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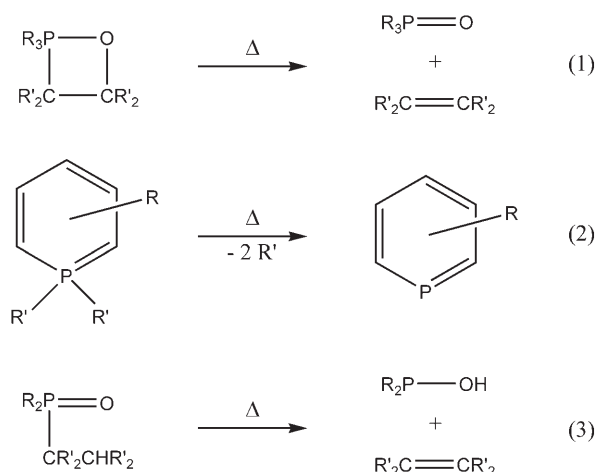
Dehydroiodination of Iodo- and Diiodomethane by a Transient Phosphinidene Complex**

Aysel Özbolat, Arif Ali Khan, Gerd von Frantzius, Martin Nieger, and Rainer Streubel*

Dedicated to Professor Ulrich Zenneck on the occasion of his 60th birthday

Molecular organophosphorus chemistry currently offers a wide variety of different methods of P–C bond formation, but only a few provide selective P–C bond cleavage in the absence of any reagents^[1] or without valence isomerization.^[2] Knowledge about unconventional decomposition pathways, however, can be crucial for the design of stable phosphine-based catalysts. Important aspects of thermal P–C bond-breaking reactions can be illustrated by the following examples. 1) Wittig-type reactions rely on the ease of breaking the endocyclic P–C bond of intermediately formed 1 σ^5 ,2 λ^5 -oxaphosphetanes [Scheme 1, Eq. (1)];^[3] 1 σ^3 ,2 λ^3 -oxaphosphetanes, by contrast, are much less prone to this type of ring cleavage. 2) Upon heating, σ^4 , λ^5 -phosphinines with two alkyl groups at the phosphorus atom can be transformed into σ^2 , λ^3 -phosphinines, their (more) aromatic counterparts [Scheme 1, Eq. (2)].^[4] 3) Branched triorganyl phosphine oxides are known to decompose by carbon-to-oxygen β -H transfer at elevated temperatures, whereas trimethyl or triphenyl derivatives are stable up to around 700 °C [Scheme 1, Eq. (3)].^[5] Herein, we report on experimental and theoretical investigations of unprecedented P–C bond-breaking reactions of acyclic halo(diorgano)phosphine tungsten complexes, which, at the same time, represent novel examples for dehydroiodination reactions of “simple” alkyl iodides.

Recently, we studied reactions of the thermally generated electrophilic terminal phosphinidene complex [(CO)₅WPCH-



Scheme 1. Examples of thermal P–C bond-cleavage methods.

(SiMe₃)₂] (**2**) with alkyl chlorides and bromides. Surprisingly, we observed formation of a dichloro(organo)phosphine complex upon reaction of **2** with carbon tetrachloride^[6] (proving the reductive capability of **2**) as well as insertion into the C–Br bond by reaction with benzyl bromide to yield a benzyl(bromo)organophosphine complex, the latter being stable under these conditions.^[7] To get further insight into such reduction and insertion reactions we decided to treat **2** with a series of C₁ and C₂ alkyl halides. Herein, we report preliminary results using iodo- and diiodomethane.

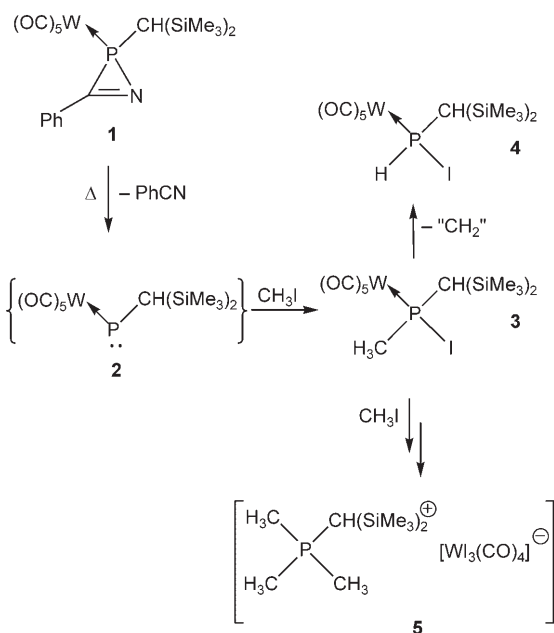
Reaction of 2*H*-azaphosphirene complex **1**^[8] with an excess of iodomethane in toluene at 75 °C yielded three major products: complex **3** by insertion of terminal phosphinidene complex **2** into the C–I bond of iodomethane, iodo-(organo)phosphine complex **4** by formal “loss” of CH₂,^[9] and {bis(trimethylsilyl)methyl}trimethylphosphonium tri-iodo(tetracarbonyl)tungstate **5** (Scheme 2). Whereas formation of complex **3** was anticipated,^[7] the formation of complex **4** and phosphonium salt **5** was a great surprise. Complex **5** resulted from an oxidation process caused by methyl iodide, in which oxidative addition of methyl iodide to the tungsten center might be the primary step. According to ³¹P NMR spectroscopic monitoring of the reaction the amount of **3** (and **4**) constantly increased within the first 55 min, but then **3** decreased in favor of **5**, whereas **4** remained approximately constant. Further studies on the reaction course revealed that toluene is not the proton source in the formation of complex **4**, as evidenced by the reaction in deuterated toluene, which yielded again **4** and not the D isotopomer.

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Scheme 2. Reaction of complex **1** with an excess of CH_3I .

Replacing iodomethane by diiodomethane (Scheme 3) gave complex **4** much faster (10 min vs. 40 min, respectively), but at the same time induced the formation of other products (ca. 85% in total), which were tentatively assigned on the basis of their NMR spectroscopic data as they could not be separated. ^{31}P NMR spectroscopic monitoring of the reaction at high temperature unambiguously showed primary formation of the C–I insertion product, complex **6** ($\delta = 41.3$ ppm, $^1J(\text{W},\text{P}) = 265.8$, $^2J(\text{P},\text{H}) = 12.7$ Hz), and subsequently either decomposition and formal loss of CHI to give complex **4** (Scheme 3, route a) or loss of HI to give (*E*)-**7** ($\delta = 242.6$ ppm, $^1J(\text{W},\text{P}) = 288.6$, $^2J(\text{P},\text{H}) = 19.1$ Hz; Scheme 3, route b). The data of **7** are in good agreement with (*E*)-Mes*P=C(H)I ($\delta =$

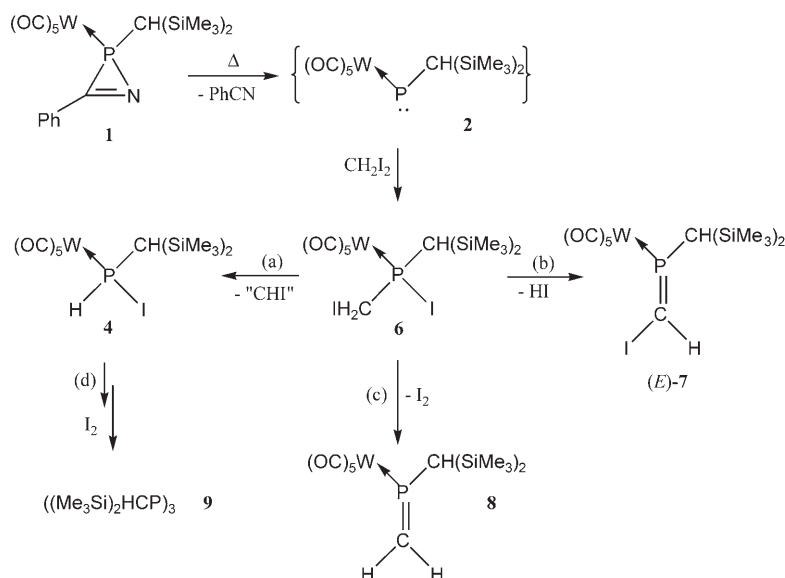
290.2 ppm, $^2J(\text{P},\text{H}) = 26.0$ Hz) but not with (*Z*)-Mes*P=C(H)I, which displays a more downfield-shifted signal and a larger P,H coupling constant magnitude ($\delta = 308.0$ ppm, $^2J(\text{P},\text{H}) = 39.9$ Hz).^[10] Unfortunately, further comparison is limited here since complexes of these phosphaaalkenes are unknown. In the case of route a we assume α -elimination by carbon-to-phosphorus H transfer,^[11] whereas formal HI elimination takes place in the case of route b. A further reaction pathway of complex **6** seems to be loss of I_2 to yield complex **8** ($\delta = 250.5$ ppm, $^1J(\text{W},\text{P}) = 255.6$, $^2J(\text{P},\text{H}) = 24.2$, $^2J(\text{P},\text{H}) = 11.4$, $^2J(\text{P},\text{H}) = 6.5$ Hz; Scheme 3, route c). This assignment is supported further by comparison with the ^{31}P and ^1H NMR data and coupling constant magnitudes of the iron complex $[\text{Fe}(\text{CO})_4(\text{Mes}^*\text{P}=\text{CH}_2)]$ ($\delta = 277.1$ ppm, $^2J(\text{P},\text{H}) = 25.8$, $^2J(\text{P},\text{H}) = 9.6$ Hz).^[12]

Cyclotriphosphine **9**^[13] ($\delta = -129.4/-155.8$ ppm, $^1J(\text{P},\text{P}) = 204.3$ Hz), observable after longer reaction times only, might result from reaction of complex **4**, for example, with I_2 and subsequent cyclocondensation (Scheme 3, route d). Upon further heating of the reaction mixture, another yet unidentified product with a ^{31}P NMR resonance at $\delta = 113.1$ ppm lacking a phosphorus–tungsten coupling was observed.

The constitutions of complexes **3–5** were unambiguously deduced from their NMR and MS data and shall not be discussed further.^[14] We were able to establish the molecular structure of complex **5** by single-crystal X-ray analysis (Figure 1).^[15] The asymmetric unit cell contains two similar ion pairs, only one of which will be discussed here. The anion consists of an octahedrally coordinated tungsten center capped by one carbonyl ligand (C1a, O1a). Two iodine atoms (I1a, I1c) and two carbonyl ligands (C1c, O1c and C1d, O1d) occupy the equatorial plane, and one iodine atom (I1b) and one carbonyl ligand (C1b, O1b) fill both slightly distorted axial corners. As anticipated, W–I bond lengthening between the tungsten atom and the equatorial iodine atoms was found, presumably owing to steric demand. The small differences between the equatorial and axial tungsten–iodine bonds (1.5 to 1.7 pm) clearly indicate the absence of any additional donor–acceptor interactions. In contrast, lengthening of the tungsten–iodine bonds induced by donor–acceptor interactions was observed in $[(\text{tert-C}_4\text{H}_9)_3\text{PI}][\text{W}(\text{CO})_4\text{I}_3]$.^[16] The phosphonium moiety of **5** has been reported previously as part of the salt $[(\text{CH}_3)_3\text{PCH}(\text{SiMe}_3)_2][\text{W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$,^[17] however, no X-ray crystal structure was obtained.

To get further insight into the reasons behind the P–C bond-breaking reactions, we performed DFT calculations.^[18] A comparison of selected geometrical data of complexes **3**, **4**, **6**, and **8** can be taken from Table 1, and the DFT structure of **6** is shown in Figure 2.

A brief look at the DFT structures and the common range of P–C single bonds^[20] reveals that all P–C bond lengths of complexes **3**, **4**, and **6** are more in the upper region, thus pointing to steric stress (Table 1). But nothing can be concluded that could be used as a structurally based prediction for the decomposition. On the



Scheme 3. Thermal reaction of complex **1** with CH_2I_2 .

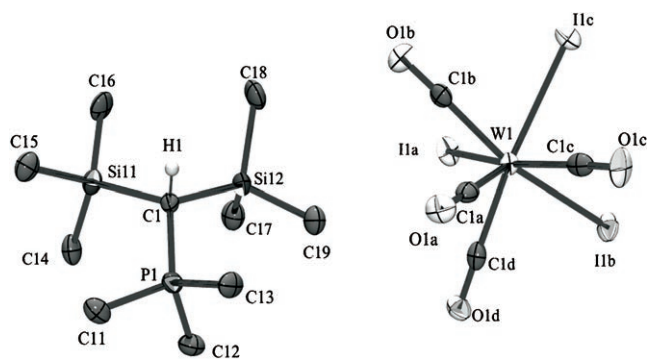


Figure 1. Displacement ellipsoid plot of one independent ion pair of complex **5** (drawn at 50% probability, hydrogen atoms except H1 are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–C1 1.779(5), P1–C11 1.787(5), P1–C12 1.781(5), P1–C13 1.783(5), W1–C1a 1.953(6), W1–C1b 2.022(6), W1–C1c 2.041(6), W1–C1d 2.009(5), W1–I1a 2.8752(4), W1–I1b 2.8575(4), W1–I1c 2.8717(4), C1a–O1a 1.167(6), C1b–O1b 1.135(6), C1c–O1c 1.127(6), C1d–O1d 1.149(5); C1a–W1–C1c 74.2(2), C1a–W1–I1a 124.29(16), C1c–W1–I1a 161.52(14), I1b–W1–I1c 90.48(1), C1b–W1–I1c 74.87(14), C1b–W1–C1d 114.0(2), C1d–W1–I1b 76.44(14), C1c–W1–I1b 76.93(14).

Table 1: Bond lengths [Å] and compliance constants (COCO, in Å²mdyn^{−1})^[19] of **3**, **4**, **6**, and **8**.^[a]

Compd	R ¹	R ²	[(OC) ₅ WP(CH(SiMe ₃) ₂)R ¹ R ²]						P–W
			P–CH(SiMe ₃) ₂	COCO	P–R ¹	COCO	P–R ²	COCO	
3	Me	I	1.863	0.443	1.851	0.380	2.558	0.876	2.573
4	H	I	1.853	0.426	1.412	0.298	2.548	0.860	2.539
6	CH ₂ I	I	1.863	0.457	1.877	0.458	2.532	0.809	2.600
8	=CH ₂	–	1.838	0.392	1.659	0.169	–	–	2.529

[a] Calculated at the B3LYP/6-311g(d,p) level, LanL2DZ at W.^[18]

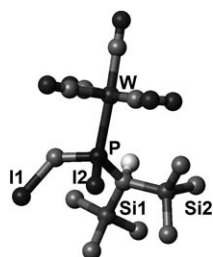


Figure 2. DFT structure of complex **6**.

other hand, P–C^{R1} compliance constants show a clear trend of bond strengths ranging from a P–C double bond in complex **8** to a weak single bond in complex **6**. In comparison with complex **6** the stronger P–Me bond of complex **3** is accompanied by a weaker P–I bond. Complex **6** has a long I···I separation (3.940 Å), which is clearly beyond the sum of covalent radii (2.66 Å) and close to the sum of van der Waals radii (3.96 Å, solid state); however, the separation is significantly shorter than the sum of van der Waals radii as determined by gas-phase kinetics (5.10 Å).^[21]

The above considerations do not, however, foster understanding of the decomposition pathways. According to calculated reaction free energies (Table 2) formation of complexes **3** and **4** from 2*H*-azaphosphirene complex **1** (or from free phosphinidene complex **2**, Scheme 2) are of

Table 2: Selected reaction free energies according to the DFT calculations.

Reactants	Products	Δ <i>G</i> [kJ mol ^{−1}]
1	→ 2 + PhCN	−8
2 + MeI	→ 3	−107
1 + MeI	→ 3 + PhCN	−115
1 + MeI + PhMe	→ 4 + PhCN + PhEt	−117
1 + 2×MeI	→ 4 + EtI + PhCN	−129
2× 2 + 2×MeI	→ 2× 4 + 2×PhCN + H ₂ C=CH ₂	−214
3 + MeI	→ 4 + EtI	−14
2× 3	→ 2× 4 + H ₂ C=CH ₂	16
2× 3	→ 4 + [(OC) ₅ WP{CH(SiMe ₃) ₂ }(Et)I]	23
3 + MePh	→ 4 + EtPh	−2

comparable probability, while formation of complex **4** from **3** by formal transfer of a carbene unit (CH₂) onto either MeI or the solvent (toluene) is accompanied by a considerably less gain of energy. All attempts to locate transition states of an intra- or intermolecular CH₂ transfer have failed so far.

All the P–C bond-forming and bond-breaking reactions at phosphorus centers presented here are highly reminiscent of well-established M–C bond-forming and -breaking reactions of coordinatively unsaturated transition-metal centers, that is, oxidative additions of CH₃I^[22] and CH₂I₂.^[23] The DFT calculations in combination with compliance constants lend further support to the view that P–C single-bond strengthening in conjunction with steric relief seems to be one driving force for geminal bond activation/cleavage processes. Although the fate of methylene and its derivatives could not be detected, it is of special interest that dehydroiodination^[24] is strictly preferred over diiodination in the reaction of complex **1** and diiodomethane, which is in marked contrast to reactions induced by metals, for example, in the system Zn/CH₂I₂.^[23]

Experimental Section

Reaction monitoring: Complex **1** (0.031 g, 0.05 mmol) was dissolved in toluene (0.2 mL) in an NMR tube, CH₃I (0.58 g, 0.25 mL, 4.0 mmol) or CH₂I₂ (1.07 g, 0.32 mL, 4.0 mmol) was added, and the solution was heated at 75 °C.

3 and 4: Complex **1** (0.617 g, 1 mmol) was dissolved in toluene (3 mL), CH₃I (0.5 mL) was added, and the solution was heated at 75 °C for 2 h. All volatile components were removed in vacuo, and the products were separated by low-temperature column chromatography (SiO₂, −10 °C, petroleum ether). Evaporation of the solvents of the first fraction and crystallization from *n*-pentane at −25 °C yielded **4** as light-yellow crystals. Yield: 0.4 g, 65%; m.p. 78–82 °C. Evaporation of the second fraction and crystallization from *n*-pentane at −25 °C yielded complex **3**, which was slightly contaminated by complex **4** (< 10%).

5: Complex **1** (0.031 g, 0.05 mmol) was dissolved in toluene (0.2 mL) in an NMR tube, CH₃I (0.58 g, 0.25 mL, 4.0 mmol) was added, and the solution was heated at 75 °C for 10 h. After a

precipitate had formed, the solution was removed with a syringe, and the crystals were washed with a small amount of diethyl ether, thus yielding **5** as golden-orange crystals. Yield: 21.0 mg, 46%; m.p. 121 °C (decomp).

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- [15] Crystal structure data for complex **5** (C₁₄H₂₈I₃O₄PSi₂W): orthorhombic, space group *Pbca* (no. 61), *a* = 17.5907(2), *b* = 17.4856(2), *c* = 34.6938(4) Å, *V* = 10671.3(2) Å³, *Z* = 16, ρ = 2.271 Mg m⁻³, μ(MoKα) = 7.966 mm⁻¹. A total of 47812 reflections were measured on a Nonius KappaCCD diffractometer using MoKα radiation (λ = 0.71073 Å) at a temperature of 123(2) K, 9412 reflections were unique (*R*_{int} = 0.0697). A semi-empirical absorption correction from equivalents was applied (min./max. transmission = 0.21995/0.41737). The structure was solved with Patterson methods and refined with full-matrix least squares against *F*² of all reflections. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined as rigid groups. *R* values [*I* > 2σ(*I*): *R*₁ = 0.0263, *wR*₂ = 0.0432. *R* values for all data: *R*₁ = 0.0457, *wR*₂ = 0.0462, min./max. difference electron density -0.918/0.750 e Å⁻³. CCDC-606431 contains 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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