Hydrogenation of White Phosphorus to Phosphane with Rhodium and Iridium Trihydrides[**]

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Francesco Vizza*

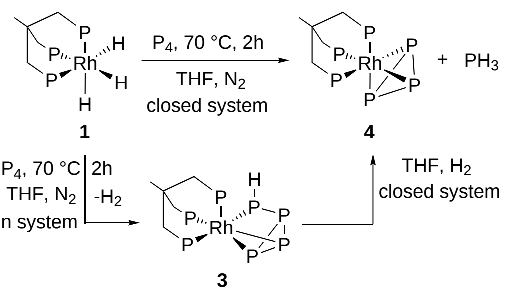
In memory of Ya. A. Dorfman

The reaction of white phosphorus with transition metal fragments results in complexes containing a large variety of P$_x$ ligands ($1 \leq x \leq 12$) most of which have been studied during the last two decades.[1] Nonetheless, there are still few examples of the functionalization of the P$_4$ molecule and of its fragmentation mediated by transition metals.[2] In particular, with the only exception of the thermal reaction of white phosphorus and Cp$_2$MoH$_2$ in toluene,[3] reactions of white phosphorus with transition metal hydrides have received little attention. As these reactions generate potentially unusual phosphorus–hydrogen compounds,[4] we decided to study the reactivity of white phosphorus towards the transition metal hydrides [(triphos)MH$_3$] (M = Rh (**1**),[5a] Ir (**2**);[5b] triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane).

In keeping with the well-documented ability of **1** and **2** to behave as hydrogenating reagents toward different organic substrates,[6] we accumulated strong evidence for the stoichiometric hydrogenation of one of the phosphorus atoms of P$_4$ to produce phosphane PH$_3$. A mechanism which encompasses the formation of the intermediate species [(triphos)MH(η^1:η^1-P$_4$)] and [(triphos)M(η^1:η^2-HP$_4$)] is proposed here.

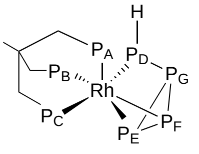
White phosphorus dissolved in tetrahydrofuran (THF) under dinitrogen reacts with the rhodium trihydride [(triphos)RhH$_3$] (**1**) at about 70 °C to afford an orange solution. After evaporation of the solvent under reduced pressure yellow microcrystals of the novel complex [(triphos)Rh(η^1:η^2-HP$_4$)] (**3**) are obtained (Scheme 1). On carrying out the same experiment in a closed system in the presence of dihydrogen (p(H$_2$) $\geq$ 1 atm), the known *cyclo*-triphosphorus complex [(triphos)Rh(η^3-P$_3$)][7] (**4**) is formed in high yield.

It was unambiguously shown by multinuclear and multidimensional NMR spectroscopy that **3** contains the unprecedented hydrogen tetraphosphide HP$_4^-$ ion as a η^3-six-electron ligand. Key experimental evidences were the ^{31}P{^{1}H} NMR spectrum, which exhibited a temperature-invariant eight-nuclei ABCDEFGX spin system and the ^{31}P–^{31}P 2D COSY NMR spectrum, which allowed us to unravel the network of several P–P connections. The presence of the monohydrophosphido moiety was clearly supported by a combination of ^{31}P DEPT (DEPT-90 and DEPT-135) and heteronuclear ^{1}H–^{31}P HMQC NMR experiments. In particular, the 2D NMR experiment points to a strong one-bond correlation between the P$_D$ resonance ($\delta = -280.22$) and the doublet of multiplets centered at $\delta = 0.01$ in the ^{1}H NMR spectrum. The ^1J(H,P) coupling constant of approximately 120 Hz matches well with the values reported by Baudler and co-workers for the extremely reactive alkali metal salts of the HP$_4^-$ ion.[8]



Scheme 1. Reaction of white phosphorus with [(triphos)RhH$_3$].

By monitoring the reaction of **1** with P$_4$ by ^{31}P{^{1}H} NMR spectroscopy (in a sealed NMR tube, N$_2$ (or H$_2$) atmosphere, [D$_8$]THF, 2 h, 70 °C) it is found that, irrespective of the gas used, one of the four phosphorus atoms of the P$_4$ molecule is completely hydrogenated to PH$_3$ (singlet at $\delta = -244.77$ which transforms into a quartet with ^1J(H,P) 186.9 Hz in the proton-coupled ^{31}P NMR spectrum). The remaining phosphorus atoms are efficiently scavenged by the (triphos)Rh moiety through the formation of the stable η^3-*cyclo*-triphosphorus complex **4**.



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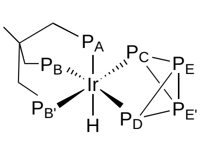

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Mechanistic information on the hydrogenation of P$_4$ is provided by in situ NMR experiments at lower temperature. Thus, when **1** in [D$_8$]THF is treated with P$_4$ at approximately 40 °C (Rh:P$_4$ = 1:2) under dinitrogen, the selective transformation of **1** into **3** occurs. During the process a resonance at $\delta = 4.75$ ascribable to H$_2$ grows in intensity in the proton spectrum before slowly disappearing. On heating at 70 °C the fast disappearance of the dihydrogen resonance is accompanied by the formation of PH$_3$ and **4**. A separate NMR experiment carried out with [D$_3$]**1** under dinitrogen indicated the total incorporation of the deuterium labels into the phosphane, confirming that all of the three hydride ligands are transferred from rhodium to one P atom.

The high stability of the Rh(η^3-P$_3$) complex means that the present hydrogenation of P$_4$ to PH$_3$ cannot be catalytic. In fact, only a stoichiometric amount of phosphane is observed when a solution of **1** and P$_4$ (Rh:P$_4$ = 1:10) in [D$_8$]THF is pressurized in a sapphire 10-mm NMR tube with up to 30 atm of H$_2$ and heated to 90 °C (HP-NMR experiment).

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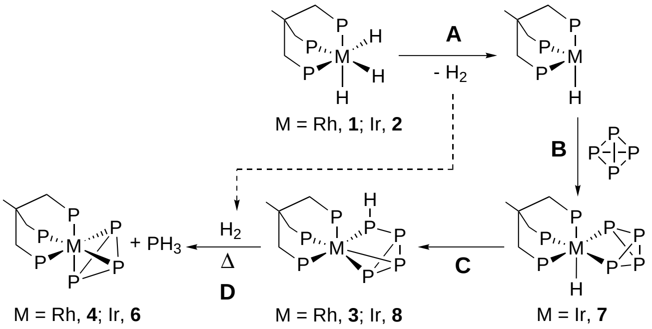
A deeper insight into the hydrogenation process of P_4 was obtained by conducting the phosphorylation reaction in the presence of the kinetically more inert iridium complexes [(triphos)IrH_3] (**2**) and [(triphos)Ir$H_2(C_2H_5)$][9] (**5**). Although **2** is also an efficient promoter for the transfer of three hydrogen atoms and leads to both PH_3 and [(triphos)Ir(η^3-P_3)][7] (**6**), no reaction occurs before 120 °C (experiment in a sealed NMR tube). At this temperature, the formation of phosphane and **6** is probably too fast to allow the detection of any intermediate species. However, on replacing **2** with the dihydridoethyl complex **5**, which reductively eliminates ethane rather than H_2,[9] pale yellow air-sensitive microcrystals of the bicyclotetraphosphane (P_4^{2-}) complex [(triphos)IrH(η^1:η^1-P_4)] (**7**) were obtained. Complex **7** is formed by oxidative addition of P_4, this being probably the first basic step of the whole process.[10] On dissolving **7** in [D_8]THF under dinitrogen a very slow reaction takes place at room temperature to afford [(triphos)Ir(η^1:η^2-HP_4)] (**8**).[11] Moreover, on saturating a solution containing **8** with H_2, PH_3 and the *cyclo*-P_3 complex **6** are formed after heating at around 70 °C.[12]

The present study provides good evidence for the direct hydrogenation of white phosphorus to PH_3 and *cyclo*-P_3 when promoted by rhodium and iridium trihydrides. A plausible mechanism is depicted in Scheme 2. The highlights of the process are: A) the generation of the transient [(triphos)MH] complex by thermal reductive elimination of H_2 from [(triphos)MH_3]; B) the oxidative addition of P_4 to afford the hydrido-(η^1:η^1-P_4) complexes [(triphos)MH(η^1:η^1-P_4)]; C) the intramolecular migration of the hydride ligand from metal to phosphorus to yield the hydrogen tetraphosphide complexes [(triphos)M(η^1:η^2-HP_4)]; and D) the final addition of H_2 to the HP_4 ligand with concomitant P–P bond cleavage.[13] Although we do not yet know how the dihydrogen molecule is transferred to the PH phosphorus atom during the last reaction step, a possible mechanism which is under investigation involves the metal-mediated heterolytic splitting of an η^2-H_2 ligand followed by the stepwise addition of H^+ and H^- to the HP_4 ligand.[14]



Scheme 2. Mechanism for the stoichiometric hydrogenation of P_4 promoted by [(triphos)MH_3] complexes.

Experimental Section

3: A solution of **1** (0.73 g, 1.00 mmol) and white phosphorus (0.25 g, 2.02 mmol) in THF (50 mL) was refluxed under dinitrogen for 2 h. After the solvent and the volatile components had been evaporated under vacuum, the residue was washed with ethanol (2 × 5 mL) and pentane (2 × 5 mL). The yellow microcrystalline material was collected by filtration under dinitrogen and washed with pentane (2 × 5 mL) before being dried under a stream of dinitrogen (yield: 0.62 g, 73 %). Elemental analysis calcd for $C_{41}H_{40}P_7Rh$: C 57.77, H 4.73, P 25.43; found; C 57.56, H 4.70, P 25.28. IR (Nujol): $\tilde{\nu} = 2213\ cm^{-1}$ (w, PH); ^1H NMR (500.13 MHz, [D_8]THF, 20 °C, TMS): $\delta = 0.01$ (ddbrm, $^1J(H,P) = 119.9$, $^2J(H,P) = 28.3$ Hz, 1H; PH); $^{31}P\{^1H\}$ NMR (81.01 MHz, [D_8]THF, 20 °C, 85 % H_3PO_4), ABCDEFGX spin systems ($X = {}^{103}Rh$): $\delta = 15.96$ (m, $J(P_A,P_B)$ 12.5, $J(P_A,P_C)$ 31.6, $J(P_A,P_D)$ 19.1, $J(P_A,P_E)$ 28.3, $J(P_A,P_F)$ 3.1, $J(P_A,P_G)$ 7.1, $J(P_A,Rh)$ 121.1 Hz, 1P, P_A), 2.81 (m, $J(P_B,P_C)$ 40.0, $J(P_B,P_D)$ 42.2, $J(P_B,P_E)$ 5.4, $J(P_B,P_F)$ 5.4, $J(P_B,P_G)$ 7.1, $J(P_B,Rh)$ 112.5 Hz, 1P, P_B), −3.33 (m, $J(P_G,P_C)$ 7.1, $J(P_G,P_D)$ 119.5, $J(P_G,P_E)$ 144.5, $J(P_G,P_F)$ 155.0, $J(P_G,Rh)$ 7.0 Hz, 1P, P_G), −10.78 (m, $J(P_C,P_D)$ 50.2, $J(P_C,P_E) \approx 0$, $J(P_C,P_F) \approx 0$, $J(P_C,Rh)$ 78.8 Hz, 1P, P_C), −180.12 (m, $J(P_E,P_D)$ 24.4, $J(P_E,P_F)$ 321.9, $J(P_E,Rh)$ 20.0 Hz, 1P, P_E), −184.98 (m, $J(P_F,P_D)$ 24.4, $J(P_F,Rh)$ 20.0 Hz, 1P, P_F), −280.22 (m, $J(P_D,Rh)$ 6.4 Hz, 1P, P_D).

7: A solution of **5** (0.70 g, 0.82 mmol) and white phosphorus (0.20 g, 1.61 mmol) in THF (or benzene) (50 mL) was refluxed under nitrogen for 5 h. Workup as above gave **7** as pale yellow microcrystals (yield: 0.73 g, 77 %). Elemental analysis calcd for $C_{41}H_{40}P_7Ir$: C 52.29, H 4.28, P 23.02; found: C 52.24, H 4.31, P 22.80. IR (Nujol): $\tilde{\nu} = 2061\ cm^{-1}$ (m, IrH); ^1H NMR (200.13 MHz, [D_6]benzene, 20 °C, TMS): $\delta = -7.09$ (dquint, $^2J(H,P_{trans}) = 141.3$ Hz, $^2J(H,P_{cis}) = 8.7$ Hz, 1H; IrH); $^{31}P\{^1H\}$ NMR (81.01 MHz, [D_8]THF, 20 °C, 85 % H_3PO_4), ABB′CDEE′ spin systems: $\delta = -31.65$ (m, $^2J(P_B,P_A) = {}^2J(P_{B'},P_A) = 16.9$, $^3J(P_{B'},P_E) = {}^3J(P_B,P_{E'}) = -14.3$, $^3J(P_B,P_E) = {}^3J(P_{B'},P_{E'}) = 18.3$ Hz, 2P, P_B and $P_{B'}$), −28.40 (m, $^2J(P_A,P_C) = {}^2J(P_A,P_D)$ −5.9 Hz, 1P, P_A), −251.28 (m, $^1J(P_C,P_D) = 160.8$, $^1J(P_C,P_E) = {}^1J(P_C,P_{E'}) = 133.0$ Hz, 1P, P_C), −255.02 (m, $^1J(P_D,P_E) = {}^1J(P_D,P_{E'}) = 141.3$ Hz, 1P, P_D), −272.7 (m, $^1J(P_E,P_{E'}) = 72.7$ Hz, 2P, P_E and $P_{E'}$).

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[11] After 12 days at room temperature a ^{31}P NMR analysis of a solution of **7** in a sealed NMR tube prepared under dinitrogen had the following composition: **7**, 35 %; **8**, 28 %; **6**, 12 %; unknown iridium compounds 25 %. The NMR spectroscopic properties of **8** are virtually the same as those for **3**. $^{31}P\{^{1}H\}$ NMR ([D$_8$]THF, 25 °C, 202.42 MHz): ABCDEFG spin system, $\delta_A = -19.60$, $\delta_B = -30.73$, $\delta_C = -45.63$, $\delta_D = -268.33$ (transforms into a doublet of multiplets in the proton-coupled ^{31}P spectrum: $^{1}J(HP) \approx 118$ Hz), $\delta_E = -217.65$, $\delta_F = -221.72$, $\delta_G = 28.87$

[12] On hydrogenation of **7**, the reductive elimination of P_4 with formation of the trihydride **2** becomes competitive with respect to the hydrogenation reaction of P_4. This finding supports the hypothesis that hydrogen migration from the metal to one of the P atoms of P_4 is mandatory to bring about the final dihydrogen transfer to give PH_3 and *cyclo*-P_3.

[13] Homolytic P–P bond cleavage of P_4 has been considered recently in the photochemical reaction of P_4 with $[Cp''(CO)_2Fe]_2$ ($Cp'' = 1,3\text{-}t Bu_2C_5H_3$): O. J. Scherer, G. Schwarz, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1996**, *622*, 951.

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Synthesis and Crystal Structure Analysis of Tetraphosphanylsilane and Identification of Tetraphosphanylgermane**

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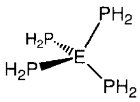
Dedicated to Professor Edgar Niecke
on the occasion of his 60th birthday

The ease with which the phosphanyl group (PH_2) can be functionalized by electrophilic and nucleophilic reagents provides facile access to a wide range of molecular phosphorus compounds. Polyphosphanyl–element compounds without organic substituents are also very promising as potential single-source precursors for chemical vapor deposition (CVD) for the synthesis of metastable element phosphides and for surface refining. Element hydrides substituted solely by PH_2 groups are not yet known, however. We have therefore been concerned with the synthesis of tetraphosphanyl compounds with elements of Group 14 (**1**–**5**). Whereas nothing is yet known about the existence of these (expectedly) extremely reactive molecules, in the case of the polyphosphanylsilanes only $HSi(PH_2)_3$[1] and related organotriphosphanylsilanes[2] could be isolated. An excellent nucleophilic transfer reagent for the PH_2 group is the tetraphosphanylalanato ion in $[LiAl(PH_2)_4]$, which reacts even at −80 °C with halogen–element compounds under halogen/PH_2 exchange. [1, 3] According to earlier studies, the reaction of SiX_4 and GeX_4 (X = halide) with $[LiAl(PH_2)_4]$ does not lead to **2** and **3**, but to a mixture of SiH- and GeH-containing phosphanyl derivatives.[4] In contrast, we ascertained that the title compounds **2** and **3** are indeed accessible when mild reaction conditions are employed and the reaction products rapidly worked-up. Whereas **2** was for the first time isolated and characterized by means of NMR and IR spectroscopy as well as by X-ray structure analysis, **3** has only been identified by gas chromatography and mass spectrometry as yet.



	1	2	3	4	5
E	C	Si	Ge	Sn	Pb

The reaction of $SiCl_4$ with $[LiAl(PH_2)_4]$ in tetraethylene glycol dimethyl ether at −30 °C leads to an orange solution,

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