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Electrophilic terminal phosphinidene complex–Lewis base adducts: Chemistry between carbon–halide bond activation and weak Lewis base adduct formation

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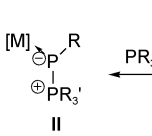
Comparative studies on the reactivity of a transiently formed terminal phosphinidene complex towards various organobromide derivatives show that carbon–bromine bond insertion is preferred with benzyl bromide, whereas formal HBr-insertion resulted with 2-bromopyridine and a surprising selectivity enhancement (of the phosphinidene complex) was observed with bromobenzene; all new products were established by elemental analyses, NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction studies.

Since Mathey and Marinetti reported the transient formation of electrophilic terminal phosphinidene (phosphanediyl) complexes[1] **I**, such complexes have emerged as important building blocks in modern organophosphorus chemistry.[2] Important reactivity features of **I** include [2+1] cycloaddition reactions, *e.g.*, with alkenes or alkynes to afford P-heterocycles, and insertion into element–element σ-bond species, *e.g.*, with alcohols or ferrocene to yield complexes with P–H functions.[1] Much less intensively studied were reactions in which zwitterionic terminal phosphinidene complex–Lewis base adducts with *strong or weak* bonds are formed, *e.g.*, phosphine complexes **II** were obtained with tertiary phosphines[3] and nitrilium phosphanylid complexes **III** were transiently formed by reaction with carbonitriles and trapped in 1,3-dipolar cycloaddition reactions (Scheme 1).[4] Since then it has been demonstrated that *weak* donor adducts of type **III**[5,6] – and related species[7–10] – are valuable new 1,3-dipoles.

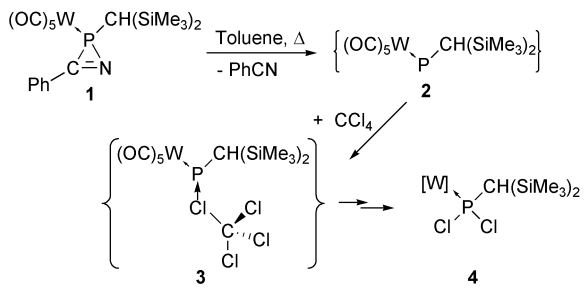
Very recently, we obtained a first hint that complexes **I** might react with carbon halides – in a surprising manner. We found that thermal decomposition of 2*H*-azaphosphirene complex **1** in tetrachloromethane afforded the dichloro(organo)phosphine complex **4** (Scheme 2). Since it is well established that **1** transiently generates complex **2**, we assumed that a terminal phosphinidene complex–Lewis base adduct **3** might be involved.[11]

Here we report that terminal phosphinidene complex **2**, generated as previously from **1**,[12] formally inserts into the carbon–bromine bond of benzyl bromide to furnish complex **6** in a clean reaction (Scheme 3); an initially formed weak Lewis base adduct **5** that subsequently rearranges to **6** seems a very reasonable explanation. Complex **6** was unambiguously characterized by NMR spectroscopy, mass spectrometry† and single-crystal X-ray diffraction‡ (Fig. 1).

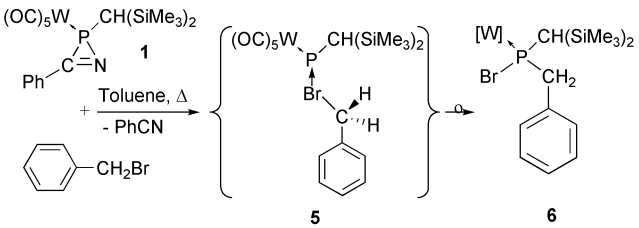
We then turned our attention to aryl bromides and carried out a comparative study using 2-bromopyridine and bromobenzene. In the case of 2-bromopyridine we obtained selectively the secondary bromophosphine complex **7** as the only phosphorus-containing product (Scheme 4); the molecular structure of **7** is shown in Fig. 2. In the *presence* of bromobenzene we



Scheme 1 Generation of strong (**II**) and weak (**III**) terminal phosphinidene complex-Lewis base adducts (R, R′ = organic substituents; [M] = transition metal complex).



Scheme 2 Thermal reaction of complex **1** in CCl_4.



Scheme 3 *Reagents and conditions:* 617 mg of complex **1**, 500 mg benzyl bromide, 3 mL toluene, 75 °C, 2 h; column chromatograpy (SiO_2, −20 °C, diethyl ether/petrol ether 40 : 60), yellow solid, yield: 65%, m.p. 146 °C (decomp.).

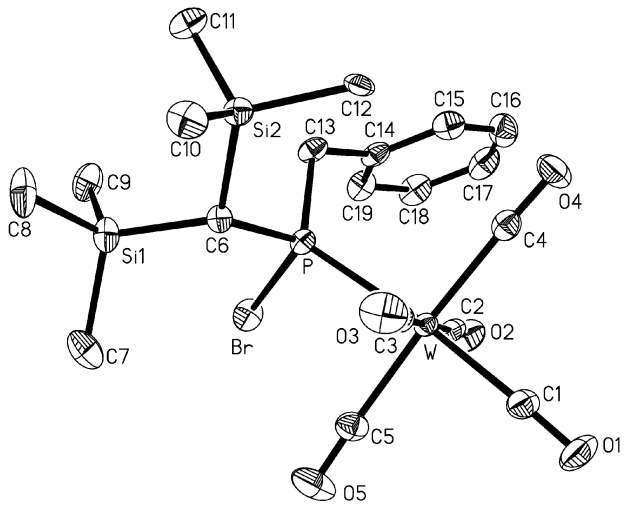


Fig. 1 Molecular structure of **6** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P–W 2.5052(7), P–C(6) 1.822(2), P–C(13) 1.859(3), P–Br 2.2693(7); Br–P–W 105.20(3), C(6)–P–C(13) 104.84(12), C(6)–P–W 117.34(9), C(6)–P–Br 106.57(8).

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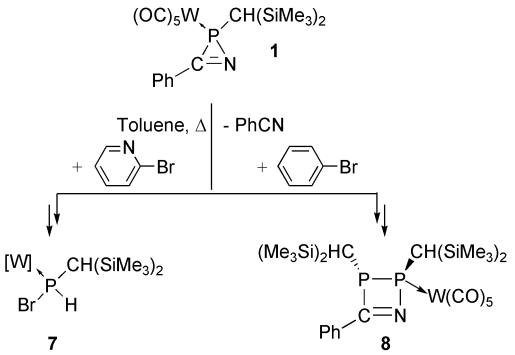

Scheme 4 *Reagents and conditions for* **7** and **8**: 617 mg of complex **1**, 500 mg 2-bromopyridine (**7**) or 500 mg bromobenzene (**8**), 3 mL toluene, 75 °C, 2 h; **7**: column chromatography (SiO_2, −10 °C, *n*-pentane), yellow solid, yield: 50%, m.p. 71 °C (decomp.); **8**[12] was purified as described before, yield: 72%.

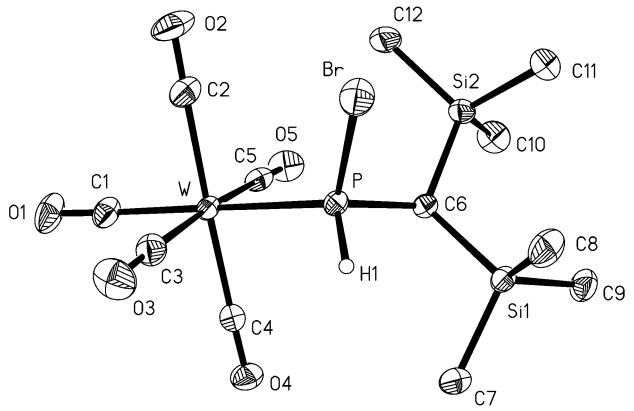

Fig. 2 Molecular structure of **7** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms, except H1, are omitted for clarity). Selected bond lengths [Å] and angles [°]: P–W 2.4568(6), P–C(6) 1.818(2), P–Br 2.2394(6), Br–P-W 116.48(2), C(6)–P–W 121.57(7), C(6)–P–Br 104.54(7).

exclusively obtained the 2,3-dihydro-1,2,3-azadiphosphete complex **8**[12] (Scheme 4).

It is remarkable that, in the *absence* of bromobenzene, **8** was obtained only as one product of a three-component mixture consisting of **8**, a dinuclear 2-aza-1,4-diphosphabutadiene tungsten complex and a 2,5-dihydro-1,3-diaza-2,5-diphosphinine tungsten complex,[12] thus showing a surprising gain in selectivity in the present case. We assume that a weak Lewis base adduct (such as **3** or **5**) between bromobenzene and the terminal phosphinidene complex **2** is transiently formed, thus changing the selectivity of complex **2**.

In conclusion, our findings not only provide evidence that *weak* Lewis base adducts – such as **5** – may be transiently formed but also that this can lead to a selectivity enhancement of electrophilic terminal phosphinidene complexes as shown in the case of **8**. We are currently investigating the reaction course leading to **7** and the option to synthesize optically active phosphine complexes *via* this method.

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Notes and references

† Satisfactory elemental analyses were obtained for complexes **6** and **7**. NMR data were recorded in $CDCl_3$ solutions (295 K) at 50.3 MHz (^{13}C), 81.0 MHz (^{31}P) and 200 MHz (^{1}H), using TMS and 85% H_3PO_4 as standard references; *J*/Hz. Selected spectroscopic data for **6** and **7**. **6**: ^{1}H NMR: δ 0.45 (s, 9H, $SiMe_3$), 0.46 (s, 9H, $SiMe_3$), 2.0 (d, ^{2}J(P,H) = 9.3 Hz, 1H, PCH), 3.72 (dd, ^{2}J(P,H) = 9.8 Hz, ^{2}J(H,H) = 13.6 Hz, 1H, PCH_2), 4.09 (pt, ^{2}J(P,H) + ^{2}J(H,H) = 13.7 Hz, 1H, PCH_2), 7.36 (m, 3H, H*arom*), 7.45 (m, 2H, H*arom*); $^{13}C\{^{1}H\}$ NMR: δ 3.4 (d, ^{3}J(P,C) = 3.6 Hz, $SiMe_3$), 4.0 (d, ^{3}J(P,C) = 2.3 Hz, $SiMe_3$), 31.0 (d, ^{1}J(P,C) = 20.0 Hz, PCH), 46.4 (d, ^{1}J(P,C) = 7.1 Hz, PCH_2), 127.9 (d, ^{2}J(P,C) = 4.1 Hz, C*arom*), 128.4 (d, ^{3}J(P,C) = 3.4 Hz, C*arom*), 131.2 (C*arom*), 133.1 (C*arom*), 133.4 (d, ^{3}J(P,C) = 3.5 Hz, C*arom*), 197.5 (d, ^{2}J(P,C) = 6.9 Hz, *cis*-CO), 199.3 (d, ^{3}J(P,C) = 32.9 Hz, *trans*-CO); $^{31}P\{^{1}H\}$ NMR: δ 108.3 (^{1}J(W,P) = 275.8, Hz); MS (70 eV, EI, ^{184}W, ^{80}Br) *m*/*z* 684 (36) [M$^+$], 628 (25) [M$^+$ − 2CO], 600 (38) [M$^+$ − 3CO], 544 (100) [M$^+$ − 5CO]. **7**: ^{1}H NMR: δ 0.27 (s, 9H, $SiMe_3$), 0.35 (s, 9H, $SiMe_3$), 1.29 (d, ^{2}J(P,H) = 6.5 Hz, 1H, PCH), 7.28 (dd, ^{1}J(P,H) = 344.5, ^{3}J(H,H) = 0.6 Hz, 1H, PH); $^{13}C\{^{1}H\}$ NMR: δ 0.1 (d, ^{3}J(P,C) = 2.8 Hz, $SiMe_3$), 1.9 (d, ^{3}J(P,C) = 4.3 Hz, $SiMe_3$), 22.9 (d, ^{1}J(P,C) = 8.8 Hz, PCH), 196.2 (d, ^{2}J(P,C) = 6.9 Hz, *cis*-CO), 198.5 (d, ^{2}J(P,C) = 27.1 Hz, *trans*-CO); $^{31}P\{^{1}H\}$ NMR: δ 23.1 (dd, ^{1}J(P,H) = 344.5 Hz), ^{1}J(W,P) = 264.0 Hz); MS (70 eV, EI, ^{184}W, ^{80}Br) *m*/*z* 594 (6) [M$^+$], 191 (45) [$HPCH(SiMe_3)_2^+$], 73 (100) [$SiMe_3^+$].

‡ *Crystal data for* **6**, $C_{19}H_{26}BrO_5PSi_2W$. Triclinic, space group $P\bar{1}$, a = 9.0099(6), b = 10.2351(6), c = 14.4398(11) Å, α = 87.965(4), β = 88.558(4), γ = 68.778(4)°, U = 1240.40 Å^3, Z = 2, μ = 6.454 mm^{-1}, MoK_α radiation, λ = 0.71073 Å ^{3}, T = 133 K. Data collection: A colourless crystal *ca*. 0.12 × 0.12 × 0.05 mm was used to record 26263 intensities on a Bruker Smart 1000 CCD diffractometer, $2\theta_{max}$ 30°); 7239 reflections were independent (R_{int} 0.0320). An absorption correction based on SADABS was applied, with transmissions 0.612–0.802. Structure refinement: The structure was solved by the heavy-atom method, all non-hydrogen atoms were refined anisotropically using full matrix least-squares procedure (SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany) based on F^2 to give $R1$ = 0.0231, $wR2$ = 0.0502 (all data). Methyl groups were refined as rigid groups and other hydrogens using a riding model.

Crystal data for **7** ($C_{12}H_{20}BrO_5PSi_2W$). Triclinic, space group $P\bar{1}$, a = 6.9656(2), b = 9.4476(3), c = 16.0750(5) Å, α = 74.990(1), β = 88.901(1), γ = 82.853(1)°, U = 1013.74(5) Å^3, Z = 2, μ = 7.880 mm^{-1}, MoK_α radiation 0.71073 Å^3, T = 133 K. Data collection: A pale yellow crystal *ca*. 0.25 × 0.24 × 0.18 mm was used to record 20897 intensities on a Bruker Smart 1000 CCD diffractometer, $2\theta_{max}$ 30°; 5896 reflections were independent (R_{int} 0.0262). An absorption correction based on SADABS was applied, with transmissions 0.29–0.49. Structure refinement: The structure was solved as above; all non-hydrogen atoms were refined anisotropically using full matrix least-squares procedures (SHELXL-97) based on F^2 to give $R1$ = 0.0192, $wR2$ = 0.0510 (all data). Methyl groups were refined as rigid groups, P–H freely and other hydrogens using a riding model. CCDC 215573 and 215574. See http://www.rsc.org/suppdata/cc/b3/b309443j/ for crystallographic data in .cif or other electronic format

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