

## E<sub>4</sub> Transfer (E = P, As) to Ni Complexes

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Dedicated to Prof. U. Siemeling on the occasion of his 60th birthday.

**Abstract:** The use of [Cp''<sub>2</sub>Zr(η<sup>1:1</sup>-E<sub>4</sub>)] (E = P (**1a**), As (**1b**), Cp'' = 1,3-di-*tert*-butyl-cyclopentadienyl) as phosphorus or arsenic source, respectively, gives access to novel stable polypnictogen transition metal complexes at ambient temperatures. The reaction of **1a/1b** with [Cp<sup>R</sup>NiBr]<sub>2</sub> (Cp<sup>R</sup> = Cp<sup>Bn</sup> (1,2,3,4,5-pentabenzyl-cyclopentadienyl), Cp''' (1,2,4-tri-*tert*-butyl-cyclopentadienyl)) was studied, to yield novel complexes depending on steric effects and stoichiometric ratios. Besides the transfer of the complete E<sub>n</sub> unit, a degradation as well as aggregation can be observed. Thus, the prismane

derivatives [(Cp'''Ni)<sub>2</sub>(μ,η<sup>3:3</sup>-E<sub>4</sub>)] (**2a** (E = P); **2b** (E = As)) or the arsenic containing cubane [(Cp'''Ni)<sub>3</sub>(μ<sub>3</sub>-As)(As<sub>4</sub>)] (**5**) are formed. Furthermore, the bromine bridged cubanes of the type [(Cp<sup>R</sup>Ni)<sub>3</sub>(Ni(μ-Br))(μ<sub>3</sub>-E)<sub>4</sub>]<sub>2</sub> (Cp<sup>R</sup> = Cp''': **6a** (E = P), **6b** (E = As), Cp<sup>R</sup> = Cp<sup>Bn</sup>: **8a** (E = P), **8b** (E = As)) can be isolated. Here, a stepwise transfer of E<sub>n</sub> units is possible, with a cyclo-E<sub>4</sub><sup>2-</sup> ligand being introduced and unprecedented triple-decker compounds of the type [((Cp<sup>R</sup>Ni)<sub>3</sub>Ni(μ<sub>3</sub>-E)<sub>4</sub>]<sub>2</sub>(μ,η<sup>4:4</sup>-E'<sub>4</sub>)] (Cp<sup>R</sup> = Cp<sup>Bn</sup>, Cp'''; E/E' = P, As) are obtained.

### Introduction

The synthesis and reactivity of polypnictogen transition metal complexes is an active field of research. Since their first discovery in the 1970s, a huge variety of such compounds has been synthesized.<sup>[1,2,3]</sup> In general, conventional synthetic methods such as the co-thermolysis or photolysis are used for their synthesis to convert white phosphorus and yellow arsenic, respectively, in the presence of corresponding transition metal complexes. These conversions often proceed under harsh conditions and, hence, the thermodynamically most stable compounds are obtained, which, however, usually results in an uncontrolled degradation and rearrangement of the E<sub>4</sub> tetrahedra. A mild activation would be of great interest as it allows the synthesis of metastable compounds. This is in line with recent activities of mild activation and fixation of small molecules such as H<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub> or CO<sub>2</sub>,<sup>[4]</sup> triggering a selective bond cleavage. For instance, recent studies have shown the ability of complexes containing β-diiminato ligands (L) to activate small molecules such as N<sub>2</sub> or P<sub>4</sub>.<sup>[5,6-9]</sup> Depending on the metal center and ligand design, white phosphorus is cleaved at r.t. in different ways by forming dinuclear complexes such as [(LM)<sub>2</sub>{(P<sub>2</sub>)<sub>2</sub>}], [(LM)<sub>2</sub>(P<sub>4</sub>)]

and [(LM)<sub>4</sub>(P<sub>8</sub>)] (M = Ni, Fe, Co).<sup>[6-10]</sup> Further examples in which only one P–P bond is opened are the formation of the butterfly complexes [(Cp<sup>R</sup>Fe(CO)<sub>2</sub>]<sub>2</sub>(μ,η<sup>1:1</sup>-E<sub>4</sub>)] (Cp<sup>R</sup> = Cp''' (1,2,4-tri-*tert*-butyl-cyclopentadienyl), Cp<sup>BIG</sup> (pentakis-(4-*n*-butyl-phenyl)cyclopentadienyl)) and [(Cp\*Cr(CO)<sub>3</sub>]<sub>2</sub>(μ,η<sup>1:1</sup>-E<sub>4</sub>)] (Cp\* = pentamethyl-cyclopentadienyl) by the reaction of E<sub>4</sub> (E = P, As) with metal carbonyl dimers.<sup>[11]</sup> By using the toluene complex [(Cp''Co)<sub>2</sub>(μ,η<sup>4:4</sup>-C<sub>7</sub>H<sub>8</sub>)], it is possible to break two P–P bonds simultaneously in E<sub>4</sub> either into two E<sub>2</sub> dumbbells to give the triple-decker complexes [(Cp<sup>R</sup>Co)<sub>2</sub>(μ,η<sup>2:2</sup>-E<sub>2</sub>)<sub>2</sub>] (E = P, As, Cp<sup>R</sup> = Cp''', Cp\*),<sup>[12]</sup> or compounds containing a *cyclo*-P<sub>4</sub> unit as end-deck as in [(Cp''Co)(η<sup>4</sup>-P<sub>4</sub>)]<sup>[13,14]</sup> or in [(CpRu(PPh<sub>3</sub>)<sub>2</sub>){CoCp'''}-(μ,η<sup>1:4</sup>-P<sub>4</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] and [(Cp<sup>BIG</sup>Mn(CO)<sub>2</sub>]<sub>2</sub>{CoCp'''}(μ,η<sup>1:1:4</sup>-P<sub>4</sub>)], respectively.<sup>[14]</sup>

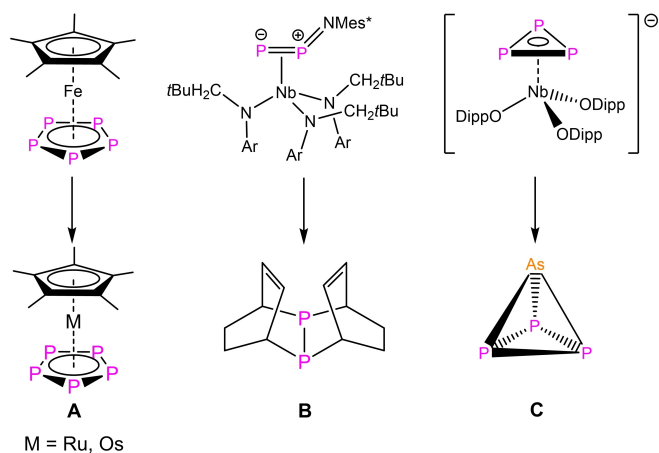
Beside a mild activation, the challenge is to avoid thermodynamic control to receive kinetic products of polypnictogen complexes. Therefore, the use of transfer reagents could be of advantage. These reactions proceed under very mild conditions and higher yields and selectivities can be achieved.<sup>[2,3,15]</sup> One interesting example was reported by Russel et al. by reacting [Cp<sub>2</sub>Zr(η<sup>1:1</sup>-(*Ct*Bu)<sub>2</sub>P<sub>2</sub>)] with ECl<sub>3</sub> (E = P, As, Sb) to obtain C<sub>2</sub>tBu<sub>2</sub>P<sub>2</sub>ECl. Subsequent reactions lead to the formation of the cationic mixed-element compound [C<sub>2</sub>tBu<sub>2</sub>P<sub>2</sub>E]<sup>+</sup>.<sup>[16]</sup>

Pentaphosphaferrocene [Cp\*Fe(η<sup>5</sup>-P<sub>5</sub>)] was also used to transfer a *cyclo*-P<sub>5</sub> unit from iron to its heavier homologues ruthenium and osmium, respectively (**A**, Scheme 1).<sup>[17]</sup> Moreover, Cummins et al. described the synthesis of the diphosphaazide complex [(η<sup>2</sup>-Mes\*NPP)Nb(N[CH<sub>2</sub>tBuAr])<sub>3</sub>] (Mes\* = 2,4,6-tri-*tert*-butyl-phenyl, Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), which upon heating liberates a P<sub>2</sub> unit that can be trapped with cyclohexa-1,3-diene to give **B** (Scheme 1).<sup>[18]</sup> In 2009, they reported the transfer of a P<sub>3</sub><sup>3-</sup> unit to AsCl<sub>3</sub> to form the neutral interpnictogen modification AsP<sub>3</sub> (**C**, Scheme 1).<sup>[19]</sup> Another remarkable example is the 2-phosphaethynolat anion [OCP<sup>-</sup>] which can act as a P<sup>-</sup>-transfer

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202101119>

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Scheme 1. Selected reactions using transfer reagents.

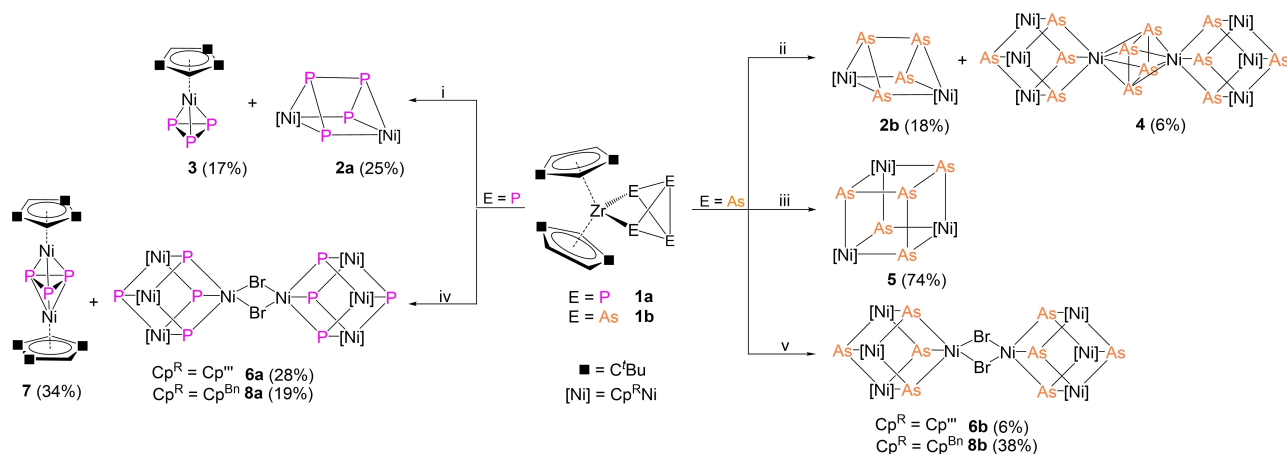
reagent.<sup>[20]</sup> For instance, using Na[OCP] Grützmacher et al. showed the transfer of a P<sub>1</sub> unit by the reaction with the imidazolium salt [DippNHC–H][Cl] to form [DippNHC=PH] (DippNHC = 1,3-bis(2,6-diisopropyl)imidazol-2-ylidene).<sup>[21]</sup>

In contrast, our group was interested in developing pnictogen-rich transfer reagents. For instance, we used the zirconium butterfly complexes [Cp''<sub>2</sub>Zr(μ<sub>1</sub>-E<sub>4</sub>)] (E = P (**1a**),<sup>[22]</sup> As (**1b**),<sup>[23]</sup> Cp'' = 1,3-di-*tert*-butyl-cyclopentadienyl) as phosphorus and arsenic sources to transfer E<sub>4</sub><sup>2-</sup> units to avoid, for example, the difficult handling of yellow arsenic. Thus, it was possible to transfer the polypnictogen unit to LSi moieties (L = PhC(NtBu)<sub>2</sub>) to form heteroaromatic sila-phospha and -arsa derivatives of benzene.<sup>[24]</sup> Furthermore, iron triple-decker complexes were formed by the reaction of **1b** with [Cp''FeBr]<sub>2</sub>. In this case, arsenic bonds were broken to form bonding isomers of [(Cp''Fe)<sub>2</sub>(μ<sub>1</sub><sup>4,4</sup>-As<sub>4</sub>)] possessing either a *cyclo*-As<sub>4</sub> or tetraarsabutadiene ligand as middle deck.<sup>[23]</sup> Since, with Cp<sup>R</sup>Fe-fragments only one type of products was obtained, the question

arose if, with the 15 VE Cp<sup>R</sup>Ni-moieties, also a selective transfer of a whole E<sub>4</sub> unit from **1a,b** can be achieved or whether fragmentation occurs, because such fragments only need a cyclo-E<sub>3</sub> unit to fulfil the 18 VE rule.<sup>[25]</sup> This intrigued us to study the reaction behavior of **1** towards [Cp''NiBr]<sub>2</sub> (R = Cp<sup>Bn</sup>, Cp'''), also in view of much better yields, if known products are formed for which a low yield synthesis is reported. Herein, we report on the selective transfer of an E<sub>4</sub> unit to Cp<sup>R</sup>Ni fragments and the formation of unprecedented triple-decker-like complexes built up by Ni<sub>4</sub>E<sub>4</sub> cubanes.

## Results and Discussion

The reaction of **1a** with in situ generated [Cp''NiBr]<sub>2</sub> in THF in a 1:1.3 stoichiometry leads to the formation of the prismane derivative [(Cp''Ni)<sub>2</sub>(μ<sub>1</sub><sup>3,3</sup>-P<sub>4</sub>)] (**2a**) and the *cyclo*-P<sub>3</sub> complex [Cp''Ni(η<sup>3</sup>-P<sub>3</sub>)] (**3**; Scheme 2). In comparison, the reaction of **1b** with [Cp''NiBr]<sub>2</sub> yields the arsenic prismane [(Cp''Ni)<sub>2</sub>(μ<sub>1</sub><sup>3,3</sup>-As<sub>4</sub>)] (**2b**) and the dimeric cubane derivative [(Cp''Ni)<sub>3</sub>Ni(μ<sub>3</sub>-As)<sub>4</sub>(μ<sub>1</sub><sup>4,4</sup>-As<sub>4</sub>)] (**4**; Scheme 2). Compounds **2** and **3** are reminiscent of the already reported compounds [Cp''Ni(η<sup>3</sup>-P<sub>3</sub>)] (Cp<sup>R</sup> = Cp\*, Cp<sup>4IPr</sup>) and [(Cp<sup>4IPr</sup>Ni)<sub>2</sub>(μ<sub>1</sub><sup>3,3</sup>-E<sub>4</sub>)] (E = P, As), respectively, obtained by cothermolysis methods, but here in much better yields.<sup>[26,27]</sup> Their full characterization is given in the Supporting Information. In the case of **2**, the whole E<sub>4</sub> unit of the starting material is transferred to two [Cp''Ni] fragments to form an E<sub>4</sub>-chain. In contrast, compound **4** consists of two [Ni<sub>4</sub>As<sub>4</sub>] subunits linked by a *cyclo*-As<sub>4</sub><sup>2-</sup> unit and represents the first nickel complex coordinated by a *cyclo*-E<sub>4</sub> unit. All nickel atoms except one in the hetero cubane are coordinated by a Cp'' ligand. The origin of the nickel atom which does not bear a Cp'' substituent is not undoubtedly clear, but it might originate from the [NiBr<sub>2</sub>-dme] used for the synthesis of [Cp''NiBr]<sub>2</sub>. To answer this question, the direct reaction of two equiv. of isolated [Cp''NiBr]<sub>2</sub> with one equiv. of **1b** was performed, leading to the formation of the entirely different

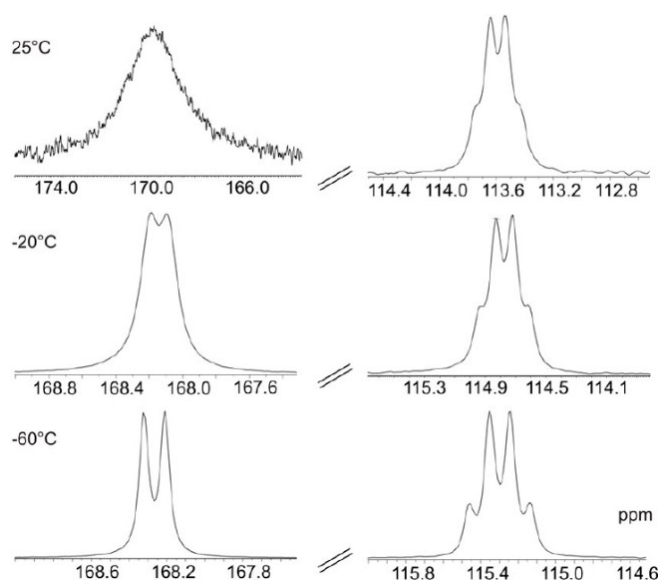


**Scheme 2.** Overview of the reactions of [Cp''<sub>2</sub>Zr(μ<sub>1</sub>-E<sub>4</sub>)] (**1a**: E = P; **1b**: E = As) with [Cp''NiBr]<sub>2</sub> (R = Cp<sup>Bn</sup>, Cp'''). i, ii) Reactions with 1.3 equiv. of [Cp''NiBr]<sub>2</sub> in *n*-hexane prepared in situ; iii) reaction with 2 equiv. of isolated [Cp''NiBr]<sub>2</sub> in THF; iv) reaction with 1.5 equiv. of [Cp''NiBr]<sub>2</sub> and 1 equiv. of [NiBr<sub>2</sub>-dme] in THF or with 2 equiv. of [Cp''NiBr]<sub>2</sub> in toluene prepared in situ; v) reaction with 1.5 equiv. of [Cp''NiBr]<sub>2</sub> prepared in situ and 1 equiv. of [NiBr<sub>2</sub>-dme] in THF or with 1 equiv. of [Cp''NiBr]<sub>2</sub> in toluene prepared in situ. In all cases, [Cp''<sub>2</sub>Zr] is eliminated; this is omitted for clarity.

reaction product  $[(Cp''Ni)_3(\mu_3-As)(As_4)]$  (**5**, Scheme 2), which is similar to the cubane  $[(Cp''Ni)_3(\mu_3-As)(As_4)]$  reported by Scherer et al., but obtained in much better yields (74 vs. 55%).<sup>[26]</sup> However, this result indicates that the nature of the  $[Cp''NiBr]_2$  source is crucial for the reaction progress. To investigate this reaction behavior in more detail, the reaction of **1a** and **1b** with 1.5 equivalents of  $[Cp''NiBr]_2$  and one equivalent of  $[NiBr_2 \cdot dme]$  was carried out, wherein the novel dimeric compounds  $[(Cp''Ni)_3\{Ni(\mu-Br)\}(\mu_3-E)_4]_2$  ( $E = P$  (**6a**),  $E = As$  (**6b**)) are formed (Scheme 2).<sup>[28]</sup> In comparison to **4**, they also consist of two  $[Ni_4E_4]$  units which are bridged by two bromine atoms. Obviously, the  $[NiBr]$ -units in **6** originate from  $[NiBr_2 \cdot dme]$ . Interestingly, in the phosphorus case, also the triple-decker complex  $[(Cp''Ni)_2(\eta^{3,3}-P_3)]$  (**7**) is formed.

To examine the influence of the Cp ligand on the reaction, we also investigated the reaction behavior of **1** towards  $[Cp^{Bn}NiBr]_2$ . The reaction of **1** with  $[Cp^{Bn}NiBr]_2$  in THF generated in situ leads to the formation of  $[(Cp^{Bn}Ni)_3\{Ni(\mu-Br)\}(\mu_3-E)_4]$  ( $E = P$ : **8a**,  $E = As$ : **8b**).

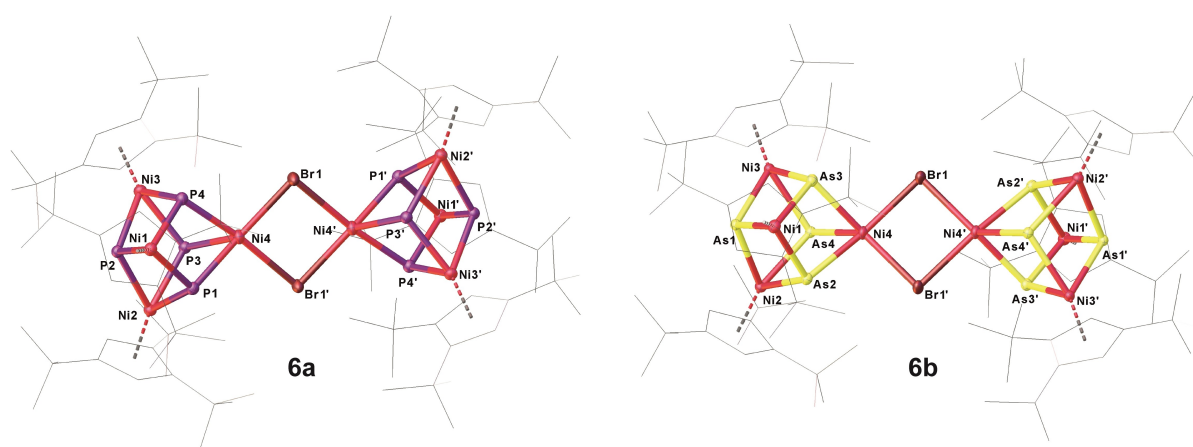
After column chromatographic workup and layering a dichloromethane solution with acetonitrile (**4**) or *n*-hexane (**6a**, **6b**, **8a**, **8b**), crystals of the dimeric cubanes suitable for single crystal X-ray diffraction analysis are obtained. The molecular structures of **6a** and **6b** are exemplified in Figure 1 (**4**, **8a** and **8b** are depicted in the Supporting Information). They consist of two cubanes linked by two bromine ligands. The central  $[Ni_2Br_2]$  ring is slightly asymmetric (**6a**, **6b**, **8a**, **8b**), showing a kite-like distortion. In **6a**, two slightly different Ni–Br distances of 2.432(2) and 2.467(2) Å exist. This trend can also be observed for the compounds **6b**, **8a** and **8b**. Usual bromine-bridged nickel compounds show Ni–Br distances in the same range.<sup>[29]</sup> The square faces of the cubanes show a kite-like distortion, which can be ascribed to the steric demand of the bulky  $Cp''$  and  $Cp^{Bn}$  ligands, respectively. Bond angles and bond lengths within the cubanes are similar to the reported values for known cubanes.<sup>[26,30]</sup> The short E...E distances within the cubanes (**6a**/**8a**: 2.5406(7) to 2.7048(6) Å; **6b**/**8b**: 2.7736(3) to 3.0186(3) Å) are remarkable. Even if they are longer than a usual single bond



**Figure 2.** Sections of the  $^{31}P\{^1H\}$  NMR spectrum of **6a** at different temperatures.

they are shorter than the sum of the van der Waals radii (P: 3.8 Å; As: 4.0 Å), indicating an E...E interaction.<sup>[31]</sup> The bonding interactions between the phosphorus atoms are also supported by the Mayer bond index (0.256 to 0.358) and localized orbitals (cf. Supporting Information, for more details exemplified for **9a** see below).

The spectroscopic data of the compounds **2a**, **3** and **7** are in agreement with the reported data of related compounds (see the Supporting Information).<sup>[26,27,32]</sup> The  $^{31}P\{^1H\}$  NMR spectrum of **6a** at room temperature shows a broad singlet at  $\delta = 169.3$  ppm and a hardly resolved quartet at  $\delta = 113.0$  ppm. In order to detect a possible dynamic behavior in solution,  $^{31}P$  NMR studies at different temperatures were carried out (Figure 2). By decreasing the temperature, both signals sharpen and, at  $-60^\circ C$ , they reveal a doublet and a quartet being in



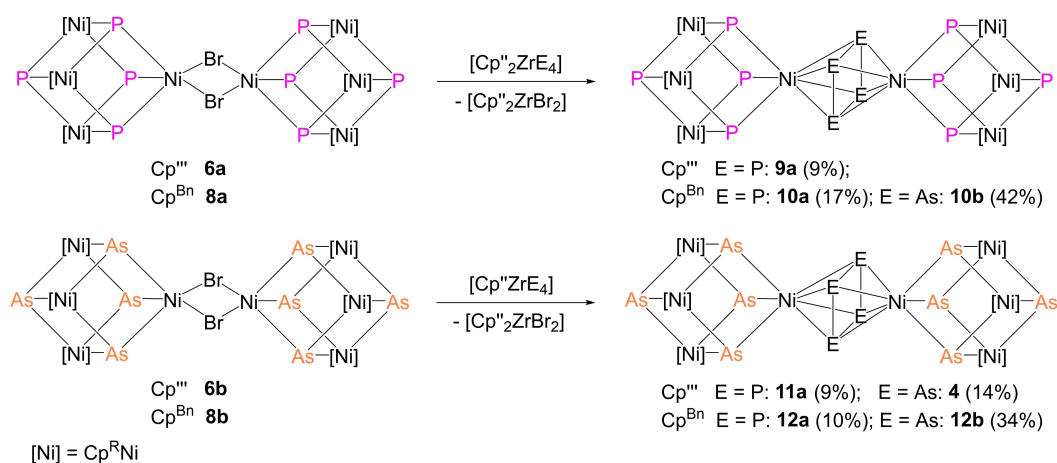
**Figure 1.** Molecular structures of **6a** (left) and **6b** (right) in the solid state with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted and the  $Cp''$  ligands are drawn in the wire frame model for clarity.

agreement with the solid-state structure of **6a** (Figure 1, left) and corresponding to an  $AX_3$  spin system with a  $^2J_{pp}$  coupling constant of 18.3 Hz. The VT NMR investigations confirm the presumption of a dynamic behavior. In contrast, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the  $\text{Cp}^{\text{Bn}}$ -substituted compound **8a** shows two sharp singlets at  $\delta = 130.8$  and 194.1 ppm, which are shifted downfield compared to **6a**. Even at low temperatures, no further splitting can be observed. The divergent behavior can be explained by the less steric bulk of the  $\text{Cp}^{\text{Bn}}$  ligands. Indeed, DFT calculations show that the dissociation of the model complex  $[(\text{CpNi})_3(\text{NiBr})(\mu_3\text{-P})_4]_2$  into the monomeric species  $[(\text{CpNi})_3(\text{NiBr})(\mu_3\text{-P})_4]$  is with  $76.75 \text{ kJ mol}^{-1}$  disfavored. The steric bulk of the  $\text{Cp}^{\text{R}}$  substituents can, however, enforce the dissociation.

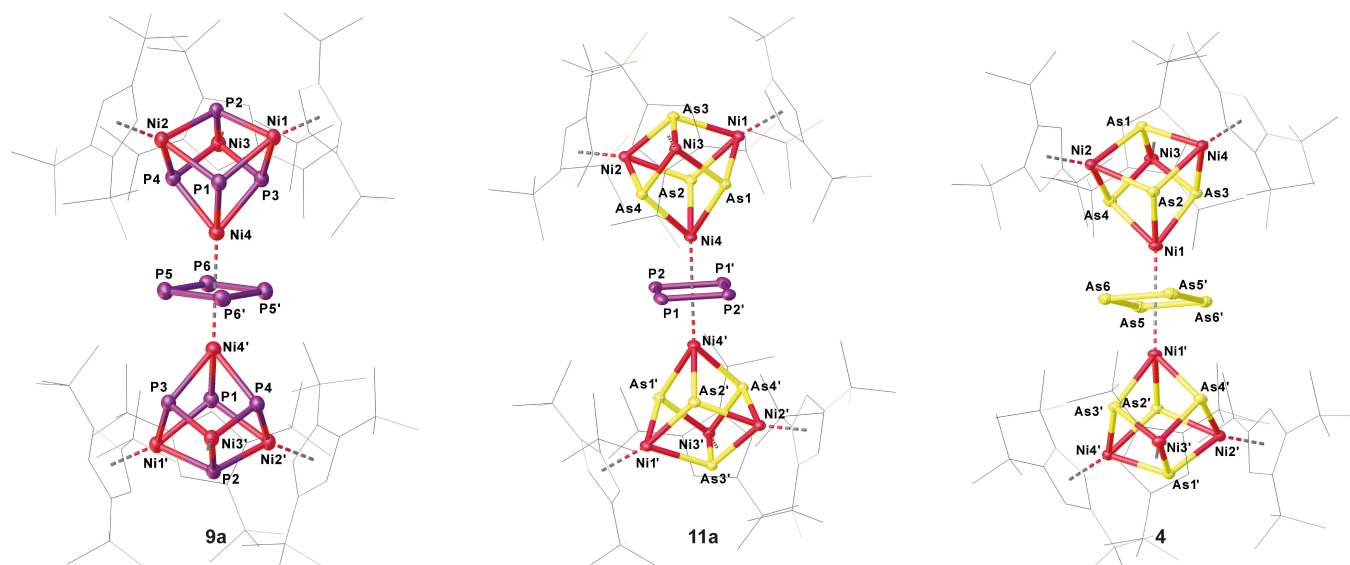
The presence of the bromide ligands in **6** and **8** enables the possibility of further functionalization. In view of the formed product **4**, a selective synthesis came into mind by a further

transfer of a whole  $E_4$  unit of **1** to the compounds **6** and **8**. Thus, the reaction of **6** and **8** with one equivalent of **1a** or **1b** results in the formation of the unprecedented triple-decker complexes  $[(\text{Cp}^{\text{R}}\text{Ni})_3\text{Ni}(\mu_3\text{-P})_4(\mu_4\text{-E}_4)]$  ( $\text{Cp}^{\text{R}} = \text{Cp}^{\text{R}}$ ,  $\text{E} = \text{P}$ : **9a**;  $\text{Cp}^{\text{R}} = \text{Cp}^{\text{Bn}}$ ,  $\text{E} = \text{P}$ : **10a**,  $\text{E} = \text{As}$ : **10b**) and  $[(\text{Cp}^{\text{R}}\text{Ni})_3\text{Ni}(\mu_3\text{-As})_4(\mu_4\text{-E}_4)]$  ( $\text{Cp}^{\text{R}} = \text{Cp}^{\text{R}}$ :  $\text{E} = \text{P}$ : **11a**,  $\text{E} = \text{As}$ : **4**;  $\text{Cp}^{\text{R}} = \text{Cp}^{\text{Bn}}$ ,  $\text{E} = \text{P}$ : **12a**,  $\text{E} = \text{As}$ : **12b**; Scheme 3). In all these reactions, the  $E_4$  unit in **1** is well transferred as a *cyclo*- $E_4^{2-}$  unit, which bridges two  $[\text{Ni}_4E_4]$  fragments. By this method, we successfully demonstrated that triple-decker complexes are accessible, even with different group 15 elements.

After column chromatographic workup and layering a dichloromethane solution with *n*-hexane or acetonitrile, crystals of the dimeric cubanes (**9a**, **10a**, **10b**, **11a**, **4**, **12a**, **12b**) suitable for single crystal X-ray diffraction analysis are obtained.<sup>[33]</sup> The molecular structures of the compounds **9a**, **11a** and **4** are depicted in Figure 3 (Figures for **10a**, **10b**, **12a**



**Scheme 3.** Overview of the reactions of **6a**, **8a**, **6b** and **8b** with another equivalent of  $[\text{Cp}''\text{Zr}(\eta^{11}\text{-E}_4)]$  ( $\text{E} = \text{P}$ : **1a**,  $\text{As}$ : **1b**).



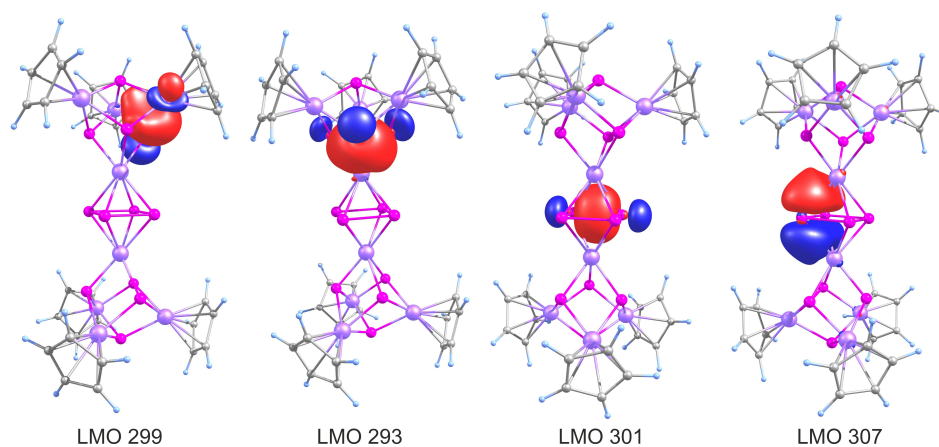
**Figure 3.** Molecular structures of **9a** (left), **11a** (middle), and **4** (right) in the solid state. Hydrogen atoms and solvent molecules are omitted and the  $\text{Cp}^{\text{R}}$  ligands are drawn in the wire frame model for clarity.



and **12b** are given in the Supporting Information). Their structural motif is exemplified based on the molecular structure of **9a**. They consist of two cubanes linked by a planar and almost rectangular *cyclo-E<sub>4</sub>* unit. Similar to the dimeric bromine-bridged cubanes they show also a kite-like distortion of the cage, due to the bulky Cp<sup>'''</sup> and Cp<sup>Bn</sup> ligands. The bond angles and bond lengths within the cubanes are in the range of values reported for similar compounds<sup>[26,30]</sup> The Ni–P distances to the P<sub>4</sub> moiety of 2.3705(14) to 2.4193(15) Å are slightly elongated compared to the distances within the cubane. There are two slightly different P–P distances of 2.1982(18) and 2.2110(18) Å within the P<sub>4</sub>-ring, which are in the range of a single bond.<sup>[34]</sup> This, and the natural charge distribution (see below), indicates that a *cyclo-P<sub>4</sub><sup>2-</sup>* moiety is present. The observed trend is also present in the other dimeric cubanes (**10a**, **10b**, **11a**, **4**, **12a**, **12b**). A comparison can also be drawn to the “free” *cyclo-E<sub>4</sub>* moieties of the compounds [K<sub>2</sub>(18-crown-6)<sub>2</sub>][P<sub>4</sub>]·3NH<sub>3</sub> and [K<sub>2</sub>(18-crown-6)<sub>2</sub>][As<sub>4</sub>] described by Korber et al., showing E–E distances in the same range (E = P: 2.160(2) to 2.172(2) Å; E = As: 2.3871(4) to 2.3898(4) Å).<sup>[35]</sup> Complexes containing a *cyclo-E<sub>4</sub><sup>2-</sup>* unit are rare and usually the moiety is coordinated end-on, as in the complexes [Cp<sup>'''</sup>Ta(CO)<sub>2</sub>(η<sup>4</sup>-P<sub>4</sub>)] or [Cp<sup>\*</sup>Nb(CO)<sub>2</sub>(η<sup>4</sup>-As<sub>4</sub>)].<sup>[36,37]</sup> The bond distances of such examples are in between a single and a double bond.<sup>[36,37,38]</sup> Also comparable triple-decker complexes with a *cyclo-E<sub>4</sub>* middle deck, for instance the ionic cobalt complexes [(Cp<sup>'''</sup>Co)<sub>2</sub>(μ<sub>3</sub>η<sup>4,4</sup>-E<sub>4</sub>)]X (E = P, As, X = BF<sub>4</sub>, [FAI {OC<sub>6</sub>F<sub>10</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}]<sup>39</sup>) or the cobalt β-diiminato compound [(L<sup>Dipp</sup>Co)<sub>2</sub>(μ<sub>3</sub>η<sup>4,4</sup>-As<sub>4</sub>)] (L = CH[CHN(2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]<sub>2</sub>), show distances in between a single and a double bond (E = P: 2.1837(8) to 2.3139(6) Å; E = As: 2.23299(5) to 2.5198(2) Å).<sup>[40]</sup> The slight elongation of the E–E bond distances of the *cyclo-E<sub>4</sub>* moiety of the compounds given here can be attributed to the bridging μ<sub>3</sub>η<sup>4,4</sup>-coordination to the more bulky [Ni<sub>4</sub>E<sub>4</sub>] cubanes. The P–P and As–As distances within the cubanes (**9a/10a**: 2.6027(15) Å to 2.725(2) Å, **4/11a/12a/12b**: 2.78276(4) to 2.9707(4) Å) are still longer than a normal single bond but shorter than the sum of the van der Waals radii, thus indicating interactions between the pnictogen atoms (see the Supporting Information).<sup>[31]</sup> This is

also confirmed by DFT calculations (TPSSh/def2-TZVP level of theory, see the Supporting Information). The Mayer bond index for the P...P interactions between P1, P3 and P4 vary from 0.31 to 0.38, for the P...P interactions involving P2 these are lower and vary from 0.28 to 0.31 (labeling according to Figure 3). The origin of the P2...P interactions is based on the P–Ni bonding orbitals to which contributions from the neighboring phosphorus atoms are mixed. The in-phase overlap of the P1, P3 and P4 orbitals with the nickel orbitals leads to a sigma-type Ni4–P bonding and to the relatively strong P...P bonding interaction. This can be nicely seen by the visualization of the localized molecular orbitals (Figure 4). The bonding interactions between the phosphorus atoms are also supported by electron localization function and localized orbital locator analysis (see the Supporting Information). Based on the natural charge distribution, for the model compound [((CpNi)<sub>3</sub>Ni(μ<sub>3</sub>-P)<sub>4</sub>)<sub>2</sub>(μ<sub>3</sub>η<sup>4,4</sup>-P<sub>4</sub>)], the *cyclo-P<sub>4</sub>* unit can be viewed as a *cyclo-P<sub>4</sub><sup>2-</sup>* ligand (nat. charge: –0.57). The Ni–Ni distances in the [Ni<sub>4</sub>E<sub>4</sub>] cubanes are too long to be indicative for considerable Ni–Ni interactions. This is also confirmed by the very low Mayer bond orders (see the Supporting Information).

Furthermore, for **9a**, **10a**, **10b**, **11a**, **4**, **12a** and **12b**, NMR investigations were carried out. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of these compounds show the corresponding sets of signals for the Cp<sup>'''</sup> or Cp<sup>Bn</sup> ligands. Interestingly, compound **9a** shows three well-resolved signals in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum already at room temperature (Figure 5). The observed signals at δ = 169.1, 122.8 and 58.4 ppm can be assigned to an A<sub>4</sub>M<sub>6</sub>X<sub>2</sub> spin system. The phosphorus atoms P<sub>X</sub> couple with three P<sub>M</sub> atoms to give the quartet at δ = 58.4 ppm with a coupling constant of <sup>2</sup>J<sub>PP</sub> = 16.8 Hz. Due to the coupling of the four P<sub>A</sub> atoms of the *cyclo-P<sub>4</sub><sup>2-</sup>* ligand with six equivalent P<sub>M</sub> atoms, a septet at δ = 169.1 ppm with a coupling constant of <sup>2</sup>J<sub>PP</sub> = 23.8 Hz arises. Furthermore, a coupling of the six P<sub>M</sub> atoms in **9a** to the P<sub>X</sub> as well as the P<sub>A</sub> atoms results in a rather broad, unresolved multiplet at δ = 122.8 ppm. The <sup>31</sup>P NMR spectroscopic data clearly shows that the solid-state structure of **9a** is retained in solution.



**Figure 4.** Selected localized molecular orbitals representing the Ni–P bonding (LMO 229 and 293) and the σ (LMO 301) and π (LMO 307) orbitals of the *cyclo-P<sub>4</sub>* unit in the model compound [((CpNi)<sub>3</sub>Ni(μ<sub>3</sub>-P)<sub>4</sub>)<sub>2</sub>(μ<sub>3</sub>η<sup>4,4</sup>-P<sub>4</sub>)] at the TPSSh/def2-TZVP level of theory.

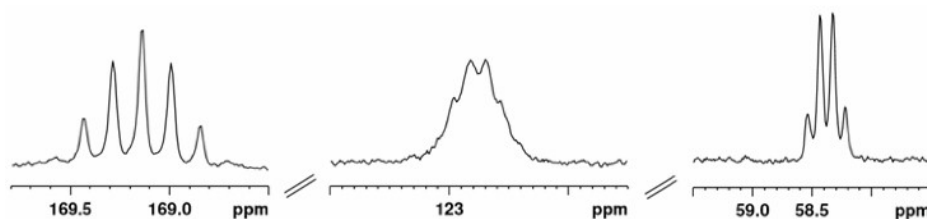


Figure 5. Sections of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **9a** at RT.

While the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **10b** shows two singlets ( $\delta = 159.6$  ppm,  $\delta = 126.8$  ppm), the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum for **10a** shows a further splitting due to the *cyclo*- $\text{P}_4^{2-}$  middle deck. A singlet at  $\delta = 118.7$  ppm can be assigned to the atoms P2/P2', while the quintet at  $\delta = 168.3$  ppm and the septet at  $\delta = 163.9$  ppm can be assigned to an  $\text{A}_6\text{X}_4$  spin system with a coupling constant of  $^2J_{\text{pp}} = 27.4$  Hz. For the compounds **11a** and **12a** containing a *cyclo*- $\text{P}_4^{2-}$  middle deck, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra display one singlet (**11a**:  $\delta = 149.5$  ppm, **12a**:  $\delta = 148.3$  ppm).

## Conclusion

In conclusion, it has been shown that the transfer of a complete  $\text{E}_4$  unit by treating  $[\text{Cp}''_2\text{Zr}(\eta^{1-1}\text{-E}_4)]$  ( $\text{E} = \text{P}$ : **1a**,  $\text{As}$ : **1b**) with  $[\text{Cp}^{\text{R}}\text{NiBr}]_2$  ( $\text{Cp}^{\text{R}} = \text{Cp}^{\text{Bn}}$ ,  $\text{Cp}^{\text{M}}$ ) leads to the formation of novel and unprecedented polypnictogen nickel complexes in high yields. Applying the concept of transfer reactions, the difficult handling and toxicity of white phosphorus and especially yellow arsenic can be avoided, and metastable, otherwise inaccessible products can be prepared. By studying the reactivity of **1** towards  $[\text{Cp}^{\text{R}}\text{NiBr}]_2$  ( $\text{Cp}^{\text{R}} = \text{Cp}^{\text{Bn}}$ ,  $\text{Cp}^{\text{M}}$ ), depending on the steric effects, reaction conditions and stoichiometry used, it could be shown that the polypnictogen units are transferred leading to products with different structural motifs. Thus, the reaction of **1** with  $[\text{Cp}^{\text{R}}\text{NiBr}]_2$  generated in situ and, in the case of **6a/6b**, additional  $[\text{NiBr}_2\cdot\text{dme}]$  leads to the formation of novel bromide-bridged cubanes  $[(\text{Cp}^{\text{R}}\text{Ni})_3\{\text{Ni}(\mu\text{-Br})\}(\mu_3\text{-E})_4]_2$  ( $\text{Cp}^{\text{R}} = \text{Cp}^{\text{M}}$ : **6a** ( $\text{E} = \text{P}$ ), **6b** ( $\text{E} = \text{As}$ ),  $\text{Cp}^{\text{R}} = \text{Cp}^{\text{Bn}}$ : **8a** ( $\text{E} = \text{P}$ ), **8b** ( $\text{E} = \text{As}$ )). By further reaction with another equivalent of **1**, it was possible to transfer another  $\text{E}_4$  unit as a *cyclo*- $\text{E}_4^{2-}$  ligand, which is stabilized by two nickel-cage fragments to build up the unprecedented triple-decker-like complexes **4**, **9**, **10**, **11a** and **12**, which also contain mixed polypnictogen ligands. Hence, we were able to transfer complete  $\text{E}_4$  units to  $\text{Cp}^{\text{R}}\text{Ni}$  fragments even though they are known to need only 3VE to fulfill the noble gas rule and prefer the formation of complexes with a *cyclo*- $\text{E}_3$  unit. Therefore, the use of  $[\text{Cp}''_2\text{Zr}(\mu, \eta^{1-1}\text{-E}_4)]$  (**1a**:  $\text{E} = \text{P}$ , **1b**:  $\text{E} = \text{As}$ ) as transfer reagents opens an improved and easily accessible way to create novel metastable polypnictogen ligand complexes.

## Experimental Section

**Single-crystal X-ray analysis:** Deposition Numbers s 2071421 (**2a**), 2071422 (**2b**), 2071423 ( $4\cdot 2\text{CH}_2\text{Cl}_2$ ), 2071424 (**5**), 2071425 (**6a**), 2071426 (**6b**), 2071396 (**8a**- $7\text{C}_7\text{H}_8$ ), 2071427 (**8b**- $6.5\text{C}_7\text{H}_8$ ), 2071428 (**9a**- $3\text{CH}_2\text{Cl}_2$ ), 2071429 (**10a**- $3\text{CH}_2\text{Cl}_2$ ), 2071430 (**11a**- $2\text{CH}_2\text{Cl}_2$ ), 2071431 (**12a**- $2.7\text{CH}_2\text{Cl}_2$ ) and 2071432 (**12b**- $3\text{CH}_2\text{Cl}_2$ ) contain 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 [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

## Acknowledgements

The authors acknowledge the Deutsche Forschungsgemeinschaft for their support within the project Sche 384/32-2. V.H. is grateful to the Fonds der Chemischen Industrie for a PhD fellowship. Open access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** arsenic · nickel · phosphorus · polypnictogen complexes · transfer reactions

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Manuscript received: March 29, 2021

Accepted manuscript online: May 10, 2021

Version of record online: June 1, 2021