

## Different thermal reactivity of a 1,2-thiaphospholo[*a*]-phosphirane in free and metal carbonyl complexed form†

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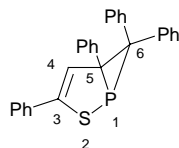
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### Supplementary Information: Full experimental, spectroscopic and analytical data

**General Remarks:** All reactions were carried out in rigorously dried glassware and under an argon atmosphere. Solvents were dried by standard procedures and kept under argon. Column chromatography was performed under hydrostatic conditions (silica gel Si60, Macherey-Nagel, 0.063–0.02 mm, column size 60×4 cm). – NMR: Bruker Bruker AMX 400 (<sup>1</sup>H: 400.1 MHz; <sup>13</sup>C: 100.61 MHz; <sup>31</sup>P 161.98 Hz); CDCl<sub>3</sub> was used as solvent. The <sup>13</sup>C spectra were recorded proton-decoupled but phosphorus-coupled; thus, the signal multiplicities reported here indicate P,C coupling. The following references were applied: internal TMS for the proton spectra, the solvent signal for the <sup>13</sup>C NMR spectra [ $\delta(\text{CDCl}_3) = 77.0$ ], and external 85% H<sub>3</sub>PO<sub>4</sub> for the <sup>31</sup>P spectra. – IR: Bruker IFS113; relative intensities are given in parentheses. – MS: Finnigan MAT SSQ 7000 (EI and CI mode). – Microanalyses: Elementar Vario EL (Division of Analytical Chemistry, University of Ulm), Heraeus CHN-O-Rapid (University of Kaiserslautern).

**Materials:** 3,5-Diphenyl-1,2-thiaphosphole (1)<sup>1</sup> and diphenyldiazomethane<sup>2</sup> were prepared according to reported methods.

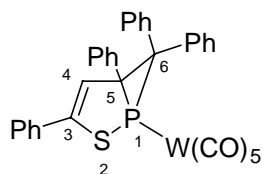
### 3,5,6,6-Tetraphenyl-2-thia-1-phospha-bicyclo[3.1.0]hex-3-ene (2)



A mixture of 3,5-diphenyl-1,2-thiaphosphole (0.508 g, 2.0 mmol) and diphenyldiazomethane (0.466 g, 2.4 mmol) in dry toluene (10 ml) was heated at 70 °C until the red colour disappeared (ca. 24 h). The solvent was removed at 20 °C/15 mbar. The resulting oil was purified by chromatography on silica gel (eluent: toluene/n-pentane (1:6)) to give the

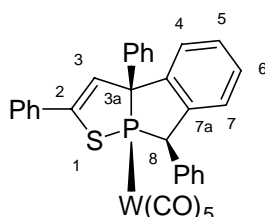
cycloadduct **2** (0.619 g, 73.7%) as colourless needles, m.p. 146 °C (acetone/CHCl<sub>3</sub>). IR (KBr):  $\nu/\text{cm}^{-1}$  1593 (w), 1574 (w), 1487 (m), 1439 (m), 1072 (w), 1028 (w), 769 (m), 747 (s), 691 (vs). <sup>1</sup>H NMR:  $\delta$  6.50 (d, <sup>3</sup>J<sub>P,H</sub> = 4.8 Hz, 1H, 4-H), 6.80–7.50 (m, 20H, H<sub>Ph</sub>). <sup>13</sup>C NMR:  $\delta$  42.1 (d, <sup>1</sup>J<sub>P,C</sub> = 48.6 Hz), 73.4 (d, <sup>1</sup>J<sub>P,C</sub> = 40.6 Hz), 127.7 (C-4); 125.6, 126.4, 126.6, 127.0, 128.2, 129.2, 129.4, 130.9, 131.5, 133.5, 137.6 and 142.2 (C<sub>Ph</sub>); 142.2 (C-3). <sup>31</sup>P NMR:  $\delta$  –81.4. MS (EI, 70 eV):  $m/z$  (%) 420 (40) [M<sup>+</sup>], 254 (3) [M<sup>+</sup>–CPh<sub>2</sub>], 165 (100). Anal. calcd for C<sub>28</sub>H<sub>21</sub>PS (420.51): C, 79.97; H, 5.03; found: C, 80.02; H, 4.97.

### 3,5,6,6-Tetraphenyl-2-thia-1-phospha-bicyclo[3.1.0]hex-3-ene P-(pentacarbonyl)tungsten (**3**)



A solution of tungsten hexacarbonyl (0.24 g, 0.68 mmol) in dry THF (120 ml) was placed in a photolysis apparatus and irradiated under cooling with water for 30 min using a medium-pressure mercury lamp, which resulted in the formation of the complex W(CO)<sub>5</sub>(thf). During this time the colour of the reaction mixture changed from colourless to yellow. Then a solution of **2** (0.252 g, 0.6 mmol) in dry THF (10 ml) was added, and the mixture was stirred for 24 h. The solvent was removed at 20 °C/15 mbar. The resulting oil was purified by chromatography on silica gel (eluent: toluene/n-pentane (1:6)) to leave a violet solid. Recrystallisation from n-pentane at 0 °C provided complex **3** (0.315 g, 70.6%) as colourless prisms, m.p. 127 °C (n-pentane). IR (KBr):  $\nu/\text{cm}^{-1}$  = 2075 (s), 1948 (vs), 1931 (vs), 1597 (w), 1489 (w), 1441 (w), 769 (m), 699 (s), 588 (m), 568 (s). <sup>1</sup>H NMR:  $\delta$  6.18 (d, <sup>3</sup>J<sub>P,H</sub> = 17.2 Hz, 1H, 4-H), 6.48 (d,  $J$  = 8.3 Hz, 2H, H<sub>Ph</sub>), 6.9–7.5 (m, 18H, H<sub>Ph</sub>). <sup>13</sup>C NMR:  $\delta$  39.9 (d, <sup>1</sup>J<sub>P,C</sub> = 23.5 Hz), 67.1 (d, <sup>1</sup>J<sub>P,C</sub> = 26.2 Hz), 127.2 (C-4); 126.0, 126.1, 126.8, 128.0, 128.2, 128.5, 128.7, 130.1, 130.2, 130.3, 130.4, 132.7, 132.8, 133.5 and 135.9 (C<sub>Ph</sub>); 142.9 (C-3), 194.2, 195.8 and 196.7 (CO). <sup>31</sup>P NMR:  $\delta$  –55.4 (t, <sup>1</sup>J<sub>P,W</sub> = 133 Hz). MS (EI, 70 eV):  $m/z$  (%) 744 (15) [M<sup>+</sup>], 716 (50) [M<sup>+</sup>–CO], 660 (100) [M<sup>+</sup>–3CO], 604 (81) [M<sup>+</sup>–5CO], 420 (8) [**2**], 357 (19), 302 (34), 262 (17), 178 (15), 165 (17). Anal. calcd for C<sub>33</sub>H<sub>21</sub>O<sub>5</sub>PSW (744.41): C, 53.24; H, 2.84; found: C, 53.28; H, 2.87.

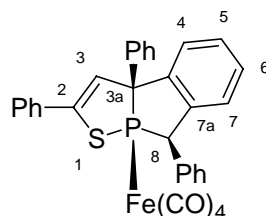
### 2,3a $\beta$ ,8 $\beta$ -Triphenyl-3a,8-dihydro-1-thia-8a-phosphacyclopenta[*a*]indene-P-(pentacarbonyl)tungsten (**5**)



A solution of tungsten complex **3** (0.05 g, 0.067 mmol) in dry toluene (10 ml) was heated at 80 °C for 3 hr. The solvent was removed at 20 °C/15 mbar. The resulting oil was purified by

chromatography on silica gel (eluent: toluene/n-pentane (1:3)) followed by recrystallisation from n-pentane/acetone at r.t. to give the rearrangement product **5** (0.038 g, 76%) as colourless prisms, m.p. 173–174 °C. IR (KBr):  $\nu/\text{cm}^{-1}$  2072 (s), 1940 (vs, br), 1597 (w), 1490 (w), 1445 (w), 1229 (w), 1073 (w), 1029 (w), 936 (w), 916 (w), 842 (w), 813 (w), 754 (m), 698 (m), 591 (m), 572 (m)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$ :  $\delta$  5.28 (d,  $^2J_{\text{P,H}} = 14.0$  Hz, 1H, 8-H), 6.30 (d,  $J_{\text{P,H}} = 18.3$  Hz, 1H, 3-H), 7.2–7.4 (m, 17H,  $\text{H}_{\text{Ph}}$ ), 7.66 (dd,  $J = 8.1$  and 1.9 Hz, 2H,  $\text{H}_{\text{Ph}}$ ).  $^{13}\text{C NMR}$ :  $\delta$  62.8 (d,  $^1J_{\text{P,C}} = 3.8$  Hz), 75.3 (d,  $^1J_{\text{P,C}} = 11.0$  Hz), 127.9 (C-3); 125.4, 127.2, 128.3, 128.8, 128.9, 129.0, 129.2, 129.3, 129.4, 129.5, 130.5, 130.6, 134.3 and 141.7 ( $\text{C}_{\text{Ph}}$ ); 142.9 (C-2); 194.3, 194.4 and 197.7 (CO).  $^{31}\text{P NMR}$ :  $\delta$  125.1 (t,  $^1J_{\text{P,W}} = 131$  Hz). MS (EI, 70 eV):  $m/z$  (%) 744 (11) [ $\text{M}^+$ ], 716 (50) [ $\text{M}^+ - \text{CO}$ ], 688 (4) [ $\text{M}^+ - 2\text{CO}$ ], 660 (100) [ $\text{M}^+ - 3\text{CO}$ ], 632 (8) [ $\text{M}^+ - 4\text{CO}$ ], 604 (96) [ $\text{M}^+ - 5\text{CO}$ ], 526 (6), 498 (12), 420 (14), 357 (23), 302 (35), 165 (11), 121 (22). Anal. calcd for  $\text{C}_{33}\text{H}_{21}\text{O}_5\text{PSW}$  (744.41): C, 53.24; H, 2.84; found: C, 53.15; H, 2.90.

### 2,3a $\beta$ ,8 $\beta$ -Triphenyl-3a,8-dihydro-1-thia-8a-phosphacyclopenta[*a*]indene-P-(tetracarbonyl)iron (**6**)



A suspension of bicyclic compound **2** (0.157 g, 0.373 mmol) and diiron nonacarbonyl (0.271 g, 0.747 mmol) in dry toluene (12 ml) was stirred at 80 °C for 30 min. The solvent was removed at 20 °C/15 mbar. The resulting oil was purified by chromatography on silica gel/florisil (eluent: toluene/n-pentane (1:6)) to give the iron complex **6** (0.038 g, 17.4%) as a rather unstable red oil. IR (film):  $\nu/\text{cm}^{-1}$  2052 (vs), 2028 (vs), 1983 (vs), 1959 (vs), 1938 (vs), 1598 (w), 1492 (m), 1446 (m), 1261 (m), 1077 (m), 1029 (m), 801 (m), 757 (m), 699 (s), 619 (s).  $^1\text{H NMR}$ :  $\delta$  5.24 (d,  $^3J_{\text{P,H}} = 14.2$  Hz, 1H, 8-H), 6.36 (d,  $J_{\text{P,H}} = 20.9$  Hz, 1H, 3-H), 6.9–7.3 (m, 17H,  $\text{H}_{\text{aryl}}$ ), 7.62 (dd,  $J = 8.1$  and 1.8 Hz, 2H,  $\text{H}_{\text{Ph}}$ ).  $^{13}\text{C NMR}$ :  $\delta$  60.4 (d,  $^1J_{\text{P,C}} = 9.1$  Hz, C-8), 72.7 (d,  $^1J_{\text{P,C}} = 16.3$  Hz, C-3a), 127.9 (C-3); 122.3–137.4 and 151.1 ( $\text{C}_{\text{aryl}}$ ); 142.1 (C-2), 210.7 and 210.9 (CO).  $^{31}\text{P NMR}$ :  $\delta$  195.2. MS (CI, 100 eV):  $m/z$  (%) 589 (100) [ $\text{MH}^+$ ], 561 (95) [ $\text{MH}^+ - \text{CO}$ ], 533 (30) [ $\text{MH}^+ - 2\text{CO}$ ], 504 (85) [ $\text{M}^+ - 3\text{CO}$ ], 476 (26) [ $\text{M}^+ - 4\text{CO}$ ], 412 (10), 357 (30), 281 (9), 238 (4), 167 (7). Due to the low stability of the compound, no correct elemental analysis could be obtained.

### Thermolysis of bicyclic compound **2**

A solution of **2** (0.100 g, 0.24 mmol) in dry mesitylene (6 ml) was heated at 120 °C for 6 h. The solvent was removed at 20 °C/15 mbar. Column chromatography (silica gel, eluent toluene/n-hexane (1:3)) gave (a) 1,3,4,4-butadiene-1-thiol (**7**) (0.028 g, 30%), (b) 1,2-thiaphosphole **1** (0.019 g, 31%) and (c) tetraphenylethene (0.015 g, 38%).

Thiol **18**: colourless solid, mp 129–130 °C ( $\text{CHCl}_3/\text{EtOH}$ ). IR (KBr):  $\nu/\text{cm}^{-1}$  2550 (w, SH), 1487 (m), 1440 (m), 770 (m), 698 (s).  $^1\text{H NMR}$ :  $\delta$  3.01 (s, 1H, SH), 6.57 (s, 1H, 2-H), 7.01–7.44 (m, 20H,  $\text{H}_{\text{Ph}}$ ).  $^{13}\text{C NMR}$ :  $\delta$  126.8 (C-2), 126.6, 127.5, 127.6, 127.7, 127.9, 128.1, 128.3, 128.5, 130.9, 131.1 and 131.4 ( $\text{CH}_{\text{Ph}}$ ); 133.6, 136.5 and 140.3 (C-1, C-3, C-4); 142.5,

143.1, 143.2 and 143.7 ( $C_{Ph}$ ). MS (EI, 70 eV):  $m/z$  (%): 390 (100) [ $M^+$ ], 357 (48) [ $M^+ - SH$ ], 313 (34) [ $M^+ - Ph$ ], 279 (40), 268 (23), 252 (11), 223 (12), 202 (7), 191 (18), 178 (13), 165 (13), 139 (13), 121 (36), 91 (6), 77 (6). Anal. calcd for  $C_{28}H_{22}S$  (390.56): C, 86.11; H, 5.68; found: C, 85.35; H, 5.65.

Tetraphenylethene: m.p. 221 °C (lit. 221–223 °C).

## References

- 1) I. Shinoda, A. Takahashi, T. Saito and T. Uchida, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2785–2794.
- 2) W. Schroeder and L. Katz, *J. Org. Chem.*, 1954, **19**, 718–720.