Reactivity of E$_4$ (E$_4$ = P$_4$, As$_4$, AsP$_3$) towards Low-Valent Al(I) and Ga(I) Compounds

Maria Haimerl,[a] Martin Piesch,[a] Ravi Yadav,[b] Peter W. Roesky,[b] and Manfred Scheer*[a]

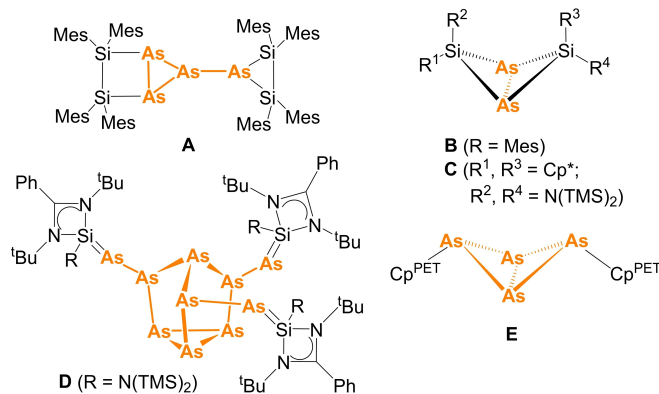*Dedicated to Professor Dieter Fenske on the occasion of his 80th birthday.*

Abstract: The reactivity of yellow arsenic and the interpnictogen compound AsP$_3$ towards low-valent group 13 compounds was investigated. The reactions of [LAl] (**1**, L = [{N(C$_6$H$_3$iPr$_2$-2,6)C(Me)}$_2$CH]$^-$) with As$_4$ and AsP$_3$ lead to [(LAl)$_2$(μ,$\eta$$^{1:1:1:1}$-E$_4$)] (E$_4$ = As$_4$ (**3 b**), AsP$_3$ (**3 c**)) by insertion of two fragments [LAl] into two of the six E—E edges of the E$_4$ tetrahedra. Furthermore, the reaction of [LGa] (**2**) with E$_4$ afforded [LGa($\eta$$^{1:1}$-E$_4$)] (E$_4$ = As$_4$ (**4 b**), AsP$_3$ (**4 c**)). In these compounds, only one E—E bond of the E$_4$ tetrahedra was cleaved. These compounds represent the first examples of the conversion of yellow arsenic and AsP$_3$, respectively, with group 13 compounds. Furthermore, the reactivity of the gallium complexes towards unsaturated transition metal units or polypnictogen (E$_n$) ligand complexes was investigated. This leads to the heterobimetallic compounds [(LGa)(μ,$\eta$$^{2:1:1}$-P$_4$)(LNi)] (**5 a**), [(Cp'''Co)(μ,$\eta$$^{4:1:1}$-E$_4$)(LGa)] (E = P (**6 a**), As (**6 b**), Cp''' = η^{5}-C$_5$H$_2$^{t}Bu$_3$) and [(Cp'''Ni)($\eta$$^{3:1:1}$-E$_3$)(LGa)] (E = P (**7 a**), As (**7 b**)), which combine two different ligand systems in one complex (nacnac and Cp) as well as two different types of metals (main group and transition metals). The products were characterized by crystallographic and spectroscopic methods.

Introduction

Yellow arsenic (As$_4$) is the isostructural higher homolog of white phosphorus, with both of them representing at room temperature kinetically stable and at the same time the most reactive group 15 allotropes. While the reactivity of white phosphorus towards transition metal and main group compounds has been extensively investigated,[1] there are just a few examples of the conversion of As$_4$ with main group compounds. The reason for this lies in its thermodynamic instability, light- and air sensitivity and the lack of storage possibilities of yellow arsenic.[2] The deficiencies in the characterization of product mixtures present another problem, since the ^{75}As NMR spectroscopic method only works for very symmetric compounds such as As$_4$. *West* et al. reported the reactivity of yellow arsenic towards silicon compounds.[3] The reaction of [Mes$_2$Si=SiMes$_2$] (Mes = mesityl) with As$_4$ leads to 1-arsa-2,3-disilacyclopropyl-1,4,5-triarsa-2,3,-disilabicyclo[2.1.0]pentane (**A**, Scheme 1) and 1,3-diarsa-2,4-disilabicyclobutane products (**B**, Scheme 1). When heating this mixture to 95 °C, a conversion of **A** to the Si$_2$As$_2$ butterfly compound **B** takes place. The reaction of P$_4$ with different disilenes leads to products similar to **B**. A totally different outcome was observed for the reaction of yellow arsenic with silylene [PhC(N^{t}Bu)$_2$SiN(SiMe$_3$)$_2$] which gave an As$_{10}$ cage with a nortricyclane core stabilized by three arsasilene fragments (**D**, Scheme 1). In contrast, treatment of the disilene [(Me$_3$Si)$_2$N(η^{1}-Me$_5$C$_5$)Si=Si(η^{1}-Me$_5$C$_5$)N(SiMe$_3$)$_2$][4] with As$_4$ leads to [Cp*{(SiMe$_3$)$_2$N}SiAs]$_2$ (**C**, Cp* = η^{5}-C$_5$Me$_5$, Scheme 1) with a butterfly-like central core. By using a main group radical (Cp$^{PET·}$, Cp^{PET} = η^{5}-C$_5$(4-EtC$_6$H$_4$)$_5$), the first organo-substituted As$_4$ butterfly compound [Cp^{PET}$_2$As$_4$][5] (**E**, Scheme 1) was synthesized. This compound was able to release yellow arsenic under thermal or

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Scheme 1. Examples of the conversion of yellow arsenic with main group compounds.

photochemical conditions. All known examples of the conversion of yellow arsenic with main group compounds are from group 14 reactivities. In contrast to yellow arsenic, the binary interpnictogen compound AsP_3[6] is stable, isolatable and can be handled as easily as P_4. However, within the last decade, only a few examples of the reaction of AsP_3 with main group and transition metal compounds were reported.[7]

Moreover, the groups of *H. W. Roesky*, *R. A. Fischer* and *J. J. Weigand* reported the reaction of the main group metal compounds [LAl] (**1**, L = [{N(C_6H_3^iPr_2-2,6)C(Me)}_2CH]^−)[8] and [LGa] (**2**)[9] with white phosphorus. Here the formation of [(LAl)_2(μ,η^{1:1:1}-P_4)] (**3a**),[10] [LGa(η^{1:1}-P_4)] (**4a**)[11] and other polyphosphines stabilized by two {LGa} fragments was observed.[12] Moreover, **2** was reacted with the antimony reagent [Cp*Sb]_4 to form [(LGa)_2(μ,η^{1:1:1}-Sb_4)].[13]
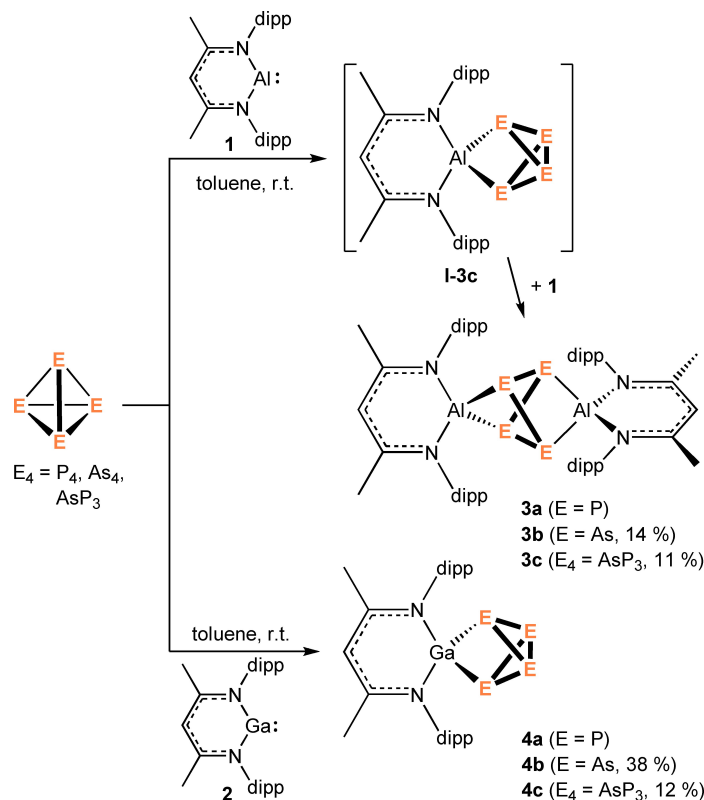
Motivated by these results of the reactivity of white phosphorus towards group 13 metal complexes, the question arose if there are similarities or differences in their reactivity towards yellow arsenic and AsP_3. Furthermore, the reactivity of such products towards unsaturated metal fragments is of interest. On the basis of our results regarding the reactivity of Cu(I) nacnac (β-diketiminato ligand (L)) complexes towards E_n ligand complexes,[13] the question arose as to what extent the E—E bonds in E_n ligand complexes can be activated or cleaved by main group fragments. Herein, we present the conversion of yellow arsenic and AsP_3 with Al(I) (**1**) and Ga (I) (**2**) compounds, the first examples of the conversion of yellow arsenic and AsP_3 with group 13 metal compounds to obtain [(LAl)_2(μ,η^{1:1:1}-E_4)]

($E_4 = As_4$ (**3b**), AsP_3 (**3c**)) and [LGa(η^{1:1}-E_4)] ($E_4 = As_4$ (**4b**), AsP_3 (**4c**)). Furthermore, the reactivity of the resulting gallium compounds towards unsaturated metal compounds and E_n ligand complexes was investigated.

Result and Discussion

The reaction of [LAl] (**1**) and [LGa] (**2**) with an excess of yellow arsenic in toluene at room temperature leads to [(LAl)_2(μ,η^{1:1:1}-As_4)] (**3b**) and [LGa(η^{1:1}-As_4)] (**4b**), which are isolated as orange (**3b**) and yellow (**4b**) air-sensitive solids in crystalline yields of 14% and 38%, respectively (Scheme 2). Reacting **1** and **2** with AsP_3, yields dinuclear [(LAl)_2(μ,η^{1:1:1}-AsP_3)] (**3c**) and mononuclear species [LGa(η^{1:1}-AsP_3)] (**4c**), respectively, as orange and yellow air-sensitive solids in isolated crystalline yields of 11% (**3c**) and 12% (**4c**), respectively (Scheme 2).

The reaction of **1** with an excess of P_4 also leads to **3a**, the $^{31}P\{^1H\}$ NMR spectrum shows only traces of a mononuclear species (see Supporting Information). According to DFT calculations at the B3LYP/def2-SVE level of theory, the formation of the dinuclear species is, in the case of aluminum, by 112 (**3a**), 95 (**3b**) and 116 (**3c**) kJ mol^{−1} more likely than the formation of the mononuclear species. A similar behavior is calculated for the gallium compounds, the dinuclear species should be favored by 25 (**4a**), 31 (**4b**) and 29 (**4c**) kJ mol^{−1}. Even after changing the reaction conditions (e.g. temperature, stoichiometry), the reaction of **2** with As_4 only leads to **4b**.[14] In

Scheme 2. Reaction of As_4 and AsP_3 with **1** and **2** (dipp = 2,6-diisopropylphenyl).

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comparison with the lighter homolog phosphorus, the reaction of **2** with white phosphorus in a 1:0.75 ratio at 180°C[15] leads to the formation of **4a** and $[(LGa)_2(P_n)]$ (n = 4, 6, 8, 12, 14, 16).[12] Freshly dissolved **3b** in C_6D_6 was characterized by ^1H NMR spectroscopy at room temperature, showing one set of signals for the two equivalent nacnac ligands. Similarly, the ^1H NMR spectrum of **4b** (C_6D_6, r.t.) reveals a full set of signals for the nacnac ligand. The $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixture of **3c** and **4c** show the formation of various compounds (see Supporting Information), but only compounds **3c** and **4c** could be isolated (see below). The $^{31}P\{^1H\}$ NMR spectrum of crystals of **4c** dissolved in C_6D_6 shows two sets of signals corresponding to two isomers indicating different chemical and magnetic environments, which can be explained by the different position of the arsenic atom in the AsP_3 unit (Figure 1). The formation of isomers of **4c** depends on the different bond cleavage of the AsP_3 tetrahedron. According to DFT calculations, the cleavage of an As–P bond is preferred by 25 kJ mol^{-1} vs. a P–P bond.[7d] If the P–As bond is broken, the major isomer **4c1** is formed, with the gallium atom being coordinated to the arsenic atom (Figure 3). A P–P bond cleavage leads to the formation of the minor isomer **4c2**, with the arsenic atom being located at the bridgehead position of the ligand (Figure 3). In the $^{31}P\{^1H\}$ NMR spectrum of **4c**, both isomers are visible. For the major isomer **4c1**, a triplet at $\delta = 179.1$ ppm and a doublet at $\delta = -319.8$ ppm ($^1J_{PP} = 155$ Hz) in an integral ratio of 1:2 can be detected. The signals for the isomer **4c2** revealing a doublet at $\delta = 227.6$ ppm and a triplet at -279.4 ppm ($^1J_{PP} = 164$ Hz) in an integral ratio of 2:1. The ratio of the compounds **4c1** and **4c2** according to the $^{31}P\{^1H\}$ NMR spectrum of the crystals is determined to be 1:0.1. There are also traces of **4a** visible ($^{31}P\{^1H\}$: $\delta = -328.7$ (t) and 212.7 ppm (t)), due to P_4 impurities in AsP_3.

The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction solution of [LAl] with AsP_3 shows two sets of signals corresponding to two mononuclear isomers of a compound that is analogous to **4c**. For one isomer, a doublet at $\delta = 117.7$ ppm ($^1J_{PP} = 162$ Hz, 2P) and a triplet at $\delta = -284.8$ ppm ($^1J_{PP} = 162$ Hz, 1P) can be detected, while for the other isomer there is a triplet at $\de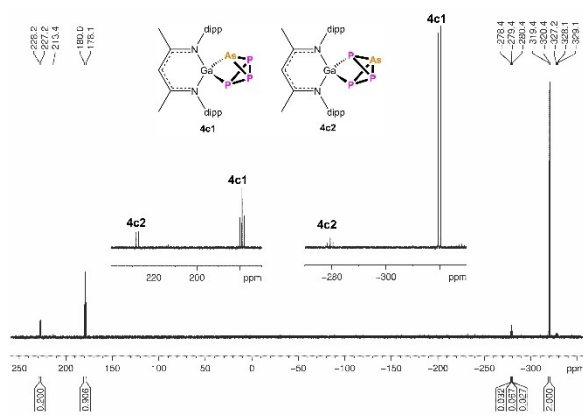lta = 67.4$ ppm ($^1J_{PP} = 151$ Hz, 1P) and a doublet at $\delta = -324.9$ ppm ($^1J_{PP} = 151$ Hz, 2P). Both isomers are in an integral ratio of 3:2. Based on the striking similarity of the $^{31}P\{^1H\}$ NMR spectroscopic data of the two isomers and **4c** (see above), the two isomers represent the analogs of **I-3c** in which the As atom possesses a wing tip and is located in the bridgehead position, respectively. Furthermore, signals are detected for **3c**, which is the only product that was obtained by crystallization regardless of numerous attempts. The ^1H NMR spectrum of a sample prepared by dissolved crystals of **3c** in C_6D_6 at room temperature shows two sets of signals for the Me-groups and the α-H atoms, due to the magnetically nonequivalent ligands. This is caused by the position of the arsenic atom within the AsP_3 unit. In the $^{31}P\{^1H\}$ NMR spectrum of the same sample of **3c**, a doublet at $\delta = 62.1$ ppm ($^1J_{PP} = 24$ Hz) and a triplet at $\delta = 50.0$ ppm ($^1J_{PP} = 24$ Hz) in an integral ratio of 2:1 can be detected. In the $^{31}P\{^1H\}$ NMR spectrum of **3c**, also a small signal for **3a** is visible (**3a**: $^{31}P\{^1H\}$: $\delta = 78.6$ ppm[10]). The small $^1J_{PP}$ coupling constants could be explained by the pronounced 3p character of the P–P bond and the predominantly 3s character of the phosphorus lone-pairs, which leads to a small s-overlap integral for the P–P bond and was reported also for diphosphines.[17] NBO analysis nicely shows the high p character of the E–E bonds (P1-P2: sp$^{9.4}$, P2-As3: sp^{10}, As3-P4: sp^{10}, P1-P4: sp$^{9.2}$). In the LIFDI-MS spectra of **3b**, **4b** and **4c**, the corresponding molecular ion peaks are detected.

The molecular structures of **3b** and **3c** reveal dinuclear compounds bearing a strongly folded As_4 or AsP_3 ring, coordinating in an $\eta^{1:1}$ fashion to both {LAl} fragments, which are twisted (**3b**: 97.70(11)°; **3c**: 81.99(11)°) to each other (Figure 2). The arsenic atom in **3c** is disordered over all four pnictogen positions (for the occupation of the phosphorus and arsenic positions see Table 1). The As–As distances in **3b** are between 2.5096(6) and 2.5220(6) Å, which is elongated in comparison to an As–As single bond.[18] The Wiberg bond
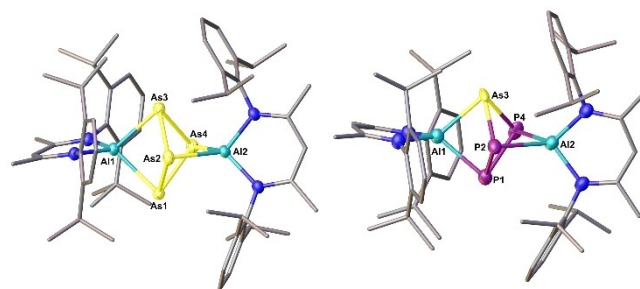
Figure 2. Molecular structure of **3b** (left) and **3c** (right, one of the four isomers) in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level (T = 123 K). Hydrogen atoms are omitted for clarity.

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **4c** in C_6D_6 at room temperature.

Table 1. Occupation of the phosphorus and arsenic positions in compound **3c** and **4c** as determined by single crystal X-ray crystallography.

	atom E	1	2	3	4
3c	P	0.91	0.90	0.69	0.67
	As	0.09	0.10	0.31	0.33
4c	P	0.49	0.65	0.98	0.97
	As	0.51	0.35	0.02	0.03

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indices show the integrity of the As–As bonds (all WBIs around 0.93). A similar M_2As_4 core was observed in [(Cp*Co-(CO))$_2$(μ,η$^{1:1:1:1}$-As$_4$)] (**F**).[19] The As1···As3 and As2···As4 distances (3.329 and 3.341 Å) of **3b** are clearly longer than those in **F** (2.838(2) and 2.881(2) Å), which indicates a complete bond cleavage of two As–As edges of the As$_4$ tetrahedra. The P–As distances in **3c** are in the range of 2.28(2) and 2.561(14) Å, the P–P distances are in between 2.301(7) and 2.407(8) Å (WBIs between 0.93 and 0.96). The average Al–As distance in **3b** is 2.4513 Å, which is comparable to the one of the recently reported compound [LAl(AsH$_2$)$_2$] (L=[{N(C$_6$H$_3$^{i}Pr$_2$-2,6)C-(Me)}$_2$CH]$^-$) (Al-As$_{(av.)}$ 2.474(3) Å).[20]

The molecular structures of **4b** and **4c** each reveal a mononuclear compound bearing an As$_4$ or AsP$_3$ butterfly ligand, coordinating in η$^{1:1}$ fashion to the {LGa} fragment (Figure 3). The arsenic atom in **4c** is disordered over all four pnictogen positions. The major isomer **4c1** with the gallium-coordinated arsenic atom and the minor isomer **4c2** with the arsenic atom in the bridgehead position of the ligand were determined to be in a ratio of 85:6 (9% are **4a**) in the solid state (for the occupation of the phosphorus and arsenic positions see Table 1). According to DFT calculations at the B3LYP/def2-SVE level of theory, **4c1** is just by 0.3 kJ mol^{-1} more stable than **4c2**.

The six-membered GaN$_2$C$_3$ ring is nearly perpendicularly oriented (**4b**: 91.8°; **4c**: 87.9°) to the E1–Ga–E2 plane. The As1···As2 distance with 3.452 Å lies in a non-bonding range for **4b** (WBI: 0.1). The E1···E2 distances of **4c** are 3.291(13), 3.365(10) and 3.295(13) Å and lie in a non-bonding range, respectively. The As–As distances of **4b** are all between 2.4608(5) and 2.4693(6) Å, except for the As3-As4 length which is as short as 2.3830(6) Å. A similar trend of the As–As distances within the As$_4$ butterfly moiety was also found in [Cp*Co(CO)(η$^{1:1}$-As$_4$)][19] and [(Cp^{R}M(CO)$_n$)$_2$(μ,η$^{1:1}$-As$_4$)][21] (Cp$'''$, M=Fe, n=2; Cp*, M=Cr, n=3). The P–As distances in **4c** are in the range between 2.315(4) and 2.52(4) Å, the P–P distances are in between 2.155(4) and 2.301(5) Å which matches the values of **4a** well.[11] Moreover, the WBIs of all E–E bonds distances were calculated and show the integrity of the bonds. The Ga–As distances are 2.4259(5)/2.4415(5) Å for **4b** and 2.412(3)/2.421(8) Å for compound **4c**. This is comparable to the Ga–As distances found in [Ga(Cp*)L(GaL)(μ,η$^{3:2}$-As$_3$)], which exhibit Ga–As bond lengths of the η^2-coordinated Ga of 2.4183(3) and 2.4224(3) Å. The E–E bond in the bridgehead of the butterfly unit of **4a** can be

further activated in the case of phosphorus with another molecule of **2**.[12] Despite numerous attempts, such a reactivity of a main group compound could not be found for the arsenic compound **4b**. Thus, the question arose if such gallium complexes are able to react further with unsaturated transition metal complexes and if this would also be the case for the As$_4$ derivative **4b**. We focused especially on the synthesis of heterometallic mixed main group (group 13 metals) and transition metal complexes which, surprisingly, have only been little explored.[22] In order to investigate the reactivity of **4a** and **4b** towards unsaturated transition metal fragments, they were reacted with 0.5 equivalents of [(LNi)$_2$tol][23] and [(Cp$'''$Co)$_2$(μ,η$^{4:4}$-C$_7$H$_8$)][24] to deliver just one metal fragment, leading to the quantitative formation of [(LGa)(μ,η$^{2:1:1}$-P$_4$)(LNi)] (**5a**) and [(Cp$'''$Co)(μ,η$^{4:1:1}$-E$_4$)(LGa)] (E=P (**6a**), As (**6b**)), which are isolated as orange (**5a**) or green (**6a**, **6b**) air-sensitive solids in crystalline yields of 61% (**5a**, Scheme 3) and 59% (**6b**, Scheme 3), respectively. The reaction of **4a** with [(Cp$'''$Co)$_2$tol] is not as selective as that of **4b**. In addition to [(Cp$'''$Co)(μ,η$^{4:1:1}$-P$_4$)(LGa)] (**6a**), [(Cp$'''$Co)(μ,η$^{2:2}$-P$_2$)$_2$] (**G**) is also formed during this reaction showing that **4a** can deliver P$_4$ units to {Cp$'''$Co} fragments.[25] To examine if [LGa] is also able to open an E–E bond of a *cyclo*-E$_n$ complex, [Cp$'''$Co(η^4-P$_4$)] (**H**) and [Cp$'''$Ni(η^3-E$_3$)] (E=P, As) (**I**) is reacted with **2** (Scheme 3). The reaction of **H** with **2** leads to the selective formation of **6a**. By the reaction of **I** with **2**, compounds [(Cp$'''$Ni)(η$^{3:1:1}$-E$_3$)(LGa)] (E=P (**7a**), As (**7b**)) are formed as orange air-sensitive solids in crystalline yields of 40% (**7a**) and 69% (**7b**), respectively (Scheme 3). These products represent novel neutral, heterometallic compounds containing mixed main group and transition metals.

Whereas the ^{31}P{^{1}H} NMR spectrum of **5a** in C$_6$D$_6$ at room temperature is silent, the ^{1}H NMR spectrum displays broad and shifted signals revealing a paramagnetic compound. The effective magnetic moment (μ$_{eff}$) is determined by the Evans method to be 2.29 μ$_B$ corresponding approximately to one unpaired electron. The paramagnetic nature of **5a** is confirmed by X-band EPR spectroscopy at room temperature and at 77 K (r.t.: g=2.156, 77 K: g$_1$=2.236, g$_2$=2.121 and g$_3$=2.038, Figure 4). DFT calculations (B3LYP/def2-SVE level) show that the spin density is delocalized over the nickel atom and all four phosphorus atoms (Figure 4), which is in agreement with the observed hyperfine coupling. The ^{1}H NMR spectrum of the
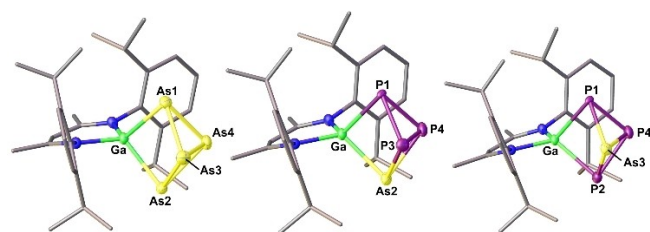

Figure 3. Molecular structure of **4b** (left), one of the major isomers **4c1** (middle) and one of the minor isomers **4c2** (right) in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level (T=123 K). Hydrogen atoms are omitted for clarity.
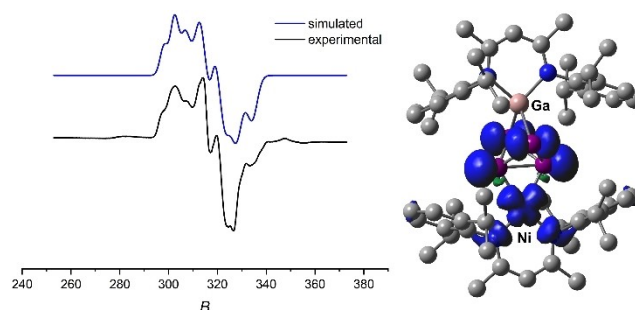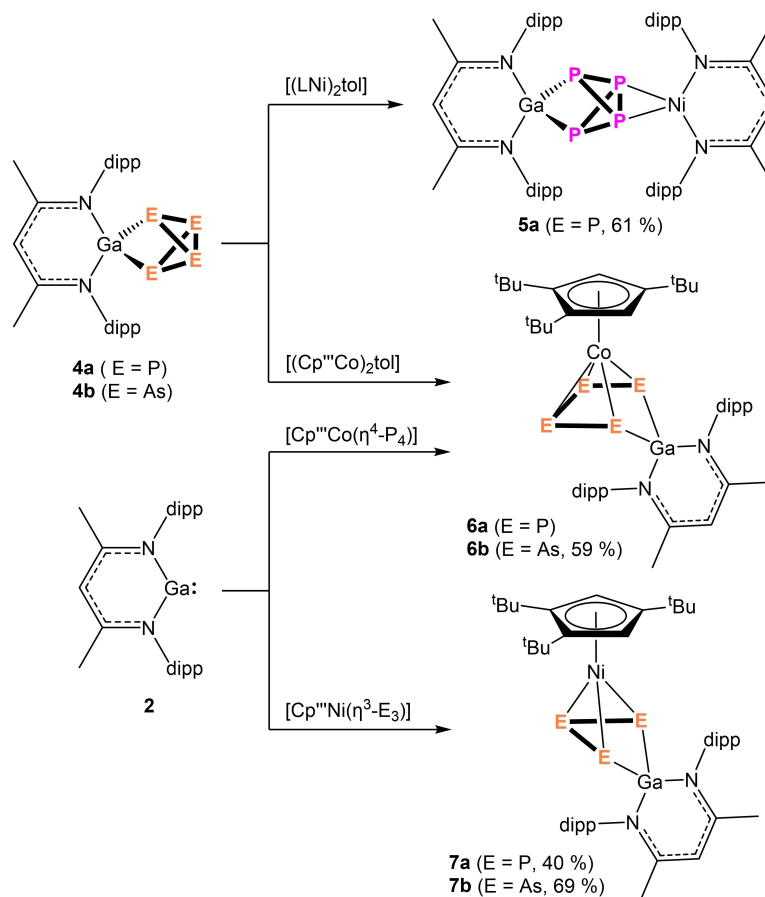

Figure 4. left: X-band EPR spectrum of **5a** (B in [mT], frozen toluene solution 77 K (black), simulation (blue)); right: spin density distribution in **5a**, calculated at the B3LYP/def2-SVE level.

Scheme 3. Reaction of **4** with unsaturated transition metal complexes and reaction of **2** with E_n ligand complexes (dipp = 2,6-diisopropylphenyl, Cp''' = $C_5H_2{}^tBu_3$).

reaction of **4b** with [(LNi)$_2$tol] exhibits broad and shifted signals similar to **5a**, crystallization, however, was not possible, regardless of numerous attempts.

The ^{1}H NMR spectra of the reaction solutions of **6b** and **7b**, respectively, in C_6D_6 indicate that the reactions are very selective, they exhibit four doublets centered at $\delta = 1.90$, 1.63, 1.19 and 0.82 ppm (**6b**); $\delta = 1.67$, 1.60, 1.14 and 1.04 ppm (**7b**) and two septets centered at $\delta = 3.95$ and 2.58 (**6b**) or $\delta = 1.56$ and 1.48 (**7b**) for the isopropyl groups, respectively. This indicates that the chemical environment of all isopropyl groups is different. Similar signals could be obtained for **6a** and **7a** in the ^{1}H NMR spectrum. The ^{31}P{^{1}H} NMR spectrum of **6a** in C_6D_6 reveals two multiplets centered at $\delta = 94.0$ and -54.0 ppm, respectively, with an integral ratio of 1:1 displaying an AA'XX' spin system (see Supporting Information). This shows high similarities to the anionic heterobimetallic complex [K-(dme)$_2${(^{Mes}BIAN)Co($\mu,\eta^{4:1:1}$-P$_4$)(LGa)] (^{Mes}BIAN = 1,2-bis(2,4,6-dimethylphenylimino)acenaphthene).[22b] The ^{31}P{^{1}H} NMR spectrum of **7a** in C_6D_6 reveals a doublet at $\delta = 163.8$ ppm (2P, $^1J_{PP} = 325$ Hz) and a triplet at $\delta = 109.1$ ppm (1P, $^1J_{PP} = 325$ Hz).

The molecular structure of **5a** displays a heterobimetallic complex bearing a P$_4$ butterfly unit, coordinating in $\eta^{1:1}$ fashion to the {LGa} fragment and in η^2 fashion to the {LNi} fragment (Figure 5). The P1···P2 distances of compound **5a** are 3.178(2) Å,

which is in the same range as for **4a** (3.173(3) Å[11]) and in a non-bonding area (WBI: P1···P2 0.12). The P–P bond distances of **5a** are all between 2.237(2) and 2.239(2) Å (all WBIs around 0.9), except for the P3-P4 bond distance which is elongated to 2.2566(15) Å (WBI: 0.78). Compound **5a** is a rare example of a mixed main group transition metal nacnac complex. To the best of our knowledge, only one example of a similar compound with mixed metal nacnac ligands is known, namely the nickel silicon compound [(LSi)($\mu,\eta^{2:1:1}$-P$_4$)(LNi)].[22c]

Compounds **6b**, **7a** and **7b** are heterodinuclear sandwich complexes with an {LM} fragment η^4- or η^3-coordinated to the As$_4$ or E$_3$ chain and an {LGa} fragment in $\eta^{1:1}$-coordination mode (Figure 5). In comparison to **4b**, in **6b**, two more As–As bonds are broken. Compounds **7a** and **7b** show an insertion of the {LGa} fragment into the cyclo-E$_3$ unit. The butadiene-like As$_4$ unit of **6b** is nearly planar (deviation 2.8 °). The As1-As2 and As3-As4 distances in **6b** are 2.3227(6) and 2.3270(6) Å, the As2-As3 bond distance is slightly longer (2.4018(6) Å). The E–E bond distances are 2.1586(11) and 2.1818(11) Å for **7a** and 2.4059(4) and 2.4095(4) Å for **7b**, respectively. The As1···As4 (**6b**), P1···P3 (**7a**) and As1···As3 (**7b**) distances are with 3.4434(6) Å (**6b**), 3.0939(9) Å (**7a**) and 3.2753(6) Å (**7b**) in the non-bonding area and slightly shorter than the comparable distance in **4b** (3.452 Å). Compound **6b** reveals a Ga–As distance (2.4271(5)
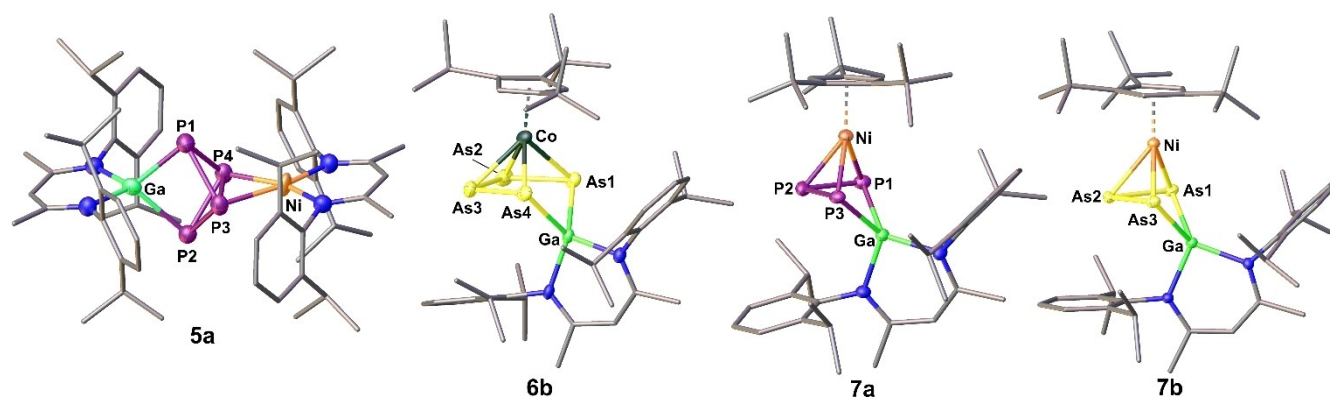
Figure 5. Molecular structures of **5a**, **6b**, **7a** and **7b** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level (T = 123 K (**5a**, **7a**); 100 K (**6b**, **7b**)). Hydrogen atoms and solvent molecules are omitted for clarity.

and 2.4481(5) Å) similar to **4b**. The six-membered GaN_2C_3 ring is nearly perpendicular (**6b**: 92.4°, **7a**: 95.9° **7b**: 89.6°) to the E1–Ga–E4/E3 plane, which is folded by 113.7° (**6b**), 126.0° (**7a**) or 120.5° (**7b**) to the $E_{4/3}$ unit. Compound **6b** contains a core that is similar to the one of the homodinuclear compound $[(Cp^*Co)(\mu,\eta^{4:1:1}\text{-}As_4)(Co(CO)Cp^*)]$.[19]

Conclusion

In summary, we reported the synthesis of novel homobimetallic compounds $[(LAl)_2(\mu,\eta^{1:1:1:1}\text{-}E_4)]$ (E = As (**3b**), AsP_3 (**3c**)) and the mononuclear compounds $[LGa(\eta^{1:1}\text{-}E_4)]$ (E = As (**4b**), AsP_3 (**4c**)), the first examples of the conversion of yellow arsenic and AsP_3 with low-valent group 13 compounds. We have shown that, in the case of AsP_3, the occurrence of an As–P bond activation is more likely than that of a P–P bond activation. The $^{31}P\{^1H\}$ NMR spectrum of **4c** shows two isomers depending on the position of the arsenic atom. The crude reaction solution of **3c** also indicates the formation of a mononuclear compound in solution, representing the first step on the reaction pathway to a double substitution. In the case of the gallium complexes, further reactivities towards unsaturated metal complexes or E_n (n = 3, 4) ligand complexes were investigated. Thus, the heterometallic compounds $[(LGa)(\mu,\eta^{2:1:1}\text{-}P_4)(LNi)]$ (**5a**), $[(Cp'''Co)(\mu,\eta^{4:1:1}\text{-}E_4)(LGa)]$ (E = P (**6a**), As (**6b**)) and $[(Cp'''Ni)(\mu,\eta^{3:1:1}\text{-}E_3)(LGa)]$ (E = P (**7a**), As (**7b**)) were synthesized. These complexes unite different ligand systems (Cp and nacnac) and also different, merged metal moieties, main group as well as transition metals, and thus revealing unprecedented examples of mixed main group/transition metal complexes.

Experimental Section

The full experimental details and characterization data can be found in the Supporting Information.

Deposition Number(s) 2192193 (**3b**), 2192194 (**3c**), 2192195 (**4b**), 2192196 (**4c**), 2192197 (**5a**), 2192198 (**6b**), 2192199 (**7a**) and

2192200 (**7b**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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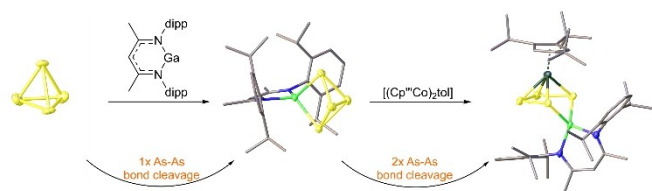
Bond by bond. The conversion of yellow arsenic with the group 13 metal compound [LGa] (L = [{N-(C₆H₃ⁱPr₂-2,6)C(Me)}₂CH]⁻) leads to one As—As bond cleavage in [LGa($\eta^{1:1}$-As₄)]. By reacting this product with an unsaturated metal complex, two further As—As bonds are broken, to form a butadiene-like As₄ chain stabilized in the coordination sphere of transition metals as well as main group metals.

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Reactivity of E₄ (E₄ = P₄, As₄, AsP₃) towards Low-Valent Al(I) and Ga(I) Compounds