and distilled into the reaction vessel by high-vacuum gas phase transfer. NMR spectra were recorded on a Varian VXR-400 spectrometer (^1H, 400 MHz; ^{13}C, 100.4 MHz). Cp_2NbH_3 was prepared as earlier described.[7] Satisfactory elemental analyses could not be obtained due to formation of carbides.

Preparation of $Cp_2NbH_2(HAsEt_2)Br$ (6). Excess of $BrAsEt_2$ (1 mL, 8.12 mmol) was added dropwise to 100 mL of a toluene solution of Cp_2NbH_3 (1.46 g, 6.46 mmol). A white voluminous precipitate was formed immediately. After filtration of the reaction solution, the powder was washed with an additional 50 mL of toluene and dried in vacuo. Yield: 2.34 g (5.34 mmol, 82.6%).

Preparation of $Cp_2NbH_2AsEt_2$ (7). A 2.34 g (5.34 mmol) sample of **6** was suspended in 100 mL of ether, 1.008 g of $NaN(SiMe_3)_2$ in 50 mL of ether was added, and the mixture thus obtained was stirred for 1 h, until the precipitate was almost completely dissolved. Volatiles were removed in vacuo, 50 mL of toluene was added, and the resulting yellow solution was filtered. Solvent was removed in vacuo, yielding 1.77 g (4.95 mmol, 93%) of a yellow crystalline substance.

Preparation of $Cp_2NbH_2(AsEt_2AsEt_2)Br$ (8). A 0.35 mL quantity of Et_2AsBr was added dropwise to a solution of 0.80 g (2.24 mmol) of **7** in 100 mL of toluene. In a few minutes, an orange powder

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Table 3. Crystal Data and Parameters of the Crystallographic Data Collection and Refinement

empirical formula	$C_{14}H_{22}AsNb$	$F(000)$	720
color, habit	yellow needles	temp, K	173
crystal system	monoclinic	2θ range, deg	2−50
space group	$P2_1/n$ (No. 14)	scan mode	θ−2θ
unit cell parameters		no. of rflns collected	3145
a, Å	8.087(2)	no. of obs rflns ($F > 4.0\sigma(F)$)	2353
b, Å	15.071(3)	no. of params	145
c, Å	12.261(2)	data/param ratio	16.22
β, deg	108.45(3)	weighting scheme	$w^{-1} = [\sigma^2(F) + 0.000000(F^2)]^{-1}$
V, Å^3	1417.6(1.1)	final R indices (obs data)[a]	$R = 0.0490$
Z	4		$R_w = 0.046$
radiation, Å	λ(Mo Kα) = 0.71069	final R indices (all data)	$R = 0.0661$
diffractometer	Siemens P4		$R_w = 0.0581$
monochromator	graphite	goodness of fit	2.00
density (calc), g/cm^3	1.678	max resid, e/Å^3	0.8637
abs coeff, cm^{-1}	31.00	min resid, e/Å^3	−0.9220

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{0.5}$.

precipitated. This was filtered off, washed with ether, and dried in vacuo. Yield: 1.00 g (1.54 mmol, 68.6%).

X-ray Diffraction Study of 7. Crystals suitable for X-ray diffraction study were grown from a solution of **7** in diethyl ether. A Siemens P4 four-circle diffractometer was employed to collect the data. Positional parameters and their estimated standard deviations are given in Table2, and the crystal data and parameters of crystallographic data collection and refinement are presented in Table 3. Unit cell parameters were determined from least-squares refinement of a set of 25 centered reflections. Two reflections were measured every 2 h as orientation and intensity checks; significant decay of intensity was not observed. The data were corrected for Lorentz, polarization, and absorption (ψ scan mode). The structure was solved by direct methods and refined by full-matrix least-squares procedures (SHELXS-86[14]) with anisotropic temperature factors for all the non-hydrogen atoms. Hydrogen atoms, including hydrides, were found from a difference map and refined groupwise together with the positions of the corresponding carbon atoms by a riding model with fixed isotropic thermal parameters ($U = 0.05$). Contributions of hydrides were taken into account in the last refinement, all their parameters being fixed.

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Supplementary Material Available: Tables of NMR, IR, and HRMS data and for **7** tables of anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom positional parameters, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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