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Notes

Synthesis and X-ray Crystal Structures of Pnictogen-Bridged, Bimetallic Complexes Containing Main Group Metal and Tricarbonylnickel Fragments

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Summary: Reactions of monomeric, base-stabilized aluminum pnictines of the type dmap−Al(Me)$_2$E(SiMe$_3$)$_2$ (dmap = 4-(dimethylamino)pyridine, E = P, As, Sb) with Ni(CO)$_4$ lead to the formation of pnictogen-bridged complexes of the type dmap−Al(Me$_2$)E(SiMe$_3$)$_2$−Ni(CO)$_3$ (E = P ***1****, As* ***2****, Sb* ***3****). This reaction for the first time offers a simple and general pathway to bimetallic pnictogen-bridged complexes containing both a main group metal and a tricarbonylnickel fragment.* ***2*** *and* ***3*** *were characterized by single-crystal X-ray diffraction and represent the first examples of a bimetallic arsenic and antimony complex of this type.*

Introduction

The coordination of triorganopnictines R$_3$E to transition metal compounds ML$_n$ is one of the basic reactions in coordination chemistry. Apart from simple complexes with a 1:1 molar ratio of pnictogen and transition metal, metal-rich complexes containing a bridging pnictogen center between two equal or different transition metals are also well known.[1] Bimetallic complexes including a group 13 metal fragment (R$_x$M′) and a transition metal fragment (ML$_n$) have been studied to a far lesser extent. Considering the steadily growing number of complexes with a direct bond between a transition metal and a group 13 metal,[2] surprisingly few pnictogen-bridged compounds are known. The handful of structurally characterized compounds are simple Lewis acid−base adducts of group 13 trialkyls R$_3$M′ or trihalides Cl$_3$M′ and transition metal complexes of the type L$_n$Fe−E=CR$_2$ (E = P, As)[3] and LW≡P.[4] Me$_3$N−Al(CH$_2$SiMe$_3$)$_2$-PPh$_2$−Cr(CO)$_5$, which was synthesized by cleavage of a group 13 phosphide heterocycle, [(Me$_3$SiH$_2$C)$_2$AlPPh$_2$]$_2$, with (Me$_3$N)Cr(CO)$_5$,[5] is the only structurally characterized example of this desired class of compounds containing a M′−E σ-bond.[6] Similar compounds containing the higher homologues of group 15, Sb and Bi, are unknown, so far. Since the number of group 13/15 heterocycles is steadily growing, in particular those containing the higher homologue of group 15, Sb,[7] this last type of reaction seemed very promising for the synthesis of the desired complexes. Unfortunately, Beachley et al. succeeded only in very few cases. They suggested that the reactivity of the heterocycles toward (Me$_3$N)Cr(CO)$_5$ depends on the degree of association and the Lewis acidity of the heterocycle in solution.[8] In addition, metathetical reactions of transition metal diorganophosphide anions with main group metal halides were not successful.[9] Until now, there is no generally applicable reaction pathway.

Recently we published the synthesis and X-ray structures of several monomeric, Lewis base-stabilized group 13/15 compounds of the type base−M′(R$_2$)E(SiMe$_3$)$_2$ (R = Me, Et, *i*-Bu; M′ = Al, Ga; E = P, As, Sb, Bi), which were obtained by ring cleavage reactions of group 13/15 heterocycles [R$_2$M′E(SiMe$_3$)$_2$]$_x$ with the strong Lewis base 4-(dimethylamino)pyridine (dmap).[10] Since these

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compounds already are monomeric with a lone pair at the pnictogen center, they should be suitable starting compounds for the synthesis of bimetallic pnictogen-bridged complexes. We therefore studied reactions of monomeric aluminum pnictines dmap−Al(Me$_2$)E(SiMe$_3$)$_2$ with Ni(CO)$_4$, which lead under elimination of carbon monoxide in good yield to the formation of pnictogen-bridged, bimetallic compounds of the type dmap−Al(Me$_2$)E(SiMe$_3$)$_2$−Ni(CO)$_3$ (E = P **1**, As **2**, Sb **3**).

Experimental Section

General Considerations. All manipulations were performed in a glovebox under an argon atmosphere or by standard Schlenk techniques.[11] Solvents were dried and distilled from sodium benzophenone ketyl or Na/K alloy prior to use. Ni(CO)$_4$ was commercially available from Strem Chemicals and used as received. dmap−Al(Me$_2$)P(SiMe$_3$)$_2$, dmap−Al(Me$_2$)As(SiMe$_3$)$_2$,[10c] and dmap−Al(Me$_2$)Sb(SiMe$_3$)$_2$[10a] were prepared by literature methods. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} spectra were recorded using a Bruker AMX 300 and a Bruker AC 200 P spectrometer and are referenced to internal C$_6$D$_5$H (δ(^{1}H) 7.154, δ(^{13}C) 128.0) or external H$_3$PO$_4$ (δ(^{31}P) 0.0), respectively. Infrared spectra were recorded as pentane solutions between KBr plates using a Nicolet Magna 550 FT-IR spectrometer. Melting points were measured in sealed capillaries and are not corrected. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.

General Preparation of dmap−Al(Me$_2$)E(SiMe$_3$)$_2$−Ni(CO)$_3$. At room temperature 0.26 g (1.5 mmol) of Ni(CO)$_4$ was added to a solution of dmap−Al(Me$_2$)E(SiMe$_3$)$_2$ (1 mmol; E = P, 0.36 g; As, 0.40 g; Sb, 0.45 g) in 20 mL of pentane. The initial rapid gas evolution finished in the course of 15 min, and the resulting clear, slightly yellow solution was stirred for another 15 min. Storage of the solutions at −30 °C yields **1**−**3** as slightly brown, crystalline solids slowly darkening upon prolonged evacuation. **2** and **3** can be recrystallized from pentane solutions at 0 °C to yield colorless crystals suitable for X-ray analysis.

dmap−Al(Me$_2$)P(SiMe$_3$)$_2$−Ni(CO)$_3$, 1: M = 499.31 g/mol; 0.42 g (0.84 mmol, 84%); mp 102−110 °C (dec). Anal. for C$_{18}$H$_{34}$AlPN$_2$NiO$_3$Si$_2$ found (calcd): C 43.18 (43.30); H 6.75 (6.86). ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C): δ −0.02 (d, $^3J_{PH}$ = 2.6 Hz, 6 H, AlMe$_2$), 0.47 (d, $^3J_{PH}$ = 4.6 Hz, 18 H, SiMe$_3$), 1.87 (s, 6 H, NMe$_2$), 5.71 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, C(3)−H), 8.09 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, C(2)−H). ^{13}C{^{1}H} NMR (50 MHz, C$_6$D$_6$, 25 °C): δ −6.1 (d, $^2J_{PC}$ = 16.1 Hz, AlMe$_2$), 3.4 (d, $^2J_{PC}$ = 8.4 Hz, SiMe$_3$), 38.5 (NMe$_2$), 107.0 (C(3)−H), 146.6 (C(2)−H), 155.9 (C(4)), 199.5 (d, $^2J_{PC}$ = 1.6 Hz, CO). ^{31}P NMR (120 MHz, C$_6$D$_6$, 25 °C): δ −275.2. IR (pentane): ν 1961, 1975 (ν_{CO}, E), 2048 (ν_{CO}, A$_1$) cm^{-1}.

dmap−Al(Me$_2$)As(SiMe$_3$)$_2$−Ni(CO)$_3$, 2: M = 543.26 g/mol; 0.52 g (0.95 mmol, 95%); mp 72 °C (dec). Anal. for C$_{18}$H$_{34}$AlAsN$_2$NiO$_3$Si$_2$ found (calcd): C 39.61 (39.80); H 6.44 (6.34). ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C): δ −0.02 (s, 6 H, AlMe$_2$), 0.49 (s, 18 H, SiMe$_3$), 1.91 (s, 6 H, NMe$_2$), 5.73 (d, $^3J_{HH}$ = 6.3 Hz, 2 H, C(3)−H), 8.04 (d, $^3J_{HH}$ = 6.3 Hz, 2 H, C(2)−H). ^{13}C{^{1}H} NMR (50 MHz, C$_6$D$_6$, 25 °C): δ −5.8 (AlMe$_2$), 4.0 (SiMe$_3$), 38.5 (NMe$_2$), 107.0 (C(3)−H), 146.6 (C(2)−H), 155.9 (C(4)), 199.8 (CO). IR (pentane): ν 1959, 1971 (ν_{CO}, E), 2046 (ν_{CO}, A$_1$) cm^{-1}.

dmap−Al(Me$_2$)Sb(SiMe$_3$)$_2$−Ni(CO)$_3$, 3: M = 590.09 g/mol; 0.54 g (0.91 mmol, 91%); mp 94 °C (dec). Anal. for C$_{18}$H$_{34}$AlN$_2$NiO$_3$SbSi$_2$ found (calcd): C 36.49 (36.61); H 5.92 (5.83). ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C): δ 0.03 (s, 6 H, AlMe$_2$), 0.56 (s, 18 H, SiMe$_3$), 1.91 (s, 6 H, NMe$_2$), 5.72 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, C(3)−H), 7.97 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, C(2)−H). ^{13}C{^{1}H} NMR (50 MHz, C$_6$D$_6$, 25 °C): δ −5.1 (AlMe$_2$), 4.6 (SiMe$_3$), 38.6 (NMe$_2$), 107.2 (C(3)−H), 146.4 (C(2)−H), 155.8 (C(4)), 200.9 (CO). IR (pentane): ν 1957, 1971 (ν_{CO}, E), 2042 (ν_{CO}, A$_1$) cm^{-1}.

Table 1. Crystallographic Data and Measurements for dmap−Al(Me$_2$)As(SiMe$_3$)$_2$−Ni(CO)$_3$ (2) and dmap−Al(Me$_2$)Sb(SiMe$_3$)$_2$−Ni(CO)$_3$ (3)

	2	3
molecular formula	C$_{18}$H$_{34}$AlAsN$_2$NiO$_3$Si$_2$	C$_{18}$H$_{34}$AlN$_2$NiO$_3$SbSi$_2$
fw	543.26	590.09
cryst syst, space group	triclinic, $P\bar{1}$ (no. 2)	triclinic, $P\bar{1}$ (no. 2)
a, Å	9.0967(3)	9.2518(7)
b, Å	9.3364(3)	9.4009(8)
c, Å	17.3256(6)	17.4533(12)
α, deg	101.305(2)	101.828(4)
β, deg	94.918(2)	94.941(5)
γ, deg	107.955(2)	107.267(4)
V, Å^3	1355.69(8)	1401.16(19)
Z	2	2
D_{calcd}, g cm^{-3}	1.331	1.399
temp, K	123(2)	123(2)
radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ, mm^{-1}	2.066	1.771
cryst dimens, mm	0.35 × 0.20 × 0.10	0.12 × 0.06 × 0.03
2θ_{max}, deg	50	50
no. of reflns rec	19065	15026
no. of nonequiv reflns	4755	4875
R_{merg}	0.060	0.072
no. of params refined	255	255
R1;[a] wR2[b]	0.026, 0.071	0.038, 0.075
goodness-of-fit[c]	1.078	0.967
final max., min. $\Delta\rho$, e Å^{-3}	0.467, −0.527	0.559, −0.598

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ (for $I > 2\sigma(I)$). [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] goodness of fit $= \{\sum[w(|F_o^2| - |F_c^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$.

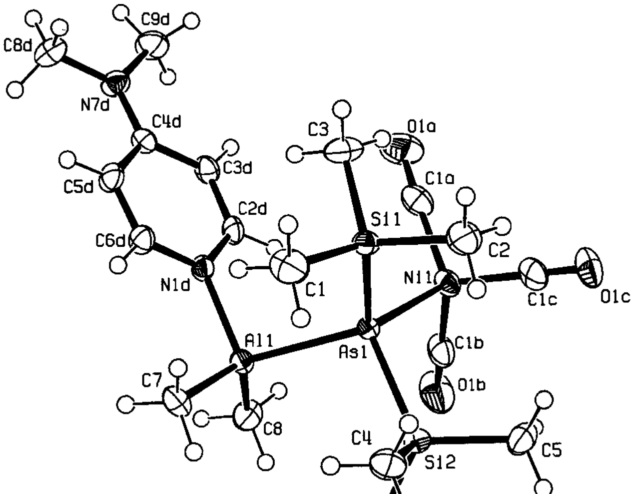

Figure 1. Molecular structure of **2** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Al1−N1d 1.966(2), Al1−As1 2.479(1), Al1−C7 1.967(2), As1−Si1 2.344(1), As1−Ni1 2.419(1), Ni1−C1a 1.789(2), C1c−O1c 1.140(2), C7−Al−C8 117.7(1), Si1−As1−Si2 105.8(1), N1d−Al1−As1 102.1(1), Ni1−As1−Al1 119.7(1), Si1−As1−Ni1 109.4(1).

X-ray Structure Solution and Refinement. Crystallographic data of **2** and **3** are summarized in Table 1. Figures1 and 2 show the ORTEP diagrams of the solid state structures including selected bond lengths and angles of **2** and **3**. Data

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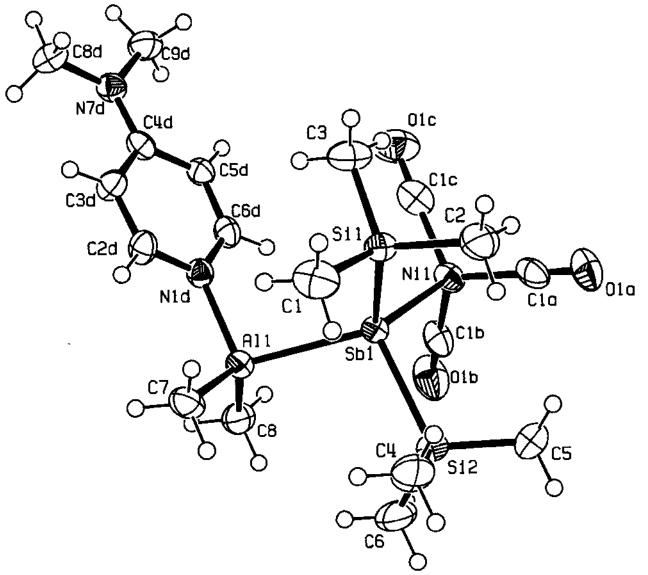
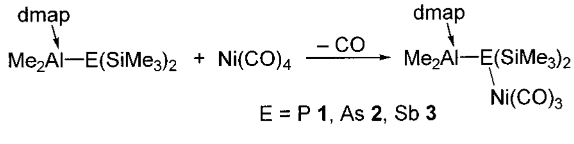


Figure 2. Molecular structure of **3** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Al1−N1d 1.965(4), Al1−Sb1 2.680(1), Al1−C7 1.966(4), Sb1−Si1 2.546(2), Sb1−Ni1 2.558(1), Ni1−C1b 1.774(5), C1b−O1b 1.144(5), C7−Al−C8 118.2(2), Si1−Sb1−Si2 104.0(1), N1d−Al1−Sb1 101.2(1), Ni1−Sb1−Al1 123.0(1), Si1−Sb1−Ni1 109.3(1).

were collected on a Nonius Kappa-CCD diffractometer. The structures were solved by Patterson methods (SHELXS-97)[12] and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[13] The crystallographic data of **2** and **3** (without structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-144765 (**2**) and CCDC-144766 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44)-1223/336033; e-mail: deposit@ccdc.cam-ak.uk).

Results and Discussion

Reactions of $Ni(CO)_4$ with monomeric, Lewis base-stabilized 13/15 compounds dmap−$Al(Me_2)E(SiMe_3)_2$ lead to the formation of pnictogen-bridged, bimetallic complexes of the type dmap−$Al(Me_2)E(SiMe_3)_2$−$Ni(CO)_3$ (E = P **1**, As **2**, Sb **3**).



$$\underset{\mathrm{Me_2Al{-}E(SiMe_3)_2}}{\overset{\mathrm{dmap}}{\downarrow}} + \mathrm{Ni(CO)_4} \xrightarrow{-\mathrm{CO}} \overset{\mathrm{dmap}\ \downarrow}{\mathrm{Me_2Al{-}E(SiMe_3)_2}}\underset{\mathrm{Ni(CO)_3}}{} \qquad (1)$$

E = P **1**, As **2**, Sb **3**

Upon storage at −30 °C **1**−**3** can be isolated as colorless crystalline solids. ^1H and ^{13}C NMR spectra show resonances due to the organic ligands bound to the Al and pnictogen centers shifted to higher field compared to the starting compounds. The formation of the complexes **1**−**3** is also confirmed by the presence of the carbonyl resonances in the ^{13}C NMR spectra (199.5 (**1**), 199.8 (**2**), and 200.9 (**3**) ppm) and the carbonyl stretching vibrations in the infrared spectra.[14] The increasing downfield shift of the carbonyl resonances and the decreasing wavenumber of the A_1 vibration (2048 (**1**), 2046 (**2**), 2042 (**3**) cm^{-1}) compared to $Ni(CO)_4$ (δ 191.9 ppm, C_6D_6; ν 2057 cm^{-1}) point to a decrease in C≡O and an increase in Ni−C bond order. On the background of the synergistic σ-donor/π-acceptor bonding concept, the change of the bond orders is ascribable to a slight increase in σ-donor/π-acceptor ratio with increasing atomic number of the pnictogen center. Comparable results have been observed for more than 100 transition metal pnictine complexes $(R_3E)ML_n$ (E = group 15 element) in an extensive ^{13}C NMR study by Bodner et al.[15] Since the variation of the organic ligands on the pnictogen center usually had a larger effect on the carbonyl resonances than variation of the pnictogen center itself,[15] comparisons with similar bimetallic complexes of gallium and indium, whose synthesis is currently under investigation, seem very interesting.

2 and **3**, which could be obtained as single crystals of X-ray quality from solutions in pentane at 0 °C, are isostructural and crystallize in the triclinic space group $P\bar{1}$ (no. 2). They represent the first examples of arsine and stibine complexes bridging a transition metal and a group 13 metal fragment. The ligands bound to the Al and the pnictogen center adopt a staggered conformation in relation to one other. Despite the coordination of a $Ni(CO)_3$ fragment, which should lead to an increased sterical pressure within the compounds, the Al−E and Al−N bond lengths within the main group fragment of **2** (Al−As 2.479(1) Å, Al−N 1.966(2) Å) and **3** (Al−Sb 2.680(2) Å, Al−N 1.965(4) Å) and the average Al−C (1.965 Å **2**, 1.966 Å **3**), As−Si (2.349 Å), and Sb−Si distances (2.550 Å) are comparable to those found for the starting compounds dmap−$Al(Me_2)E(SiMe_3)_2$ (E = As, Sb).[10a,c] In contrast to the almost unchanged bond lengths, the sum of the bond angles at the pnictogen atoms (Si−E−Si and Al−E−Si) are significantly increased in both cases. The widening by about 13° (304.1° to 317.7° (**2**) and 302.4° to 314.3° (**3**)) clearly reveals the smaller steric demand of the bonding E−Ni electron pair compared to the *lone pair* in the starting compounds. This was already demonstrated by Haaland for dative bonds of pnictines to group 13 Lewis acids[16] and meets the expectations of the VSEPR concept. It also indicates a partial rehybridization of the E−Al/Si bonding electron pairs, which had a high p-character in the starting compounds,[10c] toward a formally sp^3-hybridized orbital. The former *lone pair*, which had a high s-character, simultaneously gets more p-character. The As−Ni (2.419(1) Å (**2**)) and Sb−Ni (2.558(1) Å (**3**)) bond lengths are not necessarily comparable to other E−Ni bond lengths since, to the best of our knowledge, no other structurally characterized compounds with a higher pnictogen center (E = As, Sb, Bi) coordinated to a $Ni(CO)_3$ fragment are known, so far. However, As−Ni bond lengths in As−Ni(0) complexes range from 2.25

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[12] Sheldrick, G. M. *SHELXS-97*, Program for Structure Solution. *Acta Crystallogr. Sect. A* **1990**, *46*, 467−473.

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[14] The splitting of the E vibration is due to the disturbance of the local C_{3v} symmetry of the $Ni(CO)_3$ fragment.

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Å (polyhedral Ni_xAs_y carbonyl clusters[17]) to 2.50 Å (diarsine chelate complexes[18]), while Sb−Ni distances in Sb−Ni(0) complexes range from 2.46 Å ($[Ni(CO)_2]_2$-$[Ph_2SbOSbPh]_2$) to 2.60 Å (polyhedral Ni_xSb_y carbonyl clusters), respectively.[19] There are also some E−Ni(I) and E−Ni(II) compounds, which show comparable As−Ni[20] and Sb−Ni distances.[21] Compared to pure $Ni(CO)_4$ (average Ni−C 1.816 Å),[22] the average Ni−C bond lengths in **2** (1.791 Å) and **3** (1.779 Å) are slightly shorter, while the C−O distances are slightly elongated ($Ni(CO)_4$, 1.127 Å; **2**, 1.139 Å; **3**, 1.146 Å). Both findings confirm the results of the NMR and IR studies, which pointed to an increase of the Ni−C and decrease of the C−O bond order in the complexes compared to pure $Ni(CO)_4$. As was found in the spectroscopic studies, the σ-donor/π-acceptor ratio for **3** seems to be larger than for **2**.

Pnictogen-bridged, $Ni(CO)_3$ complexes seem to be generally available by the described reaction pathway. Compared to the method described by Beachley et al., which suffers from the lack of suitable M′−E heterocycles, our method starts from monomeric, base-stabilized compounds, which are easily available by ring cleavage reaction of M′−E heterocycles with dmap. Therefore, this pathway may offer a wide synthetic potential for the synthesis of similar compounds. Reactions of the monomeric aluminum pnictines toward transition metal complexes with different metal centers as well as metals in different oxidation states are currently under investigation.

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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