# ORGANOMETALLICS

# **Oligomerization of Terminal Phosphinidene Complexes**

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Supporting Information

ABSTRACT: The thermolysis of a 7-phenyl-7-phosphanorbornadiene pentacarbonylchromium complex yields a mixture of the cyclic trimer and tetramer of  $[PhP-Cr(CO)_5]$ . In the presence of CuCl and  $W(CO)_6$  at 60 °C, the decomposition of 7-R-7-phosphanorbornadiene pentacarbonyltungsten complexes affords the corresponding diphosphene  $\sigma_{,\pi}$  complexes [RP=PR][W(CO)\_5]\_3 (R = Me, CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et, 2-thienyl, 2-N-methylpyrrolyl). The Me derivative has been characterized as its [4+2] cycloadduct with 2,3-dimethylbutadiene. The three others have been characterized by X-ray crystal



structure analysis, NMR, and UV, and the electronic structure of the thienyl derivative has been studied by DFT calculations.

### INTRODUCTION

The reduction of dihalophosphines or the condensation of dihalophosphines with primary phosphines lead, in most cases, to a mixture of cyclopolyphosphine oligomers [RP],, the value of *n* decreasing with the steric hindrance of R. When R is extremely bulky, a diphosphene with a P=P double bond can be obtained as shown by Yoshifuji in his pioneering work of 1981.<sup>1,2</sup> Kinetic stabilization of the small oligomers (n = 2, 3, 4) can also be achieved by using bulky complexing groups on the phosphorus lone pairs. For example, Huttner has shown that PhP=PPh can be stabilized by two  $[Cr(CO)_5]$  units.<sup>3</sup> On our side, we have studied the oligomerization of the transient terminal phosphinidene complex  $[PhP-W(CO)_5]$  and obtained a variable mixture of products with n = 2, 3, or 4 according to the experimental conditions.<sup>4,5</sup> In view of the mildness of these conditions (no base, no reducing metal), it appeared interesting to check whether this approach has some generality. This is the subject of the present report.

### RESULTS AND DISCUSSION

It is known from theoretical calculations<sup>6</sup> that the P–M bond strength in  $R_3P-M(CO)_5$  varies in the order P-W > P-Cr >P-Mo. This implies that, in the 7-phosphanorbornadiene family, the stabilization of the bicyclic structure is the highest for tungsten and the weakest for molybdenum. This phenomenon has been experimentally demonstrated when devising a precursor of  $[FP-Mo(CO)_5]$ .<sup>7</sup> Thus, we decided to first check the influence of the metal on the formation of the phosphinidene oligomers. To our surprise, the thermal decomposition of the molybdenum complex  $(1_b)$  takes place slowly at 120 °C, but yields only a complex mixture of paramagnetic decomposition products (eq 1). On the contrary, the chromium complex  $\mathbf{1}_{a}$ rapidly decomposes at 120  $^{\circ}$ C to give a mixture of trimer (2) and tetramer (3).



The formula of 2 was established by exact mass measurement and <sup>31</sup>P NMR spectroscopy. The NMR spectrum shows a ABX system with two inequivalent noncomplexed phosphorus nuclei at -121.8 and -142.5 ppm and the complexed phosphorus at -42.3 ppm in  $CDCl_3$ . The formula and the stereochemistry of 3 were established by X-ray crystal structure analysis (Figure 1). The  $P_4$  ring is folded around the  $P_2-P_4$  axis, with an interplane angle of 128.5°. The stereochemistry is identical to that of the tetramer obtained with tungsten under more drastic conditions.<sup>5</sup> As can be seen, the less bulky chromium favors the formation of the tetramer, whereas, logically, the more bulky tungsten favors the trimer. It is known that the steric bulk of R favors the lower  $(RP)_n$  oligomers. For example, the Mg reduction of RPCl<sub>2</sub> gives the pentamer for R = Ph and the trimer for  $R = {}^{t}Bu.{}^{8}$ 

At lower temperature with CuCl as a catalyst, the tungsten complex  $\mathbf{1}_{c}$  is known to yield the tricomplexed dimer.<sup>4,5</sup> This reaction cannot be transposed to chromium and molybdenum since, in these cases, the copper chloride catalysis proved to be ineffective. We first decided to study what happens when the phenyl is replaced by an alkyl substituent. In the methyl case, the expected dimer is produced (we observe a <sup>31</sup>P resonance at -44.8 ppm) but is too reactive for isolation. We allowed it to react

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**Figure 1.** X-ray crystal structure of tetramer **3**. Selected bond lengths (Å) and angles (deg): P1-P2 2.2454(6), P2-P3 2.2267(6), P3-P4 2.2270(6), P1-P4 2.2370(7), P1-Cr1 2.3921(5); P2-P1-P4 82.40(2), P1-P2-P3 85.52(2), P2-P3-P4 83.05(2), P3-P4-P1 85.72(2).

in situ with 2,3-dimethylbutadiene and obtained the [2+4] cycloadduct (4), which was purified and characterized by NMR spectroscopy and HRMS (eq 2).



A positive outcome was also observed with the  $CH_2-CH_2-CO_2Et$  substituent. In this case, the dimer **5** is sufficiently stable and was isolated (eq 3).

$$(OC)_{5}W \xrightarrow{R} CO_{2}Me \xrightarrow{CuCl, W(CO)_{6}, \text{ toluene}}_{60 °C, 2-6 h} (3)$$

$$(1e-g) \xrightarrow{R} \xrightarrow{P \longrightarrow P} \xrightarrow{R} W(CO)_{5}$$

$$(OC)_{5}W \xrightarrow{P \longrightarrow P} \xrightarrow{W(CO)_{5}} W(CO)_{5}$$

$$(OC)_{5}W \xrightarrow{W(CO)_{5}} (5) e: R = CH_{2}CH_{2}CO_{2}Et (20\%) (6) f: R = \bigvee_{N} (20\%)$$

$$(7) g: R = \bigvee_{S} (20\%)$$

On the contrary, with the  $CH_2CH_2CN$  substituent, the CuCl catalysis does not work and no dimer is formed. It is known that  $Ph_2PCH_2CH_2CN$  coordinates to Ru(II) via its cyano group.<sup>9</sup> Besides, on the basis of DFT calculations, Lammertsma has suggested that the phosphorus extrusion from 7-phosphanorbornadiene complexes proceeds via a transition state where copper is tricoordinated to W, P, and one carbon at the bridgehead.<sup>10</sup>



Figure 2. X-ray crystal structure of dimer 6. Selected bond lengths (Å) and angles (deg): C1-P1 1.823(11), W1-P1 2.556(2), W3-P1 2.615(2), P1-P2 2.156(4), C11-P2 1.834(11), W2-P2 2.564(3), W3-P2 2.605(2); C1-P1-P2 104.9(4), C1-P1-W1 117.4(3), C1-P1-W3 106.9(3), C11-P2-P1 104.7(4), P1-W3-P2 48.79(8).

Obviously, the coordination of copper by the cyano group will prevent the formation of this transition state. Also of interest is the fact that adding acetonitrile to the reaction medium during the thermal decomposition of **1e** does not kill the extrusion catalysis but suppresses the formation of the dimer. It is clear from the work of Lammertsma<sup>10,11</sup> and our work<sup>12,13</sup> that copper chloride remains coordinated to the extruded phosphinidene. Thus, we suggest that the formation of the dimer takes place by oxidative coupling in the coordination sphere of copper (eq 4).

We also carried out our dimerization experiments with the N-methyl-2-pyrrolyl and 2-thienyl substituents. Both dimers have been characterized by X-ray crystal structure analysis (Figures 2 and 3). In 6, the C1-P1-P2-C11 unit displays a quasi-perfect *trans* arrangement (torsion angle 157.1°), but the two tungsten atoms coordinated to phosphorus are repelled by the  $\pi$ -complexed tungsten (W1-P1-P2-W2 138.14°). In 7, some disorder is observed, but the overall structure is similar. The most striking phenomenon when comparing the structures of 6 and 7 is that all of the distances (P-C, P-P, P-W) are systematically shorter in 7 than in 6. It seems that the thiophene ring interacts more strongly with the P<sub>2</sub>W<sub>3</sub> unit and strengthens it more efficiently than the pyrrole ring does. From the previous data on the phenyl derivative,<sup>4</sup> it seems that phenyl more resembles pyrrole than thiophene from this standpoint. The comparison of the UV spectra confirms that 7 stands apart from 6 and the phenyl derivative (Figure 4). This led us to investigate in more depth the electronic structure of 7 by DFT calculations. The data are provided in the Supporting Information. Both the structure and the UV spectrum were satisfactorily reproduced. The most important findings are that the P-P bond order is 1 (Wiberg indices) and that both the

HOMO and the LUMO do not have any significant contributions from the thiophene substituent. Some contribution from the localized  $\pi$  orbital in the two thiophene rings occurs only in the second highest occupied orbital (HOMO-1). Thus, this  $P_2W_3$  unit cannot be used as a conjugation transmitter within a polythiophene chain.

The possibility to synthesize functional diphosphenes such as **5** as stable tungsten complexes offers interesting synthetic opportunities that we are currently exploring.



Figure 3. X-ray crystal structure of dimer 7. Selected bond lengths (Å) and angles (deg): C1-P1 1.807(9), W1-P1 2.522(2), W3-P1 2.591(2), P1-P2 2.140(3), C10-P2 1.810(12), W2-P2 2.522(2), W3-P2 2.596(3); C1-P1-P2 106.0(3), C1-P1-W1 112.1(3), C1-P1-W3 110.6(3), C10-P2-P1 103.7(12), P1-W3-P2 48.73(7).

#### EXPERIMENTAL SECTION

NMR spectra were obtained on a JEOL ECA400 or JEOL ECA400SL spectrometer. All spectra were recorded at 298 K unless otherwise specified. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in ESI mode on a Finnigan MAT95XP HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon. Silica gel (230–400 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers. The phosphanorbornadiene precursors were synthesized as described in the literature.<sup>14,15</sup>

**Thermal Decomposition of 1a.** A solution of complex 1a (3 g, 5.7 mmol) in toluene (10 mL) was heated at 120 °C for 1 h. The reaction was complete, as checked by <sup>31</sup>P NMR. After evaporation, the residue was chromatographed on silica gel to give 2 and 3 as yellow powders.

Complex 2: eluent hexane, yield 0.2 g (20%). <sup>31</sup>P NMR (CDCl<sub>3</sub>): ABX, the two noncomplexed phosphorus atoms resonate at - 121.81(A) and -142.48(B). The complexed phosphorus appears at - 42.30 (X). Exact mass: calcd For C<sub>23</sub>H<sub>15</sub>O<sub>5</sub>P<sub>3</sub>Cr [M + H] 516.9616; found 516.9624.

Complex 3: eluent hexane/CH<sub>2</sub>Cl<sub>2</sub> (9:1), yield 0.36 g (45%). <sup>31</sup>P NMR (CDCl<sub>3</sub>): the spectrum shows three types of phosphorus atom at -70.24 (1P), -20.00 (2P), and 43.20 (1P). Exact mass: calcd for C<sub>29</sub>H<sub>20</sub>O<sub>5</sub>P<sub>4</sub>Cr [M + H] 624.9745; found 624.9737. Single crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub>/hexane.

Synthesis of Tetrahydro-1,2-diphosphinine (4). A solution of 1d (0.6 g, 1.13 mmol), W(CO)<sub>6</sub> (0.25 g), and CuCl (0.03 g) in toluene (5 mL) was heated at 60 °C. Monitoring by <sup>31</sup>P NMR showed that the reaction was complete after 12 h of heating. 2,3-Dimethylbutadiene (2.3 mL, 2 equiv) was added, and the solution was heated for 5 h at 110 °C. The solvent was removed under high vacuum, and the residue was chromatographed on silica gel with hexane/CH<sub>2</sub>Cl<sub>2</sub> (9:1) as eluent: 0.115 g of 4 was isolated (28% yield). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  –23.8 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.87 (pseudo t,  $\Sigma J$ (H–P) = 5.8 Hz, 6H, P-Me), 1.90 (s, 6H, Me), 2.68 (d, J(A–B) = 14.6 Hz, 2H, H<sub>A</sub> CH<sub>2</sub>P), 2.82 (d pseudo t,  $\Sigma J$ (B–P) = 8.2 Hz, 2H, H<sub>B</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  19.36 (pseudo t,  $\Sigma J$ (C–P) = 33.5 Hz, P-Me), 2.213 (s, Me), 38.72 (pseudo t,



Sample 1			Sample 2			Sample 3		
λ / nm	Absorbance	ε x 10 <sup>5</sup>	$\lambda / nm$	Absorbance	ε x 10 <sup>5</sup>	$\lambda / nm$	Absorbance	ε x 10 <sup>5</sup>
305	0.68645	6.86	310	0.51793	5.18	317	0.80945	8.09
368	0.27214	2.72	369	0.28412	2.84	369	0.37658	3.77
468	0.17434	1.74	480	0.14253	1.43	478	0.24828	2.48

Figure 4. UV spectra of  $[PhP=PPh][W(CO)_5]_3$  (sample 1), 6 (sample 2), and 7 (sample 3) in dichloromethane.

 $\Sigma J(C-P) = 9.6 \text{ Hz}, \text{ CH}_2), 126.97 (s, =C), 196.23 (s, <math>\Sigma J(C-P) = 0 \text{ Hz}, cis \text{ CO})), 197.77 (pseudo t, <math>\Sigma J(C-P) = 25.8 \text{ Hz} trans \text{ CO})$ . Exact mass: calcd for  $C_{18}H_{16}O_{10}P_2W_2$  819.9282; found 819.9287.

Synthesis of Diphosphene Complex 5. A solution of 1e (1 g, 1.6 mmol), CuCl (0.08 g), and W(CO)<sub>6</sub> (0.7 g) in toluene (15 mL) was heated at 60 °C for 2 h, under monitoring by <sup>31</sup>P NMR. The solvent was removed under high vacuum, and the compound was chromatographed at -2 °C on silica gel with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:7) as eluent: 0.2 g of 5 was isolated (20% yield). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  –27.0 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.25 (t, <sup>3</sup>J(H−H) = 7.2 Hz, 6H, Me), 2.07 (m, 2H, CH<sub>2</sub>), 2.76 (m, 4H, CH<sub>2</sub>), 2.79 (m, 2H, CH<sub>2</sub>), 4.15 (q, 4H, OCH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.16 (s, Me), 36.31 (s, CH<sub>2</sub>), 36.75 (pseudo-t,  $\Sigma J$ (C−P) = 18.1 Hz, CH<sub>2</sub>-P), 61.56 (s, OCH<sub>2</sub>), 170.21 (pseudo-t,  $\Sigma J$ (C−P) = 19.0 Hz, CO<sub>2</sub>), 195.98 (CO), 197.66 (CO). The presence of only two CO resonances indicates some fluxionality of the carbonyls.

Synthesis of 7-Phosphanorbornadiene (1f). A solution of 1-(1-methyl-2-pyrrolyl)-3,4-dimethylphosphole<sup>16</sup> 1-(1-methyl-2-pyrrolyl)-3,4-dimethylphosphole<sup>16</sup> pentacarbonyltung-sten complex ( $\delta^{31}P(CDCl_3)$  –15.3 ppm, <sup>1</sup>J(<sup>31</sup>P–<sup>183</sup>W) = 212.4 Hz) (1.6 g, 3 mmol) and dimethyl acetylenedicarboxylate (1.4 mL, 11 mmol) in toluene (1.5 mL) was heated at 75 °C for three nights. After evaporation, the organic residue was chromatographed on silica gel with hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:3) as the eluent. Yield of 1f: 1.1 g (60%). <sup>31</sup>P NMR  $(CDCl_3): \delta 194.2 \text{ ppm}, {}^{1}J({}^{31}P - {}^{183}W) = 242.7 \text{ Hz}. {}^{1}H \text{ NMR} (CDCl_3): \delta$ 2.00, 2.01 (s, 6H, Me), 3.60, 3.70, 3.80 (m, 11H, N-Me, OMe, bridge CH), 6.14 (m, 2H, CH=CHN, =CH-N), 6.62 (d, <sup>1</sup>H, NCCH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 16.20 (s, Me), 35.32 (s, Me-N), 52.46 (s, OMe), 59.07  $(d, {}^{1}J(C-P) = 25.2 \text{ Hz}, \text{CH-P}), 62.11 (d, {}^{1}J(C-P) = 15.2 \text{ Hz}, \text{CH-P}),$ 108.64 (d, J(C-P) = 7.4 Hz, =H pyr), 115.75 (d, J(C-P) = 9.6 Hz, CHpyr), 126.63 (s, CH-pyr), 131.85 (d,  ${}^{1}J(C-P) = 22.9$  Hz, P-C-N), 137.11 (d,  ${}^{2}J(C-P) = 17.1 \text{ Hz}$ , Me-<u>C</u>=), 137.85 (d,  ${}^{2}J(C-P) = 18.1 \text{ Hz}$ , Me-<u>C</u>=), 143.55 (s, =<u>C</u>-CO<sub>2</sub>Me), 146.49 (s, =<u>C</u>-CO<sub>2</sub>Me), 164.37 (s, COMe), 165.72 (s, COMe), 195.81 (d,  ${}^{2}J(C-P) = 6.6$  Hz, *cis* CO), 198.75 (d,  ${}^{2}J(C-P) = 26.7$  Hz, trans CO). The two sides of the phosphanorbornadiene appear to be inequivalent. This is probably due to the blocked rotation of the pyrrolyl substituent due to the NMe group.

Synthesis of Diphosphene Complex 6. A solution of 1f (0.65 g, 1 mmol) and CuCl (0.06 g) in toluene (5 mL) was heated at 60 °C for 6 h under monitoring by <sup>31</sup>P NMR. The solvent was removed under high vacuum, and the compound was chromatographed on silica gel with hexane/CH<sub>2</sub>Cl<sub>2</sub> (2:1) as the eluent: 0.095 g of 6 was isolated as redbrown crystals (20% yield). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –38.3 ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  4.21 (s, 6H, NMe), 6.13 (m, 2H, H $\beta$ ), 6.47 (m, 2H, H $\beta$ ), 6.96 (m, 2H, H $\alpha$ ). Exact mass: calcd for C<sub>20</sub>H<sub>11</sub>N<sub>2</sub>O<sub>10</sub>P<sub>2</sub>W <sub>2</sub> (M – W(CO)<sub>5</sub> – H) 868.9037; found 868.9039. Single crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub> at –20 °C.

**Synthesis of 7-Phosphanorbornadiene (1g).** A solution of 1-(2-thienyl)-3,4-dimethylphosphole<sup>17</sup> pentacarbonyltungsten complex  $(\delta^{31}P(CDCl_3) - 5.1 \text{ ppm}, {}^{1}J({}^{31}P^{-183}W) = 221.0 \text{ Hz})$  (1.6 g, 3 mmol) and dimethyl acetylenedicarboxylate (1.6 mL, 12 mmol) in toluene (2 mL) was heated at 75 °C for three nights. After evaporation, the organic residue was chromatographed on silica gel with hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:1) as the eluent. Yield of **1g**: 1.0 g (50%). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  2.25 (s, 6H, Me), 3.68 (d, {}^{2}J(H-P) = 2.72 \text{ Hz}, 2H, CH-P), 3.83 (s, 6H, OMe), 7.02-7.44 (m, 3H, CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  15.79 (s, Me), 52.95 (s, OMe), 61.34 (d, {}^{1}J(C-P) = 20.0 \text{ Hz}, CH-P), 127.44 (d, J(C-P) = 7.6 \text{ Hz}, Th=CH), 129.16 (d, {}^{1}J(C-P) = 62.3 \text{ Hz}, Th C-P), 129.95 (s, Th =CH), 132.25 (d, J(C-P) = 6.7 \text{ Hz}, Th=CH), 138.28 (d, {}^{2}J(C-P) = 18.1 \text{ Hz}, =C-Me), 145.47 (d, {}^{2}J(C-P) = 4.8 \text{ Hz}, =C-CO\_2Me), 164.64 (s, COMe), 195.80 (d, {}^{2}J(C-P) = 6.7 \text{ Hz}, cis CO), 198.66 (d, {}^{2}J(C-P) = 26.7 \text{ Hz}, trans CO).

Synthesis of Diphosphene Complex 7. Same as for 6. Eluent hexane/CH<sub>2</sub>Cl<sub>2</sub> (4:1); 0.09 g of 7 was isolated as red-brown crystals (20% yield). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  – 36.1 ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 

7.17 (m, 2H, H $\beta$ ), 7.46 (m, 2H, H $\beta$ ), 7.67 (m, 2H, H $\alpha$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  128.79, 133.60, 137.70 (s, =CH), 140.36 (pseudo t, =C), 190.22 (s,  $\pi$  WCO, fluxional), 195.99 (s, *cis* CO), 198.54 (pseudo t, *trans* CO). Exact mass: calcd for C<sub>18</sub>H<sub>6</sub>O<sub>10</sub>P<sub>2</sub>S<sub>2</sub>W<sub>2</sub> (M – W(CO)<sub>5</sub> – 2H) 873.7941; found 873.7938. Single crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub>.

## ASSOCIATED CONTENT

**Supporting Information.** X-ray crystal structure analyses of compounds **3**, **6**, and **7**. Computational details for **7**. This material is available free of charge via the Internet at http://pubs. acs.org.

#### AUTHOR INFORMATION

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