structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167142. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[23] The solid-state arrangement of **3** is derived from a distorted CsCl packing in which the almost spherical $\mathrm{Al(OR)_4^-}$ ions form a cubic primitive lattice in which the cubic interstices are occupied by the $\mathrm{P_5Br_2^+}$ ion.

[24] A search of the chemical abstracts data base with Scifinder and the Cambridge structural database CSD with the program Conquest did not reveal a precedent of this $\mathrm{P_5}$ cage. However, similar C_{2v}-symmetric $\mathrm{MP_4}$ units (i.e. M = Ir) formally containing a $\mathrm{P_4^{2-}}$ unit are known.[25]

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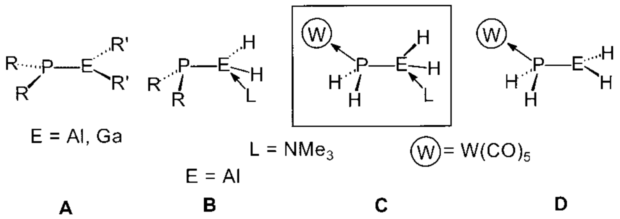
Lewis Acid/Base Stabilized Phosphanylalane and -gallane**

Ulf Vogel, Alexey Y. Timoshkin, and Manfred Scheer*

Dedicated to Professor Max Herberhold
in occasion of his 65th birthday

Bulky substituents at the main group atoms are necessary for the synthesis of monomeric phosphanylalanes and -gallanes of the type **A**.[1] In contrast to the strong π bonding in B–N, B–P, and B–As derivatives, only very weak π interactions combined with an increase of ionic bond contributions is supposed for the heavier Group 13 elements.[1] Thus, the lone pair of electrons at the heavier Group 15 element and the presence of an adjacent empty orbital at the Group 13 element leads to a head-to-tail dimerization or trimerization if the substituents are not sufficiently bulky. These compounds are mainly synthesized by salt elimination reactions;[1] however, it was shown recently that the cleavage of cyclic oligomers $[\mathrm{R_2PER'_2}]_n$ (E = P, As; R = Me; R′ = $\mathrm{SiMe_3}$; $n = 2, 3$) by a Lewis base, such as 4-(dimethylamino)pyridine (DMAP), leads to monomeric complexes.[2] To our knowledge, the parent compounds $[\mathrm{H_2EPH_2}]$ (E = Al, Ga) have not yet been synthesized or even detected in matrix isolation experiments,[3a] but ab initio calculations have been carried out for both compounds.[3, 4] It has been suggested that they play important roles in the formation of aluminum phosphide and gallium phosphide semiconductors starting from $\mathrm{PH_3}$ and $\mathrm{EH_3}$, respectively, by chemical vapor deposition (CVD) processes.[5] In 1993 Cowley and Jones reported the synthesis of monomeric base-stabilized phosphanyl- and arsanylalanes of type **B** by a metathetical reaction.[6] In **B** the P atom still contains bulky mesityl substituents, whereas the $\mathrm{AlH_2}$ moiety was stabilized by a Lewis base.



Our interest in this field concerns the synthesis of unsubstituted[7] oligomers and polymers of mixed ligands of elements of Group 13 and 15. By using our general concept of the stabilization of unstable moieties by fixation of the phosphorus lone pair of electrons by metal carbonyl complexes,[8] we report herein on the first synthesis of Lewis acid/base stabilized phosphanylalane and -gallane of type **C**.

According to our denisty functional theory (DFT) calculations[9a] (Table 1), the additional coordination of a Lewis base, such as $\mathrm{NMe_3}$, at $[\mathrm{H_2AlPH_2}]$ stabilizes the resulting adduct by 108 kJ mol^{-1}. The additional coordination of a Lewis acid such as $[\mathrm{W(CO)_5}]$ leads to a further increase of stabilization by 154 kJ mol^{-1}. On the other hand, if $[\mathrm{H_2AlPH_2}]$ is only coordinated by the Lewis acid $[\mathrm{W(CO)_5}]$ (compound **D**) the stabilization energy is only −135 kJ mol^{-1}. $[\mathrm{H_2AlPH_2\{W(CO)_5\}}]$ (**D**) tends to display an intramolecular (O)C⋯Al interaction that stabilizes the unsaturated Al center. Therefore, for steric as well as thermodynamic reasons, it seems to be essential for the molecule $[\mathrm{H_2AlPH_2}]$ to possess both Lewis base and acid stabilization, as realized in a molecule of type **C**; the stabilization energy of −262 kJ mol^{-1} is higher than the dimerization energy of $[\mathrm{H_2AlPH_2}]$ (−147 kJ mol^{-1}; Table 1). Furthermore, it is interesting that the Gibbs energies of $\mathrm{H_2}$ elimination reactions between unprotected $\mathrm{AlH_3}$ and $\mathrm{PH_3}$ [reaction (9)] and between their donor–acceptor complexes [reaction (7)] are similar and, therefore, the presence of the used protecting groups does not change the thermodynamics of the elimina-

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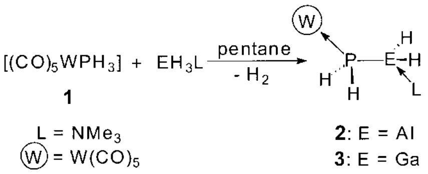
Table 1. Calculated standard enthalpies ΔH^0_{298} [kJ mol^{-1}], Gibbs energies ΔG^0_{298} [kJ mol^{-1}], and entropies ΔS^0_{298} [J K^{-1} mol^{-1}] of gas-phase reactions. B3LYP/6-31G*(ECP on W) level of theory.

Reaction		ΔH^0_{298}	ΔS^0_{298}	ΔG^0_{298}
$2\,H_2AlPH_2 = [H_2AlPH_2]_2$	(1)	– 147.4	– 181.4	– 93.3
$H_2AlPH_2 + NMe_3 = [Me_3N \cdot H_2AlPH_2]$	(2)	– 108.3	– 160.4	– 60.5
$H_2AlPH_2 + [W(CO)_5] = [H_2AlPH_2\{W(CO)_5\}]$	(3)	– 134.9	– 180.6	– 81.1
$H_2AlPH_2 + NMe_3 + [W(CO)_5] = [Me_3N \cdot H_2AlPH_2\{W(CO)_5\}]$	(4)	– 262.2	– 333.6	– 162.8
$AlH_3 + NMe_3 = [Me_3N \cdot AlH_3]$	(5)	– 117.0	– 150.6	– 72.1
$PH_3 + [W(CO)_5] = [H_3P\{W(CO)_5\}]$	(6)	– 129.5	– 138.1	– 88.3
$[Me_3N \cdot AlH_3] + [H_3P\{W(CO)_5\}] = [Me_3N \cdot H_2AlPH_2\{W(CO)_5\}] + H_2$	(7)	– 44.6	– 52.6	– 28.9
$AlH_3 + PH_3 = H_3AlPH_3$	(8)	– 49.4	– 121.3	– 13.3
$AlH_3 + PH_3 = H_2AlPH_2 + H_2$	(9)	– 28.8	– 7.6	– 26.5
$AlH_3 + PH_3 = \frac{1}{2}[H_2AlPH_2]_2 + H_2$	(10)	– 102.5	– 98.3	– 73.2
$[W(CO)_5] + NMe_3 = [Me_3N \cdot W(CO)_5]$	(11)	– 111.5	– 163.2	– 62.9
$[Me_3N \cdot H_2AlPH_2\{W(CO)_5\}] = H_2AlPH_2 + [Me_3N \cdot W(CO)_5]$	(12)	150.7	170.4	99.9

tion reaction, but prevents subsequent reactions of the formed product. Compound $[Me_3N \cdot H_2AlPH_2\{W(CO)_5\}]$ is found to be stable at 298 K with respect to dissociation into the components [reaction (4)] as well as with respect to possible dissociation into $[H_2AlPH_2]$ and $[Me_3N \cdot W(CO)_5]$ [reaction (12)].

Since sterically unprotected Group 13/15 σ-bound compounds are sensitive towards donor solvents such as THF, for the experimental approach to complexes of type **C**, the H_2 elimination reaction[10] appears to us to be the method of choice. Indeed, reactions of $[W(CO)_5PH_3]$ (**1**) with $EH_3 \cdot NMe_3$ in hydrocarbons as solvent lead to the novel complexes $[\{(CO)_5W\}H_2PEH_2 \cdot NMe_3]$ (**2**: E = Al, **3**: E = Ga) in good yields. Experiments to synthesize the corresponding boron-substituted complex in a similar manner have failed so far due to the low reactivity of the borane trimethylamine complex towards **1** [Eq. (13)].



(13)

Compounds **2** and **3** form colorless crystals, which rapidly turn yellowish on exposure to light. They are soluble in hydrocarbon solvents without decomposition at room temperature.[11] The appropriate molecular ion peaks are observed in the mass spectra of both compounds. The ^{31}P NMR spectrum of **2** reveals a broad triplet at $\delta = -250$ ($^1J(P,H) = 283$ Hz), which is shifted to higher field compared to that of the starting compound $[W(CO)_5PH_3]$ ($\delta = -184$) as one would expect for the substitution of a proton by the electropositive aluminum atom. In accordance with this, the ^{31}P NMR spectrum of **3** shows a triplet of triplets at $\delta = -240$ due to the coupling of the phosphorus atom to the protons at the P and Ga atom, respectively. The Raman spectrum of **2** shows four bands at 1894, 1917, 1966, and 2077 cm^{-1} for the CO stretching frequencies, as well as a band for the P–H vibration mode at 2323 cm^{-1} and one for the Al–H absorption at 1819 cm^{-1}, which are in good agreement with the calculated frequencies.[9b] Furthermore, the broad absorption found at 1680 cm^{-1} indicates the presence of Al–H···Al hydride bridges. This assumption for **2** is confirmed by the X-ray structure analysis, which shows a H-bridged dimer in the solid state (Figure 1, the H atoms on the phosphorus and aluminum atoms could be located and freely refined).

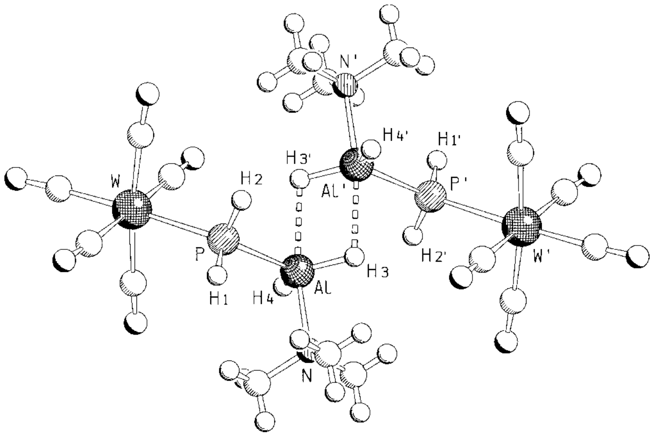


Figure 1. Molecular structure of **2** in the crystal. Selected bond lengths [Å] and angles [°]: Al-P 2.367(1), W-P 2.5491(9), Al-N 2.036(3), Al-H4 1.532, Al-H3 1.553, Al′···H3 2.053; W-P-Al 118.44(4), P-Al-N 103.28(8), W-P-Al-N 118.5, H2-P-Al-H3 11.3.

In the molecular structure of **2**[12] (Figure 1) the aluminum atom adopts a distorted trigonal-bipyramidal coordination sphere (P-Al-N 103.28(8)°) with a Al···H3′ distance to the second molecule of 2.053 Å (compare with 1.553 Å for the intramolecular Al–H3 distance). Similar long hydride bridges were found in the dimer $[H_3Al(NMe_3CH_2Ph)]_2$ (2.07(2) Å).[13] The local geometry around the Al–P axis is almost eclipsed (torsion angle H2-P-Al-H3 11°) and is therefore not consistent with the calculated structure of free $[H_2AlPH_2]$, for which a *gauche* conformation is established with an almost planar geometry around the Al center (torsion angle: 45°). Owing to the weak π interaction combined with the ionic bond contribution, the Al–P bond length in H_2AlPH_2 (2.335 Å[3c]) is shorter than that in **2** (2.377(1) Å), for which such a π interaction is not possible. The Al–P bond length in **2** is close to that in known monomeric compounds with organic substituents, but it is significantly shorter than that in $[(CO)_5CrPPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$ (2.485(1) Å),[14] probably due to the steric repulsion of the substituents at the Al and

P atom, respectively, in the latter compound. In **2** the W–P bond length (2.549(1) Å) and the Al–N bond length (2.036(3) Å) are similar to those in $[W(CO)_5PH_3]$ (**1**) (2.491(2) Å),[15] $[W(CO)_5PMe_3]$ (2.516(2) Å),[16] and $[W(CO)_5PPh_3]$ (2.545(1) Å),[17] and to those in $AlH_3\cdot N(C_2H_4)_3CH$ (1.991(4) Å)[18] and $[(CO)_5CrPPh_2Al(CH_2SiMe_3)_2\cdot NMe_3]$ (2.049(3) Å),[14] respectively.

The structural optimization of $[\{(CO)_5W\}H_2PAlH_2\cdot NMe_3]$ by density functional methods[9] under no symmetry restrictions and tight convergence criteria resulted in the *cis*-orientated isomer being 5 kJ mol^{-1} more stable than the experimentally observed *trans* isomer. Since this difference is very small, the influence of other interactions in the solid-state structure of **2** together with the intermolecular dimerization to form Al⋯H bridges may play an important role in the preference for the experimentally observed *trans* orientation of the substituents in the solid state.

Like **2** complex **3** also crystallizes in the space group $P2_1/c$. The compounds are, however, not isostructural since **3** is monomeric and lacks intermolecular H bonds. The monomeric nature of **3** leads to a slightly staggered geometry (Figure 2, torsion angle H1-P-Ga-H4 81.4°) in contrast to the eclipsed configuration of the dimeric Al complex **2**. The free $[H_2GaPH_2]$ molecule displays a torsion angle of 44°.[4] The Ga–P bond length in **3** (2.349(2) Å) is slightly longer than the calculated distance in the free molecule $[H_2GaPH_2]$ (2.328 Å) and in the monomeric compounds stabilized by bulky substituents (e.g. tBu$_2$GaP(Mes*)SiPh$_3$, 2.295(3) Å, Mes* = 2,4,6-tri-*tert*-butylphenyl[19]). In the latter compounds the lone pair at the phosphorus atom interacts with the vacant orbital at the planar Ga atom, which is consistent with the flattened geometry at the P center. The Ga–P bond is lengthened if the steric repulsion between the substituents is further increased (e.g. tBu$_2$PGaTmp$_2$, 2.4225(8) Å, Tmp = 2,2,6,6-tetramethylpiperidinate[20]).

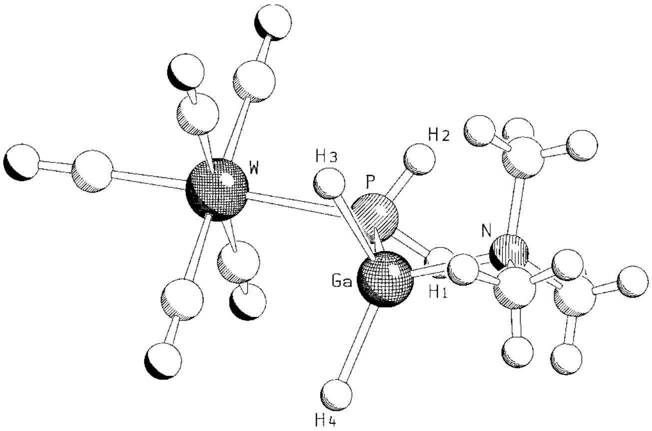


Figure 2. Molecular structure of **3** in the crystal. Selected bond lengths [Å] and angles [°]: Ga-P 2.349(2), W-P 2.537(2), Ga-N 2.039(7); W-P-Ga 114.72(7), P-Ga-N 107.4(2), W-P-Ga-N 158.95, H1-P-Ga-H4 81.4.

The results presented show that Lewis acid/base stabilization is necessary to stabilize the parent compounds of phosphanylalane and -gallane. Owing to their high tendency to lose H_2, the novel compounds open new perspectives for the synthesis of novel substituent-free oligomers comprising the elements of Group 13 and 15 fixed on transition metal centers. Furthermore, their use as molecular precursors in CVD processes could be of interest.

Experimental Section

$[\{(CO)_5W\}H_2PAlH_2\cdot NMe_3]$ (**2**): $[W(CO)_5PH_3]$ (358 mg, 1.00 mmol)[15] and $AlH_3\cdot NMe_3$ (89 mg, 1.00 mmol)[21] were refluxed in *n*-hexane (50 mL) under a nitrogen atmosphere until gas evolution ceased (≈2 h). The reaction mixture was filtered and the filtrate was reduced to about 30 mL. After one day at −30 °C **2** (200 mg, 45 %) crystallized as colorless crystals. ^{1}H NMR (300 MHz, [D$_8$]toluene, −40 °C, TMS ext.): $\delta = 1.41$ (s, 9H; NMe$_3$), 1.70 (d, ^1J(H,P) = 283 Hz, 2H; PH$_2$); ^{31}P NMR (101 MHz, [D$_8$]toluene, −40 °C, H$_3$PO$_4$ ext.): $\delta = -250$ (t, ^1J(P,H) = 283 Hz); MS (FI, 10 kV, 120 °C): m/z: 445 (7) [M^++H]; Raman (solid-state) $\tilde{\nu} = 2941$ (w), 2865 (w), 2803 (w), 2323 (m), 2068 (m), 1975 (sh), 1966 (vs), 1917 (w), 1894 (m), 1819 (w), 1680 (w, br), 460 (m), 438 (m), 103 cm^{-1} (m).

$[\{(CO)_5W\}H_2PGaH_2\cdot NMe_3]$ (**3**): $[W(CO)_5PH_3]$ (358 mg, 1.00 mmol) and $GaH_3\cdot NMe_3$ (132 mg, 1.00 mmol)[22] were refluxed in *n*-pentane (50 mL) under a nitrogen atmosphere until gas evolution ceased (≈1 h). The mixture was filtered and the filtrate was reduced to about 30 mL. After crystallization at −30 °C colorless crystals of **3** were obtained, which should be handled under exclusion of light. Yield: 190 mg (39 %). ^{1}H NMR (300 MHz, [D$_8$]toluene, −40 °C, TMS ext.): $\delta = 1.46$ (s, 9H; NMe$_3$), 1.84 (dt, ^1J(P,H) = 293 Hz, ^3J(H,H) = 3 Hz; PH$_2$), 4.74 (d br, ^2J(P,H) = 46 Hz; GaH$_2$); ^{31}P{^{1}H} NMR (101 MHz, [D$_8$]toluene, −40 °C, H$_3$PO$_4$ ext.): $\delta = -240$ (s, ^1J(W,P) = 165 Hz; PH$_2$); ^{31}P NMR (101 MHz, [D$_8$]toluene, −40 °C, H$_3$PO$_4$ ext.): $\delta = -240$ (tt, ^1J(H,P) = 293 Hz, ^2J(H,P) = 46 Hz; PH$_2$); MS (EI, 80 °C): m/z: 488 (0.2) [M^+], 460 (0.2) [$M^+ -$ CO], 429 (0.1) [$M^+ -$ NMe$_3$]; Raman (solid state): $\tilde{\nu} = 2942$ (w), 2859 (w), 2806 (w), 2335 (m), 2069 (m), 1971 (vs), 1944 (m), 1919 (m), 1895 (s), 1066 (w), 433 (m), 343 (w), 108 cm^{-1} (s).

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B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**. B3LYP functional (A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–793) has been used together with standard 6-31G* basis set for H, C, N, Al, and P atoms. Effective core potential basis set of Hay and Wadt (P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310) was used for W atoms. All structures were fully optimized with subsequent vibrational analysis and correspond to the minimum on the potential energy surface; b) calculated Raman frequencies according to the B3LYP method (compare: A. Y. Timoshkin, H. F. Bettinger, H. F. Schaefer, *J. Am. Chem. Soc.* **1997**, *119*, 5668–5678): $\tilde{\nu}$(C–O): 1920, 1938, 1951, 1977, 2048; $\tilde{\nu}$(AlH): 1816, 1836; $\tilde{\nu}$(P–H): 2312, 2316 cm^{-1}.

[10] For H_2 elimination reactions which form bonds between Group 13 and Group 15 elements compare: M. Driess, S. Kuntz, K. Merz, H. Pritzkow, *Chem. Eur. J.* **1998**, *4*, 1628–1632.

[11] In toluene and CH_2Cl_2, H_2 elimination reactions occur at room temperature, whereas in donor solvents such as THF these reactions lead to rapid decomposition. The ^{31}P NMR spectra of these solutions in THF indicate an ionic decomposition product of possible formula $[\{(CO)_5W\}_2PH_2]^-$.

[12] Crystal structure analyses of **2** and **3** were performed on a STOE IPDS diffractometer with $Ag_{K\alpha}$ radiation ($\lambda = 0.56087$ Å) for **2** and $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) for **3**. The structures were solved by direct methods with the program SHELXS-93,[23a] and full matrix least-squares refinement on F^2 in SHELXL-97[23b] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms at carbon atoms were located in idealized positions and refined isotropically according to the riding model. The hydrogen atoms at the phosphorus, aluminum, and gallium atoms were freely refined. **2**: $C_8H_{13}AlNO_5PW$, $M_r = 444.99$, crystal dimensions $0.40 \times 0.20 \times 0.08$ mm^3, monoclinic, space group $P2_1/c$ (no. 14); $a = 6.562(1)$, $b = 13.495(3)$, $c = 17.295(4)$ Å, $\beta = 100.29(3)°$, $T = 210(2)$ K, $Z = 4$, $V = 1506.9(5)$ Å^3, $\rho_{calcd} = 1.961$ Mg m^{-3}, $\mu(Ag_{K\alpha}) = 4.219$ mm^{-1}, 4058 independent reflections ($R_{int} = 0.0435$, $2\theta_{max} = 46.3°$), 3637 observed with $F_o = 4\sigma(F_o)$; 173 parameters, $R_1 = 0.0246$, $wR_2 = 0.0638$. **3**: $C_8H_{13}GaNO_5PW$, $M_r = 487.73$, crystal dimensions $0.50 \times 0.30 \times 0.02$ mm^3, monoclinic, space group $P2_1/c$ (no. 14); $a = 6.629(1)$, $b = 11.533(2)$, $c = 20.112(4)$ Å, $\beta = 90.27(3)°$, $T = 200(1)$ K, $Z = 4$, $V = 1537.4(5)$ Å^3, $\rho_{calcd} = 2.107$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 9.338$ mm^{-1}, 2912 independent reflections ($R_{int} = 0.1058$, $2\theta_{max} = 52°$), 2623 observed with $F_o = 4\sigma(F_o)$; 161 parameters, $R_1 = 0.0437$, $wR_2 = 0.1137$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166049 (**2**) and CCDC-166050 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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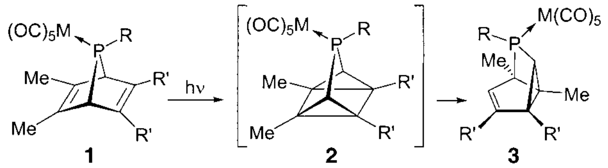
Norbornadiene–Quadricyclane Valence Isomerism for a Tetraphosphorus Derivative[**]

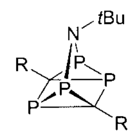
Mark J. M. Vlaar, Andreas W. Ehlers, Marius Schakel, Scott B. Clendenning, John F. Nixon, Martin Lutz, Anthony L. Spek, and Koop Lammertsma*

The photochemically induced valence isomerization of norbornadiene to the higher energy quadricyclane is well established[1] and this is also the case for the 7-oxa- and 7-azanorbornadienes.[2] The related 7-phospha analogue **1** on the other hand undergoes a UV-induced rearrangement to the tricyclic compound **3** [Eq. (1), R = Ph, Me; R′ = CO_2Me; M = W, Cr] presumably via an intermediate quadricyclane **2**, however, this has not been established definitely.[3]



1 **2** **3** (1)

Recently, we found that tetraphosphaquadricyclane **8** is formed with surprising ease, together with the polycyclic compound **7** (Scheme 1), from the reaction of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**4**) with the transient phosphinidene complex [PhPW(CO)$_5$],[4, 5] which is generated in situ by thermal degradation of **1** (R = Ph, M = W). The mechanism for the unexpected formation of **8** was not elucidated, but an intramolecular [2+2] cycloaddition of the two P=C units of an intermediate tetraphosphanorbornadiene complex, the 1,4-adduct **6**,[6] was assumed. A similar process has been proposed for the formation of quadricyclane **9**, R = alkyl, but intermediate norbornadiene derivatives were not detected in this case either.[7]



9

Norbornadienes containing two or more P atoms have been proposed as intermediates, mostly in the cyclooligomerization of phosphaalkynes,[7, 8] but to date only one triphospha-7-

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