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Selective Dimerization of Lewis-Acid/Base-Stabilized Phosphanylalanes

Michael Bodensteiner,[a] Alexey Y. Timoshkin,[b] Eugenia V. Peresypkina,[c] Ulf Vogel,[a] and Manfred Scheer*[a]

Dedicated to Professor Hartmut Bärnighausen on the occasion of his 80th birthday

Abstract: The reaction of $[\{(CO)_5W\}PRH_2]$ (R = H, Ph) with $H_3Al{\cdot}NR_3$ (R = Et, Me) leads to the formation of four-membered heterocyclic compounds $[(\{(CO)_5W\}P(H)AlH{\cdot}NEt_3)_2]$ and $[(\{(CO)_5W\}PhPAlH{\cdot}NMe_3)_2]$. Upon dissolving the solid compounds, fast equilibria between the isomers are observed on the NMR timescale. Further insight into the stability and reactivity of the isomers was gained by applying theoretical methods. DFT calculations predict that hydrogen elimination in the case of $[(\{(CO)_5W\}PhPAlH{\cdot}NMe_3)_2]$ may be reversible.

Keywords: aluminum · density functional calculations · dimerization · isomerization · phosphorus

Introduction

The storage and activation of hydrogen is an active topic in the chemistry of compounds that contain Group 13 and Group 15 elements. In particular, owing to its high hydrogen-storage capacity, ammonia–borane ($H_3B{\cdot}NH_3$) has attracted much attention.[1,2] Acids,[3] transition-metal catalysts,[4] nanoparticles,[5] and ionic liquids[6] have been successfully employed to liberate hydrogen from this system. Recently, spontaneous hydrogen elimination from aromatic amine boranes, $Ph{*}NH_2{\cdot}BH_3$, in THF, without any catalyst, was reported by Manners and co-workers.[7]

Phosphorus–boron compounds also show facile hydrogen activation in frustrated Lewis acid/Lewis base (LA/LB) pairs, such as $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$.[8] Even non-frustrated adducts can undergo hydrogen elimination to form polymers by using Rh^I catalysts.[9] Aluminum–phosphorus systems were recently used for the activation of C≡C triple bonds[10] and for chemically binding CO_2.[11] Our research focuses on the hydrogen-substituted parent compounds $H_2E{-}E'H_2$ (E = B, Al, Ga; E′ = P, As), which have only been studied theoretically owing to their instability.[12] These compounds undergo oligomerization and polymerization processes by intramolecular H_2 elimination, thereby resulting in numerous different structural motifs.[13] To avoid polymerization and to stabilize the non-existent monomers, we developed the concept of LA/LB stabilization, thereby enabling us to synthesize the first LA/LB-stabilized phosphanyl- and arsanylboranes, as well as phosphanylalanes and -gallanes,[14] by using $M(CO)_5$ (M = Cr, W) or $E(C_6F_5)_3$ (E = B, Ga) as LAs and amines or N-heterocyclic carbenes as LBs.[15] Computations predicted that stabilization of compounds of the type $H_2E{-}E'H_2$ can be achieved by using either LAs or LBs but not necessarily both; indeed, we succeeded in synthesizing the first LB-stabilized, hydrogen-substituted Group 13/15 compound, $H_2P{-}BH_2{\cdot}NMe_3$, by abstraction of the LA.[16] For the phosphanylalane analogue, abstraction of the LA is not possible; the LA/LB-stabilized compounds already easily lose hydrogen under formation of oligomers, even at ambient temperatures. Thus, the challenge is to control this process by applying appropriate conditions, such as solvent and temperature, and also the features of the LA or LB. We recently found that, depending on the solvent and the temperature, $[\{(CO)_5W\}H_2PAlH_2{\cdot}NMe_3]$ trimerized and we were able to gain mechanistic insight into this reaction.[17] We have now discovered that the LB has a decisive influence on the oligomerization process. Thus, the use of the slightly bulkier base NEt_3 results in the exclusive formation of a dimer. The NMe_3 derivative also undergoes selective dimerization if one hydrogen atom of the phosphine group is substituted by a phenyl group. Further aggregation of those four-membered rings would then lead to the tetramer. Theoretical investigations on the smaller model LA/LB substituents BH_3 and NH_3 revealed a distorted cube-shaped compound, which has already been reported by Cowley et al. for the non-LA/LB-stabilized derivative (Figure 1).[18] However, the geometries of these compounds differ significantly because they were influenced by the steric and the electronic properties of the substituents.

Herein, we investigate the role of the amine and the phenyl substituent on the oligomerization products.

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[a] Dr. M. Bodensteiner, Dr. U. Vogel, Prof. Dr. M. Scheer
Institut für Anorganische Chemie
Universität Regensburg, 93040 Regensburg (Germany)
Fax: (+49) 941-943-4439
E-mail: manfred.scheer@ur.de

[b] Prof. Dr. A. Y. Timoshkin
Department of Chemistry, St. Petersburg State University
University pr. 26, 198504 Old Peterhoff, St. Petersburg (Russia)

[c] Dr. E. V. Peresypkina
Nikolaev Institute of Inorganic Chemistry SB RAS
Ak. Lavrentiev pr. 3, 630090 Novosibirsk (Russia)

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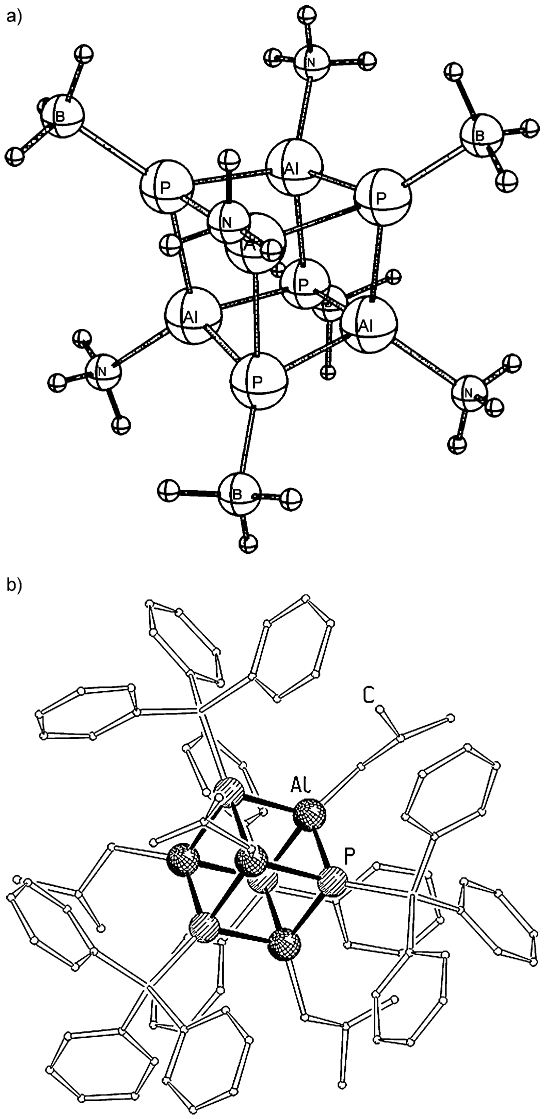


Figure 1. a) Theoretically computed $[\{(H_3B)PAl(NH_3)\}_4]$ (P–Al 2.381 Å; Al–P–Al 78.0°, P–Al–P 100.8°) and b) experimentally observed $[\{(Ph_3Si)PAl(i\text{Bu})\}_4]$ heterocubanes (P–Al 2.409(4)–2.417(4) Å; Al–P–Al 90.9(2)–92.3°, P–Al–P 87.7(2)–89.0(2)°).[18]

Results and Discussion

The triethylamine-substituted compound $[\{(CO)_5W\}H_2PAlH_2{\cdot}NEt_3]$ (**1**) can be synthesized by the reaction between $W(CO)_5PH_3$ and $AlH_3{\cdot}NEt_3$ in CH_2Cl_2, but the solution has to be cooled immediately to −78 °C to inhibit further elimination of hydrogen and aggregation. Crystals of compound **1** can be isolated in good yield (89 %) at low temperatures. As a solid, compound **1** is stable at ambient temperature, but is extremely air-sensitive. Its ^{31}P NMR spectrum shows the expected triplet at $\delta = -242$ ppm ($^1J(P,H) = 286$ Hz), which is in good accordance with the data for the NMe_3 derivative. IR spectra could not be acquired from a solid sample because, even in a glovebox, the compound rapidly decomposed during the preparation of a KBr pellet. Nevertheless, P–H (2322 cm^{-1}) and Al–H stretching frequencies (1833 cm^{-1}, 1744 cm^{-1}) were observed in CH_2Cl_2. Despite the absence of the molecular-ion peak in the mass spectrum (EI), peaks of characteristic fragments were detected. In the solid state, two molecules of compound **1** arrange through hydride bridges, thereby resulting in a distorted trigonal bipyramidal geometry at the aluminum atom (Figure 2). In comparison to $[\{(CO)_5W\}H_2PAlH_2{\cdot}NMe_3]$, the distance between the molecules is elongated, owing to the larger base (Al–Al′ 3.0067(3) Å in compound **1** compared to 2.908(2) Å). Furthermore, the W–P–Al angle is widened by more than eight degrees (127.02(10)° in compound **1**, in comparison with 118.44(4)° in $[\{(CO)_5W\}H_2PAlH_2{\cdot}NMe_3]$).

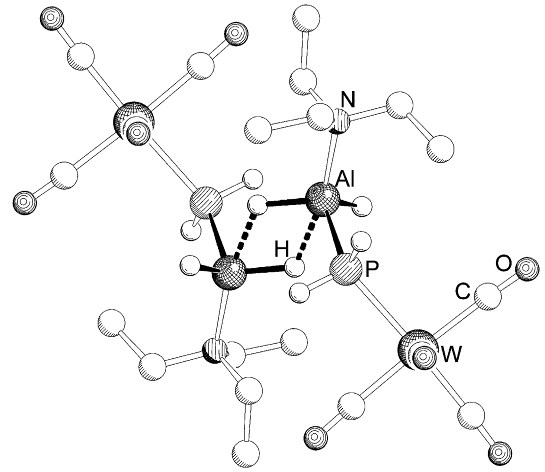


Figure 2. Hydride-bridged arrangement of compound **1** in the solid state; hydrogen atoms of the triethylamine moiety are omitted for clarity. Selected bond lengths [Å] and angles [°]: W–P 2.559(2), P–Al 2.387(3), Al–N 2.066(6); P–Al–N 105.77(19).

If the reaction mixture of $W(CO)_5PH_3$ and $AlH_3{\cdot}NEt_3$ is not cooled down, or a solution of compound **1** is warmed up to 4 °C, yellow needles of $[(\{(CO)_5W\}HPAlH{\cdot}NEt_3)_2]$ (**2**) are obtained. Surprisingly, compound **2** does not undergo trimerization, but, instead, undergoes dimerization, in comparison to the NMe_3 derivative.[17] Based on the NMR data and theoretical calculations, a four-membered-ringed intermediate, $[(\{(CO)_5W\}H_2PAlH_2{\cdot}NMe_3)_2]$, was also proposed for the trimethylamine system. However, it could not be isolated owing to its further reactivity towards the ladder-shaped compound $[(\{(CO)_5W\}HPAlH{\cdot}NMe_3)_2\{(CO)_5WPAl{\cdot}NMe_3\}]$. Similar additional aggregation was not observed for the NEt_3 derivative at all; the four-membered ring was the only product of this reaction. The $^{31}P\{^1H\}$ NMR spectrum of a solution of compound **2** in CD_2Cl_2 showed three signals (Figure 3).

In addition, in the ^1H NMR spectrum, resonances for different aminoethyl groups are detected, which indicate the presence of different isomers in solution. Discounting the possibility of ring puckering, which is expected to be an effect of the arrangement of the substituents, the structures of the possible isomers are depicted in Figure 4.

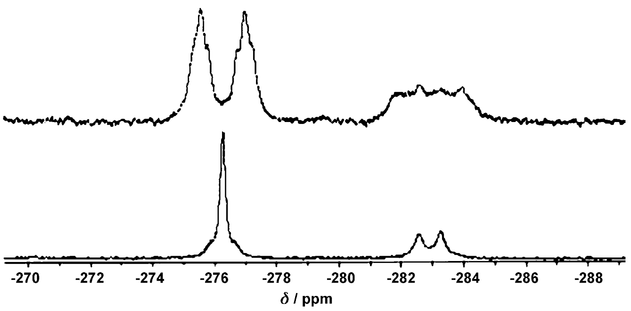


Figure 3. ^{31}P NMR (top) and ^{31}P{^{1}H} NMR spectra (bottom) of compound **2** in CH_2Cl_2 at 300 K.

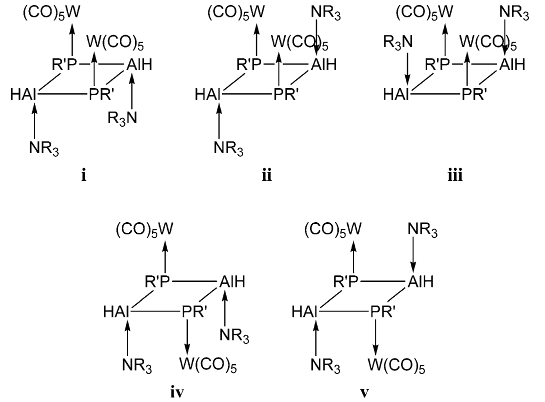


Figure 4. Possible isomers of compounds **2** (R = Et, R′ = H) and **3** (R = Me, R′ = Ph).

The isomer determined by X-ray structure analysis is **2(i)** (Figure 4). The four-membered Al_2P_2 ring is puckered by 16.8° along the Al–Al axis. DFT calculations also show that this geometry is the most stable for the hypothetical parent molecule *cis*-$(HAlPH)_2$.[19] The P–Al bond lengths (2.382(4) and 2.385(4) Å) are in good agreement with those found in compound **1**. However, the angles within the ring are bent close to 90° to allow the four-membered ring to be formed (Al1–P–Al2 84.15(15), P–Al1–P 94.62(18), P–Al2–P 94.45(18)°).

Unfortunately, all efforts to isolate other isomers in the solid state failed. The unit-cell parameters for about 100 different crystals were equal within the standard deviation range. The seven crystals that possessed the most-deviated cell parameters were fully processed in X-ray experiments and all gave the structure of compound **2** (isomer **i**; Figure 5).

If these crystals are dissolved in CD_2Cl_2 to record their ^{31}P NMR spectra, the same three signals are detected with consistent integration ratios. This observation suggests the existence of an equilibrium between the isomers that is fast on the NMR timescale. For such compounds, it is known that, in presence of a free amine, a base-exchange occurs through an intermediate that features a trigonal-bipyramidal aluminum atom with two amine ligands.[20] Even with extremely careful handling, the appearance of traces of free NEt_3 cannot be completely avoided, owing to the decomposition of some of the substance during solvation. A small signal for free NEt_3 is observed in the ^{1}H NMR spectrum of compound **2**. Such an exchange of one NEt_3 ligand leads to the formation of isomers **ii** and **iii**, which give the additional resonances in the NMR spectra (Scheme 1).

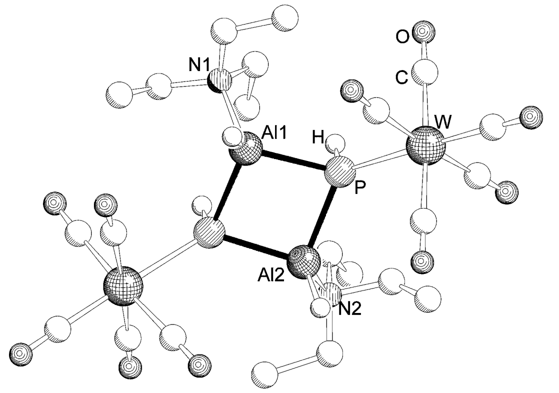
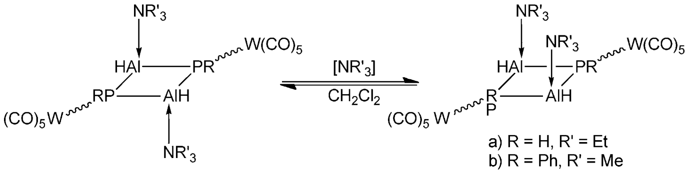


Figure 5. Puckered four-membered ring of compound **2** in the solid state; hydrogen atoms on the triethylamine moiety are omitted for clarity. Selected bond lengths [Å] and angles [°]: W–P 2.589(3), P–Al1 2.382(4), P–Al2 2.385(4), Al1–N1 2.000(13), Al2–N2 1.990(14); Al1–P–Al2 84.15(15), P–Al1–P 94.62(18), P–Al2–P 94.45(18).



Scheme 1. Isomerization equilibrium of compounds **2** and **3** in CH_2Cl_2.

Interestingly, a similar four-membered ring motif is found in the product of the reaction between the mono-phenyl-substituted phosphane $[(CO)_5WPPhH_2]$ and the amine adduct $H_3Al{\cdot}NMe_3$, even in the presence of the smaller base NMe_3. In contrast to compound **2**, isomer **v**, which features a *trans* arrangement of similar substituents, is formed in $[(\{(CO)_5W\}PhPAlH{\cdot}NMe_3)_2]$ (**3**) (Figure 6).

Moreover, the four-membered ring is perfectly planar in the solid state. The monomeric precursor compound $[\{(CO)_5W\}PhHPAlH_2{\cdot}NMe_3]$ cannot be isolated owing to a fast dimerization to afford compound **3**. However, evidence for its presence is observed in the ^{31}P NMR spectrum of the crude reaction mixture, which shows an additional doublet at $\delta = -136$ ppm ($^1J(P,H) = 296$ Hz).[21] Furthermore, as in the spectra of compound **2**, ^{31}P NMR studies of compound **3** also reveal signals for different isomers at $\delta = -138$, -140, -142, and -144 ppm and the ^{1}H and ^{31}P NMR spectra show traces of decomposition products $[(CO)_5WPPhH_2]$ and NMe_3.

Theoretical studies: Further information regarding the behavior of these four-membered rings was gained from theoretical computations. The structural features of all of the

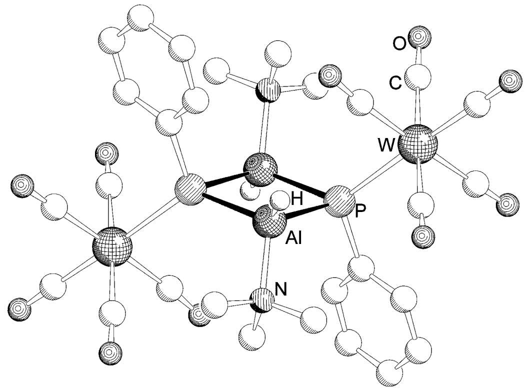


Figure 6. Planar four-membered ring of compound **3** in the solid state; hydrogen atoms at the phenyl substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: W–P 2.6256(19), P–Al 2.418(3), Al–N 1.978(6); Al-P-Al 82.81(9), P-Al-P 97.20(9).

theoretically considered isomers are summarized in the Supporting Information.[21] Theoretical computations of different isomers at the B3LYP/6-31G* (ECP on W) level of theory reveal that all five of the possible isomers of compound **2** (Figure 3) are close in energy (the maximum energy difference was only 11 kJ mol^{-1}) and that isomer **2(ii)** is predicted to be the lowest in energy (Table 1). However, the three isomers **2(i)**, **2(ii)**, and **2(v)** are very close in energy (within 4 kJ mol^{-1}), which fits well with the experimentally observed equilibrium between the isomers in solution. The negative value of the isomerization Gibbs energy indicates that isomer **2(i)** should be dominant in the gas phase at 298 K (assuming that an equilibrium between all of the isomers is achieved). In our opinion, the fact that only isomer **2(i)** could be isolated in the solid state is due to favorable packing in the crystal. Isomer **2(i)** possesses a relatively large dipole moment, which should increase the crystal lattice energy and facilitate its crystallization.

Table 1. $E°_0$, standard isomerization Gibbs energies ($\Delta G°_{298}$), dipole moments (μ), and the Debye and dihedral PAlPAl angles (θ_{PAlPAl}) for the different isomers of compounds **2** and **3**.[a]

Isomer	$E°_0$ [kJ mol^{-1}]	$\Delta G°_{298}$ [kJ mol^{-1}]	μ [°]	θ_{PAlPAl} [°]
2(i)	3.9	−3.3	5.7	29.9
	(3.9)	(−4.0)	(6.1)	(28.0)
2(ii)	0.0	0.0	2.5	17.3
	(0.0)	(0.0)	(1.9)	(17.8)
2(iii)	11.3	20.0	4.0	2.8
	(12.1)	(15.7)	(3.4)	(1.5)
2(iv)	7.4	9.5	3.2	21.7
	(7.5)	(3.7)	(1.9)	(24.1)
2(v)	3.4	5.9	6.2	15.8
	(3.4)	(0.0)	(4.2)	(11.4)
3(i)	25.7	27.7	13.5	18.6
3(ii)	10.8	16.9	14.2	17.8
3(iii)	15.6	15.8	6.5	24.9
3(iv)	9.1	7.9	4.4	18.3
3(v)	0.0	0.0	0.0	0.0

[a] Values in parenthesis correspond to the isomers of $[(\{(CO)_5W\}PHAlH{\cdot}NMe_3)_2]$. Calculations were performed at the B3LYP/6-31G* (ECP on W) level of theory.

The energy difference between the isomers of the NEt_3 and NMe_3 derivatives is very small (for comparison, data for the analogous $[(\{(CO)_5W\}PHAlH{\cdot}NMe_3)_2]$ isomers are given in parentheses in Table 1).

In contrast, the substitution of a hydrogen atom at a phosphorus site by a phenyl group leads to larger energy differences (up to 25 kJ mol^{-1}) between the five possible isomers of compound **3**, with isomer **3(v)** being 9 kJ mol^{-1} more stable than isomer **3(iv)**. The Gibbs energy values for the isomerization reactions in the gas phase suggest that isomer **3(v)** is the dominant form at standard temperature. In agreement with theoretical predictions, crystal-structure analysis revealed that isomer **3(v)** featured a planar four-membered Al_2P_2 ring (Figure 6). In contrast, the optimized structures of isomer **2(v)** and its NMe_3 analogue are asymmetric, with a puckered Al_2P_2 ring. This result suggests that the phenyl groups on the phosphorus atoms induce the planarity of the Al_2P_2 ring in isomer **3(v)**. The unique feature of isomer **3(v)** is the presence of short intramolecular Al–H···H–C distances (2.217 Å) between the negatively charged hydridic hydrogen atom at the aluminum center and the partially positively charged hydrogen atom on the phenyl group (Mulliken partial charges are −0.17 and +0.13, respectively). This interaction might be responsible for the stabilization of isomer **3(v)** in the solid state.

The planar rings of Group 13/15 elements are quite common for structures of dimeric imino compounds.[12,13] For four-membered rings of the heavier Group 15 elements, both puckered and planar structures have been observed and the planar structures are usually enforced by very bulky substituents. For example, the structurally characterized donor-only stabilized cyclic aluminum–phosphorus compound $[(i\mathrm{Pr}_3SiPAlClPy)_2]$ has a planar Al_2P_2 ring.[22] Structural and thermodynamic features of model Ga and In compounds have been theoretically explored in a recent report.[23]

The experimentally observed equilibrium between the isomers of compound **2** in solution indicates a fast ligand-exchange process. There are several plausible mechanisms to account for this exchange. Our computational data (Table 2) reveal that the dimers are quite strongly bound with respect to the dissociation of the Al_2P_2 ring into monomers. For isomers **2(ii)** and **3(v)**, such a dissociation process is endothermic by 190–196 kJ mol^{-1} (per mole of dimer). These results suggest that a dissociation process cannot be responsible for the fast isomerization of compound **2** at room temperature. To gain an insight into the exchange mechanism, we performed additional computational studies for the two most probable mechanisms, based on S_N1 and S_N2 amine-exchange reactions (Figure 7).

We found that the dissociation of NEt_3 from compound **2** is endothermic by 107–132 kJ mol^{-1} (depending on the isomer) and the dissociation of NMe_3 from compound **3** is endothermic by 95–135 kJ mol^{-1}. In both cases, the most-stable $[\{(CO)_5WPRAlH\}_2NR'_3]$ product features the $W(CO)_5$ group in a bridging position.[21] The reaction energies of the amine-base-dissociation processes are the lower

Table 2. Predicted standard enthalpies and standard Gibbs energies for the gas-phase reactions.[a]

	Process	$\Delta H°_{298}$ [kJ mol^{-1}]	$\Delta G°_{298}$ [kJ mol^{-1}]
1a	$AlH_3{\cdot}NEt_3+(CO)_5WPH_3=\mathbf{1}+H_2$	−39.1 (−38.2)	−24.9 (−27.5)
1b	$AlH_3{\cdot}NMe_3+(CO)_5WP(Ph)H_2=[(CO)_5WP(Ph)HAlH_2{\cdot}NMe_3]+H_2$	−33.4	−24.3
2a	$\mathbf{1}=[(CO)_5WPHAlH{\cdot}NEt_3]+H_2$	77.0	49.6
2b	$[(CO)_5WP(Ph)HAlH_2{\cdot}NMe_3]=[(CO)_5WP(Ph)AlH{\cdot}NMe_3]+H_2$	99.9	78.9
3a	$[(CO)_5WPHAlH{\cdot}NEt_3]=0.5\,\mathbf{2}$	−97.9	−75.2
3b	$[(CO)_5WP(Ph)AlH{\cdot}NMe_3]=0.5\,\mathbf{3}$	−95.0	−68.8
4a	$\mathbf{1}=0.5\,\mathbf{2}+H_2$	−20.9	−25.5
4b	$[(CO)_5WP(Ph)HAlH_2{\cdot}NMe_3]=0.5\,\mathbf{3}+H_2$	4.9	10.1
5a	$AlH_3{\cdot}NEt_3+[(CO)_5WPH_3]=0.5\,\mathbf{2}+2H_2$	−60.0 (−58.8)	−50.4 (−48.1)
5b	$AlH_3{\cdot}NMe_3+(CO)_5WP(Ph)H_2=0.5\,\mathbf{3}+2\,H_2$	−28.5	−14.2

[a] Values in parenthesis correspond to reactions with NMe_3 instead of NEt_3, see reference [2]. Calculations were performed at the B3LYP/6-31G*(ECP on W) level of theory.

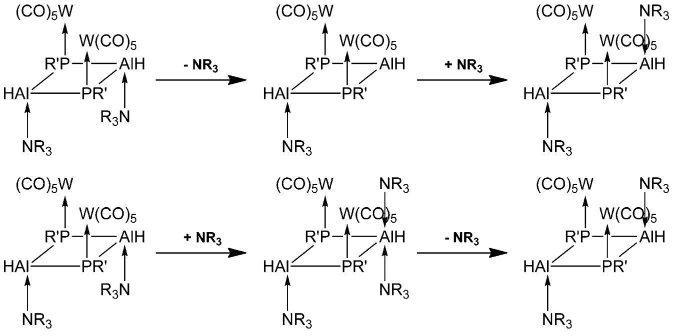


Figure 7. Proposed S_N1 (top) and S_N2 (bottom) isomerization pathways (**2**: R = Et, R′ = H; **3**: R = Me, R′ = Ph).

limits for the activation energies of the S_N1 mechanism. These values (95–135 kJ mol^{-1}) appear to be too high to account for the observed fast isomerization at room temperature. Thus, an isomerization through an S_N1 mechanism with amine dissociation can be ruled out as being too energetically demanding.

The alternative S_N2 pathway includes an addition of the amine to the dimeric ring (Figure 7, bottom). Our attempts to optimize the intermediate structures for the S_N2 mechanism (by the addition of the amine to compounds **2** and **3**) failed. Proposed intermediates with pentacoordinate trigonal-pyramidal aluminum atoms were unstable; such structures lost one amine group upon optimization. This result indicates easy removal of an amine moiety from the intermediate but does not allow us to obtain the activation energy for the first step of the S_N2 reaction pathway. The presence of free amines in solution (broad signals in the ^{1}H NMR spectra) provides a further hint at a dynamic process and is in agreement with a fast amine-base-exchange process through an S_N2 mechanism for both compounds **2** and **3** (Figure 7). The origin of the free base in solution is most probably due to minor decomposition of the compounds owing to side reactions (compounds **2** and **3** are unstable at room temperature in solution).

The first hydrogen-elimination process from the starting materials (Table 2, processes 1a and 1b) is energetically favorable. The elimination of the second hydrogen molecule with the formation of monomers $[\{(CO)_5W\}PHAlH{\cdot}NEt_3]$ and $[\{(CO)_5W\}P(Ph)AlH{\cdot}NMe_3]$ (Table 2, processes 2a and 2b) is unfavorable, but is compensated by the subsequent dimerization energies (Table 2, process 3). The overall reaction (Table 2, processes 5a and 5b) is exothermic and thermodynamically allowed for both compounds **2** and **3**.

A comparison of processes 4a and 4b shows that compound **1** is thermodynamically unstable towards H_2 evolution, whilst an analogous H_2 elimination from the $[\{(CO)_5W\}P(Ph)HAlH_2{\cdot}NMe_3]$ monomer is endergonic. The experimental isolation of the more-reactive compound **1** in the solid state may be attributed to additional hydrogen-bridge stabilization (Figure 1). A similar assembly of the phenyl-substituted derivative appears to be less favorable, owing to steric hindrance. From our theoretical computations, it appears that, in the case of the formation of compound **3**, the second hydrogen-evolution step (Table 2, process 4b) may be reversible, which is of potential interest for applications in hydrogen-storage/release. These predictions require additional experimental studies at high hydrogen pressures. Thermodynamic parameters for the reactions that lead to compounds **2** and **3** from the starting materials are summarized in Table 2, which presents results for the most-stable isomers, **2(ii)** and **3(v)**. Thus, the substitution of NEt_3 by NMe_3 only leads to minimal changes in the thermodynamics of the dehydrogenation reactions.

Conclusion

In summary, these results have shown that minor changes in the amine moiety from NMe_3 to NEt_3 in Lewis-acid/base-stabilized phosphanylalanes $[\{(CO)_5W\}H_2PAlH_2{\cdot}NR_3]$ leads to significantly different reactivity. In the case of the larger base, smaller four-membered $[(\{(CO)_5W\}HPAlH{\cdot}NEt_3)_2]$ rings are formed, which show dynamic behavior in solution. Similarly, four-membered $[(\{(CO)_5W\}PhPAlH{\cdot}NMe_3)_2]$ rings are formed in the case of the phenyl-substituted derivative. Upon dissolving the solid products, fast equilibria between different ring isomers are observed. The stability of these isomers and their interconversion pathways were calculated by using DFT methods.

Experimental Section

All procedures were either performed under an argon atmosphere in a glovebox or by using standard Schlenk techniques. Solvents were degassed and dried over appropriate drying agents. $[(\{(CO)_5W\}PH_3]$,[24] $[\{(CO)_5W\}PH_2Ph]$,[25] $H_3Al{\cdot}NEt_3$,[26] and $H_3Al{\cdot}NMe_3$[27] were synthesized according to literature procedures. All NMR spectra were acquired on a BRUKER AVANCE 400 spectrometer (^{1}H: 400.13 MHz, ^{27}Al: 104.27 MHz, ^{31}P: 161.98 MHz) and chemical shifts (δ) are given in ppm. IR spectroscopy was performed on a VARIAN FTS800 spectrometer and absorption maxima are given in cm^{-1}. MS (EI) spectra were obtained on a FINNIGAN MAT SSQ 710A.

Synthesis of compound 1: $[\{(CO)_5W\}PH_3]$ (179 mg, 0.5 mmol) and $H_3Al{\cdot}NEt_3$ (65 mg, 0.5 mmol) were stirred in CH_2Cl_2 (3 mL) at RT until the evolution of gas ceased (20 min) and the reaction mixture was immediately cooled to −78 °C. Colorless crystals of compound **1** could already be obtained during the cooling process. Yield: 217 mg (0.445 mmol, 89 %).

Analytical data for compound 1: ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, TMS): $\delta = 1.27$ (t, J(H,H) = 7 Hz; CH_3), 2.19 (br d, J(P,H) = 286 Hz; PH_2), 2.94 (q, J(H,H) = 7 Hz; CH_2), 3.8 ppm (br s; AlH_2); $^1H\{^{31}P\}$ NMR (400 MHz, CD_2Cl_2, 300 K, TMS): $\delta = 1.27$ (t, J(H,H) = 7 Hz; CH_3), 2.19 (br s; PH_2), 2.94 (q, J(H,H) = 7 Hz; CH_2), 3.8 ppm (br s; AlH_2); ^{27}Al NMR (104 MHz, CD_2Cl_2, 300 K, 1.5 M $Al(NO_3)_3$): $\delta = 141$ ppm (br s, $\omega_{1/2} = 1500$ Hz; AlH_2); ^{31}P NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4): $\delta = -242$ ppm (br t, J(P,H) = 286 Hz; PH_2); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4): $\delta = -242$ ppm (br s; PH_2); MS (EI, 70 eV): m/z (%): 429 (0.4) $[(CO)_5W(PH_2AlH_2{\cdot}NEt)]^+$, 386 (0.5) $[(CO)_5W(PH_2AlH_2)]^+$, 358 (66) $[(CO)_5WPH_3]^+$, 328 (13) $[(CO)_4WPH]^+$, 300 (71) $[(CO)_3WPH]^+$, 272 (62) $[(CO)_2WPH]^+$, 243 (41) $[(CO)WP]^+$, 215 (23) $[WP]^+$, 184 (5) $[W]^+$, 101 (19) $[NEt_3]^+$, 86 (100) $[NEt_2CH_2]^+$; IR (CH_2Cl_2): $\tilde{\nu} = 2322$ (w; PH), 2068 (s; CO), 1978 (s; CO), 1929 (vs; CO), 1833 (m; AlH), 1774 cm^{-1} (m; AlH).

Synthesis of compound 2: *Method A*. A solution of $[\{(CO)_5W\}PH_3]$ (179 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added to $H_3Al{\cdot}NEt_3$ (65 mg, 0.5 mmol) and the mixture was stirred for 80 min at RT. At 4 °C, pale-yellow crystals were obtained after 2 days. Yield: 377 mg (0.39 mmol, 78 %). *Method B.* A 0.5 mmol solution of compound **1** was stored at 4 °C; after 2 days, crystals of compound **2** start to grow. Yield: 302 mg (0.31 mmol, 70 % from compound **1**, 62 % from the starting materials).

Analytical data for compound 2: ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, TMS): $\delta = -8.4$ (br s; AlH), −8.1 (br s; AlH), −6.6 (br s; AlH), 0.52 (dt, J(P,H) = 233 Hz, J(H,H) = 5 Hz; PH), 0.73 (dm, J(P,H) = 234 Hz; PH), 0.91 (dm, J(P,H) = 232 Hz; PH), 1.42 (t, J(H,H) = 7 Hz; CH_3), 3.13 ppm (q, J(H,H) = 7 Hz; CH_2); $^1H\{^{31}P\}$ NMR (400 MHz, CD_2Cl_2, 300 K, TMS): $\delta = -8.4$ (br s; AlH), −8.1 (br s; AlH), −6.6 (br s; AlH), 0.52 (t, J(H,H) = 5 Hz; PH), 0.73 (m; PH), 0.91 (m; PH), 1.42 (t, J(H,H) = 7 Hz; CH_3), 3.13 ppm (q, J(H,H) = 7 Hz; CH_2); ^{27}Al NMR (104 MHz, CD_2Cl_2, 300 K, 1.5 M $Al(NO_3)_3$): $\delta = 158$ ppm (br s, $\omega_{1/2} = 1600$ Hz; AlH); ^{31}P NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4): $\delta = -276$ (br d, J(P,H) = 233 Hz; PH), −283 ppm (br ddm, J(P,P) = 111 Hz; PH); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4): $\delta = -276$ (br s; PH), −283 ppm (br d, J(P,P) = 111 Hz; PH); MS (EI, 14 eV): m/z (%): 356 (28) $[(CO)_5WPH]^+$, 328 (2) $[(CO)_4WPH]^+$, 299 (30) $[(CO)_3WPH]^+$, 270 (18) $[(CO)_2WP]^+$, 241 (29) $[(CO)WP]^+$, 214 (8) $[WP]^+$, 184 3) $[W]^+$, 101 (100) $[NEt_3]^+$; IR (CH_2Cl_2): $\tilde{\nu} = 2295$ (w; PH), 2068 (s; CO), 2060 (m; CO), 1977 (s; CO), 1921 (vs; CO), 1830 (m; AlH), 1774 (m; AlH).

Synthesis of compound 3: A solution of $[\{(CO)_5W\}PH_2Ph]$ (217 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was stirred with $H_3Al{\cdot}NMe_3$ (45 mg, 0.5 mmol) at RT. After the evolution of gas ceased (1 h), the yellow solution was stored at 4 °C for 5 days to obtain yellow crystals of compound **3**. Yield: 314 mg (0.30 mmol, 61 %). The NMR data were taken from the crude reaction mixture after 30 min and showed additional signals for $[\{(CO)_5W\}P(H)(Ph)AlH_2{\cdot}NMe_3]$ as an intermediate product that could not be isolated.

Analytical data of compound 3: ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, TMS): $\delta = 2.46$ (s; NMe_3), 2.77 (s; NMe_3), 4.0 (br s; AlH), 7.2–7.7 ppm (m; Ph); ^{27}Al NMR (104 MHz, CD_2Cl_2, 300 K, 1.5 M $Al(NO_3)_3$): $\delta = 147$ ppm (br s, $\omega_{1/2} = 1600$ Hz; AlH); ^{31}P NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4): $\delta = -138$ (br s; PPh), −140 (br s; PPh), −142 (br s; PPh), −144 ppm (br s; PPh); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4): $\delta = -138$ (br s; PPh), −140 (br s; PPh), −142 (br s; PPh), −144 ppm (br s; PPh); MS (EI, 14 eV): m/z (%): 866 (0.7) $[M-2Ph-Me-2H]^+$, 433 (67) $[(CO)_5WPHPh)]^+$, 377 (51) $[(CO)_3WPHPh)]^+$, 348 (100) $[(CO)_2WPPh)]^+$, 320 (44) $[(CO)WPPh)]^+$, 292 (64) $[WPPh]^+$, 242 (16) $[(CO)WP]^+$, 214 (7) $[WP]^+$; IR (CH_2Cl_2): $\tilde{\nu} = 2076$ (s; CO), 1994 (s; CO), 1942 (vs; CO), 1751 cm^{-1} (w; AlH).

NMR data of $[\{(CO)_5W\}P(H)(Ph)AlH_2{\cdot}NMe_3]$: ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, TMS): $\delta = 2.17$ (s; NMe_3), 4.0 (br s; AlH_2), 4.24 (d, J(P,H) = 296 Hz; PPhH), 7.2–7.7 ppm (m; Ph); ^{31}P NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4): $\delta = -136$ ppm (br d, J(P,H) = 296 Hz; PPhH); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4): $\delta = -136$ ppm (br s; PPhH).

Crystals of compounds **1**, **2**, and **3** were taken from a cooled (−30 °C) Schlenk flask under a stream of argon. The crystals were immediately covered with perfluorinated polyethers (Fomblin, Aldrich) and the chosen single crystal was transferred onto a nylon loop together with some oil and directly attached onto the goniometer under a stream of cold nitrogen.[28] All of the crystals were processed on an Oxford Diffraction Gemini R Ultra CCD diffractometer by using $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). For compound **1**, an analytical absorption correction was applied[29] and a multi-scan correction from equivalents was carried out for compounds **2** and **3**.[30] The structures were solved by using direct methods with SIR-92[31] and full-matrix least-squares refinement on F^2 was performed with SHELXL-97.[32] Hydrogen atoms at the phosphorus and aluminum atoms were refined isotropically with free distances; the carbon-bound hydrogen atoms were calculated geometrically and a riding model was used for refinement. The ethyl groups in compound **2** were disordered over two positions; thus, several restraints were used for refinement. Residual density was located close to the tungsten atoms. The crystals of compounds **2** and **3** were very sensitive and some decomposition from the surface could not be avoided. In addition, the thin needles only provided very weak scattering power.

Crystal data for compound 1: $C_{11}H_{19}AlNO_5PW$; $M = 487.06$; triclinic; space group $P\bar{1}$ (no. 2); $a = 7.1463(5)$, $b = 10.8385(7)$, $c = 12.0833(7)$ Å; $\alpha = 86.767(5)$, $\beta = 75.650(6)$, $\gamma = 76.089(6)°$; $V = 880.12(10)$ Å^3; $Z = 2$; $\mu = 13.656$ mm^{-1}; $F(000) = 468$; $T = 123(1)$ K; 6034 reflections measured; 2689 unique reflections ($R_{int} = 0.0486$); $R_1 = 0.0478$ and $wR_2 = 0.1267$ for $I > 2\sigma(I)$.

Crystal data for compound 2·CH_2Cl_2: $C_{23}H_{36}Al_2Cl_2N_2O_{10}P_2W_2$; $M = 1037.07$; orthorhombic; space group $Pnma$ (no. 62); $a = 29.201(4)$, $b = 17.283(4)$, $c = 7.1718(5)$ Å; $V = 3619.5(10)$ Å^3; $Z = 4$; $\mu = 14.671$ mm^{-1}; $F(000) = 2024$; $T = 104(1)$ K; 8677 reflections measured; 2007 unique reflections ($R_{int} = 0.0365$); $R_1 = 0.0418$ and $wR_2 = 0.1122$ for $I > 2\sigma(I)$.

Crystal data for compound 3: $C_{28}H_{30}Al_2N_2O_{10}P_2W_2$; $M = 1038.12$; monoclinic; space group $P2_1/c$ (no. 14); $a = 10.307(3)$, $b = 18.925(4)$, $c = 9.143(2)$ Å; $\beta = 97.87(2)°$; $V = 1766.6(7)$ Å^3; $Z = 2$; $\mu = 13.667$ mm^{-1}; $F(000) = 992$; $T = 104(1)$ K; 10142 reflections measured; 1894 unique reflections ($R_{int} = 0.0347$); $R_1 = 0.0248$ and $wR_2 = 0.0540$ for $I > 2\sigma(I)$.

CCDC-897904 (**1**), CCDC-897905 (**2**), and CCDC-897906 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262–8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118; b) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4079–4124.

[2] P. Wang, *Dalton Trans.* **2012**, *41*, 4296–4302.

[3] F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant, D. A. Dixon, *Angew. Chem.* **2007**, *119*, 760–763; *Angew. Chem. Int. Ed.* **2007**, *46*, 746–749.

[4] a) S.-K. Kim, W.-S. Han, T.-J. Kim, T.-Y. Kim, S. W. Nam, M. Mitoraj, L. Pieko, A. Michalak, S.-J. Hwang, S. O. Kang, *J. Am. Chem. Soc.* **2010**, *132*, 9954–9955; b) B. L. Conley, T. J. Williams, *Chem. Commun.* **2010**, *46*, 4815–4817; c) P. M. Zimmerman, A. Paul, C. B. Musgrave, *Inorg. Chem.* **2009**, *48*, 5418–5433; d) A. Staubitz, A. P. Soto, I. Manners, *Angew. Chem.* **2008**, *120*, 6308–6311; *Angew. Chem. Int. Ed.* **2008**, *47*, 6212–6215.

[5] a) Ö. Metin, V. Mazumder, S. Özkar, S. Sun, *J. Am. Chem. Soc.* **2010**, *132*, 1468–1469; b) J.-M. Yan, X.-B. Zhang, S. Han, H. Shioyama, Q. Xu, *Angew. Chem.* **2008**, *120*, 2319–2321; *Angew. Chem. Int. Ed.* **2008**, *47*, 2287–2289.

[6] D. W. Himmelberger, L. R. Alden, M. E. Bluhm, L. G. Sneddon, *Inorg. Chem.* **2009**, *48*, 9883–9889.

[7] H. Helten, A. P. M. Robertson, A. Staubitz, J. R. Vancel, M. F. Haddow, I. Manners, *Chem. Eur. J.* **2012**, *18*, 4665–4680.

[8] a) G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126; b) D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76.

[9] a) H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough, I. Manners, *Angew. Chem.* **1999**, *111*, 3540–3543; *Angew. Chem. Int. Ed.* **1999**, *38*, 3321–3323; b) H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 6669–6678.

[10] H. Westenberg, J. C. Slootweg, A. Hepp, J. Kösters, S. Roters, A. W. Ehlers, K. Lammertsma, W. Uhl, *Organometallics* **2010**, *29*, 1323–1330.

[11] T. Habereder, H. Nöth, R. T. Paine, *Eur. J. Inorg. Chem.* **2007**, 4298–4305.

[12] a) T. L. Allen, W. H. Fink, *Inorg. Chem.* **1992**, *31*, 1703–1705; b) T. L. Allen, A. C. Scheiner, H. F. Schaefer III, *Inorg. Chem.* **1990**, *29*, 1930–1936; c) M. B. Coolidge, W. T. Borden, *J. Am. Chem. Soc.* **1990**, *112*, 1704–1706; d) H.-J. Himmel, *Dalton Trans.* **2003**, 3639–3649; e) H.-J. Himmel, *Eur. J. Inorg. Chem.* **2003**, 2153–2163; f) A. Y. Timoshkin, *Phosphorus, Sulfur, Silicon Relat. Elem.* **2001**, *168*, 275–280.

[13] a) S. Schulz, *Adv. Organomet. Chem.* **2003**, *49*, 225–317; b) B. Neumüller, E. Iravani, *Coord. Chem. Rev.* **2004**, *248*, 817–834; c) A. Y. Timoshkin, *Coord. Chem. Rev.* **2005**, *249*, 2094–2131; d) T. J. Clark, K. Lee, I. Manners, *Chem. Eur. J.* **2006**, *12*, 8634–8648.

[14] a) U. Vogel, P. Hoemensch, K.-Ch. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515–519; b) U. Vogel, A. Y. Timoshkin, M. Scheer, *Angew. Chem.* **2001**, *113*, 4541–4544; *Angew. Chem. Int. Ed.* **2001**, *40*, 4409–4412.

[15] a) U. Vogel, A. Y. Timoshkin, K.-Ch. Schwan, M. Bodensteiner, M. Scheer, *J. Organomet. Chem.* **2006**, *691*, 4556–4564; b) A. Adolf, U. Vogel, M. Zabel, A. Y. Timoshkin, M. Scheer, *Eur. J. Inorg. Chem.* **2008**, *22*, 3482–3492.

[16] K.-Ch. Schwan, A. Y. Timoshkin, M. Zabel, M. Scheer, *Chem. Eur. J.* **2006**, *12*, 4900–4908.

[17] M. Bodensteiner, U. Vogel, A. Y. Timoshkin, M. Scheer, *Angew. Chem.* **2009**, *121*, 4700–4704; *Angew. Chem. Int. Ed.* **2009**, *48*, 4629–4633.

[18] a) A. Y. Timoshkin, *Inorg. Chem.* **2009**, *48*, 8145–8153; b) A. H. Cowley, R. A. Jones, M. A. Mardones, J. L. Atwood, S. G. Bott, *Angew. Chem.* **1990**, *102*, 1504–1505; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1409–1410.

[19] R. D. Davy, H. F. Schaefer, *J. Phys. Chem. A* **1997**, *101*, 5707–5711.

[20] U. Vogel, K.-C. Schwan, M. Scheer, *Eur. J. Inorg. Chem.* **2004**, 2062–2065.

[21] cf. supporting information.

[22] C. von Hänisch, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1496–1500.

[23] A. Y. Timoshkin, I. V. Kazakov, C. von Hänisch, *Russ. J. Gen. Chem.* **2009**, *79*, 1067–1073.

[24] U. Vogel, M. Scheer, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1593–1598.

[25] H. C. E. McFarlene, W. McFarlane, D. S. Rycroft, *J. Chem. Soc. Dalton Trans.* **1976**, 1616–1622.

[26] J. S. Cha, H. C. Brown, *J. Org. Chem.* **1993**, *58*, 3974–3979.

[27] J. K. Ruff, *Inorg. Synth.* **1967**, *9*, 30–37.

[28] J. Cosier, A. M. Glazer, *Appl. Cryst.* **1986**, *19*, 105–107.

[29] R. C. Clark, J. S. Reid, *Acta Cryst.* **1995**, *A51*, 887–897.

[30] Agilent Technologies, *CrysAlisPro* **2006–2012**, Oxford, UK.

[31] A. Altomare, G. L. Cascarano, C. Giacovazzo, A. Gualardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

[32] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112–122.

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