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Halogenation of Lewis acid/base stabilised phosphanylboranes

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Dedicated to Professor Christoph Elschenbroich on the occasion of his 70th birthday.

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ABSTRACT

The reaction pattern of the Lewis-acid/base stabilised phosphanylborane $[(CO)_5W(H_2PBH_2 \cdot NMe_3)]$ (**1**) with elemental halogens is comprehensively studied. The reaction with iodine and bromine leads to a selective halogenation at the tungstencarbonyl moiety under formation of $[WX_2(CO)_4(H_2PBH_2 \cdot NMe_3)]$ (X = I (**2**), Br (**3**)). Whereas **2** is a stable product the brominated compound **3** dimerises easily to $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)]_2$ (**4**) under lost of CO. The CO elimination reaction of **3** is extensively studied. If **3** is reacted with $[Et_4N][Br]$ the ionic compound $[Et_4N][WBr_3(CO)_3(H_2PBH_2 \cdot NMe_3)]$ (**5**) is formed. Otherwise, if **3** is combined with the donor ligand $[H_2PBH_2 \cdot NMe_3]$, the complex $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)_2]$ (**6**) is obtained. Compounds **2**–**6** are comprehensively characterised by X-ray diffraction analysis, NMR, and IR spectroscopy.

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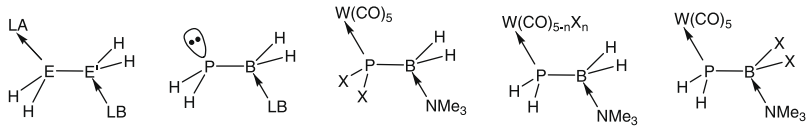
1. Introduction

Group 13/15 element compounds play an important role in the design of semiconducting layers as well as for novel inorganic polymers [1]. We are particularly interested in controlled polymerisation processes of 13/15 element compounds, which are derived from the parent compounds of the formula $[H_2EE'H_2]$ (E = P, As; E′ = B, Al, Ga). We were able to show the synthesis of the first Lewis-acid (LA) and Lewis-base (LB) stabilised parent compounds of the phosphanylalanes and gallanes [2] as well as the corresponding arsanyl- and phosphanylboranes of type **A** [3]. One of the aspects of initial investigations concerning the reactivity of the LA/LB stabilised phosphanylborane $[W(CO)_5(H_2PBH_2\ NMe_3)]$ (**1**), was the elimination of the transition metal moiety to synthesise the parent compound of the phosphanylborane **B**, stabilised only by a Lewis base. Thus, the novel primary boranylphosphine $[H_2PBH_2\ NMe_3]$ has been synthesised [4].

Another interesting question regarding the reactivity of $[W(CO)_5(H_2PBH_2 \cdot NMe_3)]$ (**1**) is the behaviour towards different halogenation reagents. Recently, we surprisingly discovered the selective double halogenation of **1** at the phosphorus atom using CX_4 (X = Cl, Br) as reactants to yield compounds of type **C** [5]. In addition to these findings we have been interested to investigate halogenation reactions with elemental dihalogens in a more general manner. Besides the halogenation at the tungsten atom (type **D**), in principle, the substitution of hydrogens at the pnictogen (type **C**) as well as at the boron atom (type **E**) is possible. In contrast to the halogenation with CX_4 to give the type **C** complexes,



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we now find that the reaction with Br_2 and I_2 leads to halogenation at the tungsten atom under the lost of CO to form type **D** complexes which show a great diversity in a subsequent reactivity pattern. The results of these investigations we report herein after.

2. Experimental

2.1. General remarks

All manipulations are performed under an atmosphere of dry nitrogen using standard glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures. NMR Spectra were recorded on a Bruker Avance 400 (400.13 MHz for ^{1}H, 192.55 MHz for ^{11}B and 161.98 MHz for ^{31}P) and the chemical shifts are referenced to external standards (^{1}H: $SiMe_4$, ^{11}B: BF_3 Et_2O, ^{31}P: 85% H_3PO_4). IR spectra were recorded either on a Bruker IFS 280 or a Varian FTS 2000 spectrometer. ESI-MS spectra were measured on a Finnigan Thermoquest TSQ 7000 mass-spectrometer. Starting materials were synthesized using published procedures: **1** [3] and $[H_2PBH_2 \cdot NMe_3]$ [4].

2.2. Preparations

2.2.1. $[WI_2(CO)_4(H_2PBH_2 \cdot NMe_3)]$ (**2**)

To a solution of $[(CO)_5W(H_2PBH_2 \cdot NMe_3)]$ (**1**) (200 mg, 0.466 mmol) in CH_2Cl_2 (25 ml) an equimolar amount of iodine (118 mg, 0.466 mmol) is added at 0 °C. The colour of the solution changes from pale yellow to yellow. After stirring for 14 h the solvent is removed in vacuo until incipient crystallisation. Compound **2** is obtained at –20 °C as pale yellow plates (250 mg, 0.383 mmol, 82%). **2**: Anal. Calc. for $BC_7H_{13}I_2NO_4PW$ (654.62): C, 12.84; H, 2.00. Found: C, 12.68; H, 1.86%. ^{1}H NMR (CD_2Cl_2, 300 K): δ = 2.81 (s, 9H, NMe_3), 4.24 ppm (dm, ^1J(H,P) = 333 Hz, 2H, PH_2), ^{31}P NMR (CD_2Cl_2, 300 K): δ = –150.3 ppm (t, br, ^1J(P,H) = 333 Hz, PH_2), ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K): δ = –150.3 ppm (s, br, PH_2), ^{11}B NMR (CD_2Cl_2, 300 K): δ = –150.3 ppm (s, br, BH_2); IR (KBr): $\tilde{\nu}$ = 3000 (w), 2963 (w), 2925 (w), 2424 (m, BH), 2401 (w, BH), 2340 (w, PH), 2300 (w, PH), 2072 (vs, CO), 2021 (vs, CO), 1981 (vs, CO), 1948 (vs, CO), 1481 (m), 1466 (m), 1411 (w), 1241 (w), 1153 (w), 1127 (m), 1098 (m), 1057 (m), 976 (w), 866 (m), 800 (m), 762 (m), 710 (w), 535 (s), 500 (m), 479 (s) cm^{-1}.

2.2.2. $[WBr_2(CO)_4(H_2PBH_2 \cdot NMe_3)]$ (**3**)

$[(CO)_5W(H_2PBH_2 \cdot NMe_3)]$ (**1**) (382 mg, 0.891 mmol) in Et_2O (15 ml) is allowed to react with 1.5 ml (0.891 mmol) of a 0.59 M Br_2 solution in pentane at –25 °C. After stirring over night the solution is concentrated by blowing a CO stream over the reaction mixture. The solution is kept at –25 °C under a CO atmosphere to give pale yellow crystals of **3** (429 mg, 0.765 mmol, 86%). Compound **3**: Anal. Calc. for $BC_7H_{13}Br_2NO_4PW$ (560.62): C, 15.00; H, 2.34. Found: C, 14.76; H, 2.66%. ^{1}H NMR (toluene-d_8, 300 K): δ = 2.79 (d, ^4J(H,P) = 1 Hz, 9H, NMe_3), 3.55 ppm (dm, ^1J(H,P) = 331 Hz, 2H, PH_2), ^{31}P NMR (toluene-d_8, 300 K): δ = –133.1 ppm (t(br), ^1J(P,H) = 333 Hz, PH_2), ^{31}P{^{1}H} NMR (toluene-d_8, 300 K): δ = –133.1 ppm (s(br), ^1J(P,H) = 333 Hz, PH_2), ^{11}B NMR (toluene-d_8, 300 K): δ = –10.1 ppm (s, br, BH_2); IR (KBr): $\tilde{\nu}$ = 3000 (w), 2964 (w), 2926 (w), 2450 (m, BH), 2409 (w, BH), 2347 (w, PH), 2301 (w, PH), 2099 (vs, CO), 2027 (vs, CO), 1990(vs, CO), 1946 (vs, CO), 1484 (m), 1465 (m), 1412 (w), 1262 (s), 1154 (w), 1128 (m), 1098 (vs), 1060 (s), 1022 (vs), 977 (w), 863 (m), 802 (vs), 760 (w), 706 (w), 536 (w), 500 (m) cm^{-1}.

2.2.3. $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)]_2$ (**4**)

To $[(CO)_5W(H_2PBH_2{\cdot}NMe_3)]$ (**1**) (125 mg, 0.292 mmol) dissolved in toluene (10 ml) 0.68 ml a 0.47 M Br_2 solution (0.32 mmol) in pentane is added dropwise at –25 °C. The mixture is vigorously stirred for 12 h. The solid residue is separated by filtration and washed twice with toluene (about 10 ml). The combined filtrate and washings are heated to 50–60 °C for a short time to complete the CO elimination. When the resulting orange solution reaches room temperature **4** is obtained as yellow needles (131 mg, 0.123 mmol, 84%). Compound **4**: Anal. Calc. for $B_2Br_4C_{12}H_{26}N_2O_6P_2W_2$ (1065.21): C, 13.53; H, 2.46. Found: C, 13.79; H, 2.80%. ^{1}H NMR (CD_2Cl_2, 300 K): δ = 2.77 (s, 9H, NMe_3), 4.18 ppm (dm, ^1J(H,P) = 339 Hz, 2H, PH_2), ^{31}P NMR (CD_2Cl_2, 193 K): δ = –116.3 ppm (t, br, ^1J(P,H) = 339 Hz, PH_2), ^{31}P{^{1}H} NMR (CD_2Cl_2, 193 K): δ = –116.3 ppm (s, br, PH_2), ^{11}B NMR (CD_2Cl_2, 300 K): δ = –9.3 ppm (s, br, BH_2); IR (KBr): $\tilde{\nu}$ = 3003 (w), 2949 (w), 2446 (m, BH), 2414 (m, BH), 2348 (m, PH), 2303 (m, PH), 2021 (vs, CO), 1935 (vs, CO), 1921 (vs, CO), 1482 (s), 1467 (s), 1261 (w), 1244 (w), 1156 (m), 1128 (s), 1094 (m), 1063 (m), 1017 (w), 975 (w), 866 (w), 784 (vs), 737 (w), 479 (w), 448 (w) cm^{-1}.

2.2.4. Synthesis of $[Et_4N][WBr_3(CO)_3(H_2PBH_2{\cdot}NMe_3)]$ (**5**)

Et_4NBr (53 mg, 0.253 mmol) is added at room temperature to $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)]_2$ (**4**) (135 mg, 0.127 mmol)) dissolved in CH_2Cl_2 (20 ml) and vigorously stirred for 12 h. Afterwards the solvent is reduced to 2 ml in vacuo. After adding THF (2–3 ml) the mixture is layered with *n*-hexane (4 ml). After 24 h, **5** crystallises at room temperature as yellow plates (162 mg, 0.218 mmol, 86%). **5**: Anal. Calc. for $B_1Br_3C_{14}H_{33}N_2O_3P_1W_1$ (742.76): C, 22.64; H, 4.48. Found: C, 22.91; H, 4.78%. ^{1}H NMR (CD_2Cl_2, 300 K): δ = 1.35 (t, ^3J(H,H) = 6 Hz, 12H, NEt_4), 2.79 (d, ^4J(H,P) = 1 Hz, 9H, NMe_3), 3.31 (q, ^3J(H,H) = 7 Hz, 8H, NEt_4), 4.11 ppm (dt, ^1J(H,P) = 338 Hz, ^3J(H,H) = 6 Hz, 2H, PH_2), ^{31}P NMR (CD_2Cl_2, 300 K): δ = –98.6 ppm (t, ^1J(P,H) = 338 Hz, PH_2), ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K): δ = –98.6 ppm (s, br, PH_2), ^{11}B NMR (CD_2Cl_2, 300 K): δ = –9.0 ppm (s, br, BH_2); positive ion MS (ESI, THF/CH_3CN): *m/z* (%): 612 ($[A]^-$, 4%), negative ion MS (ESI, THF/CH_3CN): *m/z* (%): 130 ($[K]^+$, 100%); IR (KBr): $\tilde{\nu}$ = 3006 (w), 2988 (w), 2948 (w), 2426 (m, BH), 2396 (w, BH), 2336 (w, PH), 2302 (w, PH), 2010 (vs, CO), 1940 (sh, CO), 1919 (vs, CO), 1863 (vs, CO), 1481 (m), 1460 (m), 1393 (w), 1247 (w), 1171 (w), 1129 (w), 1087 (w), 1052 (w), 1000 (w), 864 (w), 795 (s), 590 (m) cm^{-1}.

2.2.5. Synthesis of $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)_2]$ (**6**)

A mixture of $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)]_2$ (**4**) (107 mg, 0.101 mmol) in THF (10 ml) and $H_2PBH_2 \cdot NMe_3$ (0.025 ml, 21 mg, 0.201 mmol) is stirred at room temperature for 5 h. The solution is filtered over Celite and the solvent removed in vacuo. Compound **6** is obtained as a pale yellow solid (84 mg, 0.132 mmol, 66%). Compound **6**: Anal. Calc. for $B_2Br_2C_9H_{26}N_2O_3P_2W$ (637.53): C, 16.96; H, 4.11. Found: C, 17.27; H, 4.43%. ^{1}H NMR (benzene-d_6, 300 K): δ = 2.80 (s, 9H, NMe_3), 3.95 ppm (dt, ^1J(H,P) = 331 Hz, ^3J(H,H) = 7 Hz, 2H, PH_2), ^{31}P NMR (benzene-d_6, 300 K, 85% H_3PO_4 ext.): δ = –116.5 ppm (s, br, PH_2), ^{11}B NMR (benzene-d_6, 300 K): δ = –9.0 ppm (s, br, BH_2); IR (THF): $\tilde{\nu}$ = 2432 (m, BH), 2395 (m, BH), 2342 (w, PH), 2016 (vs, CO), 1932 (vs, CO), 1901 (vs, CO), 1779 (w), 1261 (s), 1082 (vs), 807 (m), 704 (w), 542 (w), 503 (w) cm^{-1}.

2.3. X-ray structure determination

The crystal structure analyses of the products were performed on a STOE IPDS diffractometer with Mo-Kα radiation (λ = 0.71073 Å) for **4** and **6** and Ag-Kα radiation (λ = 0.56087 Å) for **2** and **5a**. The crystal structure analysis of **3** and **5** was performed on an Oxford Diffraction Gemini Ultra diffractometer with Cu-Kα radiation (λ = 1.54180 Å). The structures are solved by direct methods with the program SHELXS-97 [6], and full matrix least squares refinement on F^2 in SHELXL-97 [6] is performed with aniso-

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