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# Stepwise Building of Polyphosphirene Chains

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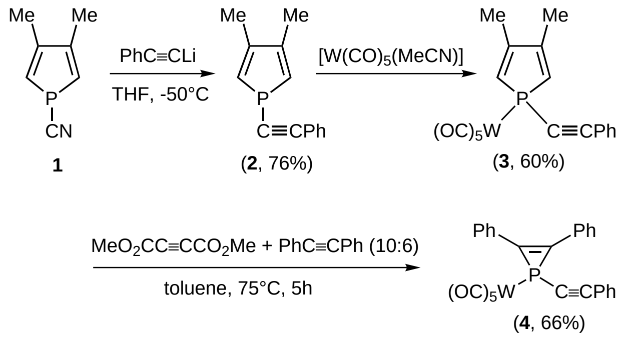
As a result of its very peculiar structural and electronic properties, the phosphirene ring occupies a special niche in carbon–phosphorus heterocyclic chemistry.[1] Whereas the foundations of its chemistry are now well established, almost nothing is known about oligomeric or macrocyclic molecules containing several phosphirene units. Recently, both 2,2′-biphosphirenes[2] and the related 2,2′-bisphosphiranes[3] have been described, but their syntheses cannot by easily extrapolated to yield higher oligomers. Herein, we wish to present an iterative approach which opens a route to a new class of polyphosphirenes.

Our initial idea was to synthesize a 1-alkynylphosphirene derivative and to investigate the reactivity of its C≡C triple bond toward terminal phosphinidene complexes. For this purpose, we needed to prepare an alkynylphosphinidene precursor. Accordingly, we first synthesized the 1-alkynylphosphole **2** and the corresponding P–W(CO)$_5$ complex **3** from the 1-cyanophosphole **1**.[4] Fearing a [P+C≡C] self-condensation of the alkynylphosphinidene intermediate, we then decided to combine the synthesis of the 7-phosphanorbornadiene precursor[5] with its generation and trapping by a reactive alkyne such as diphenylacetylene (tolan).[6] On that basis, **3** was allowed to react with a 10:6 mixture of dimethyl acetylenedicarboxylate and tolan. Tolan proved to compete efficiently with the self-condensation of the phosphinidene intermediate and the desired 1-alkynylphosphirene complex **4** was obtained in satisfactory yield (Scheme 1).



Scheme 1. Synthesis of a 1-alkynylphosphirene complex.

The C≡C triple bond of **4** is highly hindered by the phosphirenyl substituent, nevertheless, a typical terminal phosphinidene complex such as [PhPW(CO)$_5$] readily cycloadds to it to give the 1,2′-biphosphirene **6** (Scheme 2).

The $^{31}$P NMR spectrum of **6** confirms the presence of the two phosphirene rings: $\delta(^{31}P) = -186.5$ (P1), $-142.6$ (P2),

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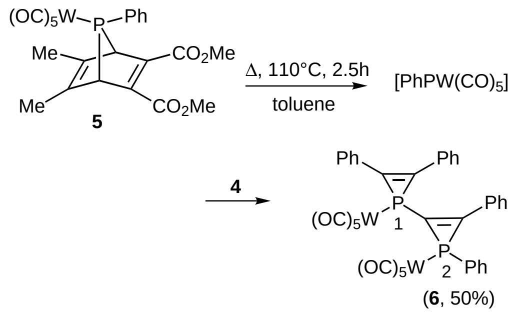
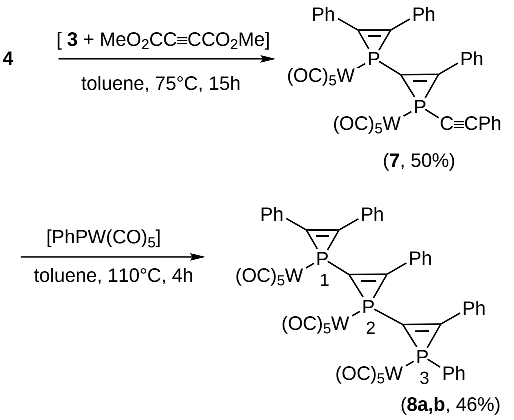


Scheme 2. Synthesis of a 1,2′-biphosphirene complex.

$^2J_{P,P} = 11$ Hz. At this point, it is interesting to recall that, in many cases, terminal phosphinidene complexes insert into the ring P–C2 bond of 2-alkynylphosphirenes, thus preventing the formation of the expected 2,2′-biphosphirenes.[7] Clearly, a 2-alkynyl substituent weakens the ring P–C bonds, whereas a 1-alkynyl substituent does not. This success led us to attempt the condensation of **4** with the system [**3**+MeO$_2$C-C≡C-CO$_2$Me], the synthetic equivalent of the 7-phosphanorbornadiene precursor of [PhC≡CPW(CO)$_5$] employed above. This new experiment was again successful (Scheme 3).



Scheme 3. Synthesis of a triphosphirene complex.

The $^{31}$P NMR parameters of **7** are very similar to those of **6**, except that the two phosphorus nuclei resonate at almost the same frequency: $\delta(^{31}P) = -184.0$ and $-187.1$, $^2J_{P,P} = 16$ Hz. Noteworthy is that **7** was formed as a minor by-product in the synthesis of **4**. The availability of **7** gave us the possibility to check the validity of our iterative approach. By using the method which converts **4** into **6** we could transform **7** into the triphosphirene **8** (Scheme 3).

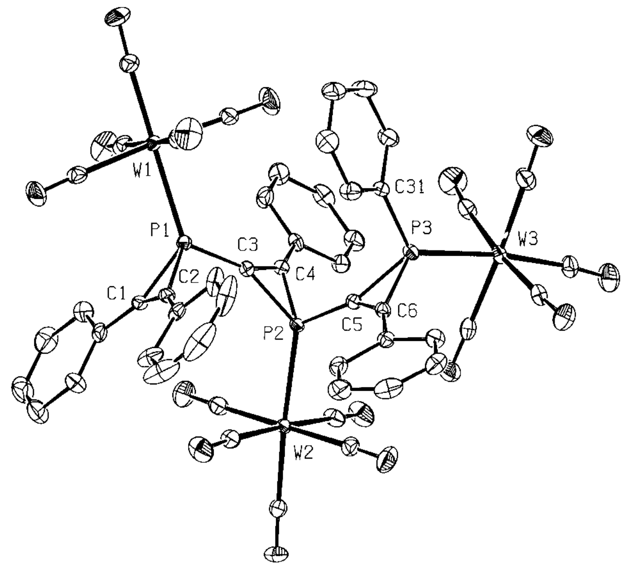


Figure 1. Structure of **8a**. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: P1-C1 1.793(5), P1-C2 1.781(5), P1-C3 1.804(5), P1-W1 2.473(1), C1-C2 1.324(7), P2-C3 1.809(5), P2-C4 1.803(5), P2-C5 1.788(5), C3-C4 1.326(6), P2-W2 2.469(1), P3-C5 1.818(4), P3-C6 1.796(5), P3-C31 1.818(5), P3-W3 2.488(1), C5-C6 1.321(7); C1-P1-C2 43.5(2), C1-P1-C3 103.5(2), C1-P1-W1 125.9(2), C2-P1-C3 104.6(2), C2-P1-W1 124.8(2), C3-P2-C4 43.1(2), C3-P2-C5 106.7(2), C3-P2-W2 129.7(1), C4-P2-C5 105.4(2), C4-P2-W2 127.5(2), C5-P3-C6 42.9(2), C5-P3-C31 106.5(2), C5-P3-W3 124.8(1), C6-P3-C31 106.5(2), C6-P3-W3 124.9(2).

The triphosphirene **8** was formed as a 1:1 mixture of two diastereomers showing characteristic $^{31}$P NMR spectra: **8a**: $\delta(^{31}P) = -188.5$ (P1), $-169.8$ (P2), $-139.3$ (P3), $^2J_{P1,P2} = 4$ Hz, $^2J_{P2,P3} = 14$ Hz; **8b**: $\delta(^{31}P) = -187.0$ (P1), $-173.8$ (P2), $-139.0$ (P3), $^2J_{P1,P2} = 9$ Hz, $^2J_{P2,P3} = 21$ Hz. These two isomers were difficult to separate by standard chromatographic procedures. However, a slow recrystallization in hexane/toluene yielded pure crystals of **8a**. The X-ray data are presented in (Figure 1).[8] The structural parameters of the first phosphirene ring (P1) are very close to those of the prototypical 1,2,3-triphenylphosphirene complex [(PhC)$_2$PhPW(CO)$_5$].[6] Both the second (P2) and third rings (P3) show elongated P–C ring bonds. This might be the result of steric compression, which tends to increase the distances between the bulky P–W units. However, as we have seen, this weakening of the ring P–C bonds does not interfere with the [P+C≡C] condensation process. This process is both original and useful, and appears to have no equivalent in the related silirene field.[9] Finally, the formation of a small amount of **7** during the synthesis of **4** indicates that the possibility exists to create longer oligophosphirene chains using a one-pot procedure. Since various techniques exist to obtain free phosphirenes from their complexes,[10] an interesting coordination chemistry can be built around such chains.

## *Experimental Section*

**2**, **3**: A solution of the lithium salt of phenylacetylene (1.3 equiv) in diethyl ether was added at $-50$ °C to a solution of 1-cyano-3,4-dimethylphosphole (**1**)[4] (7 g, $5 \times 10^{-2}$ mol) in THF (150 mL). The mixture was then stirred for 0.5 h at RT. After evaporation of the solvent, the residue was purified by chromatography on silica gel eluting with hexane/dichloromethane (4/1) to yield **2** (8 g, 76%): $^{31}$P NMR (81 MHz, THF): $\delta = -40.6$. Complex **3**: $^{31}$P NMR (CDCl$_3$): $\delta = -25.3$ ($^1J(P,W) = 219.7$ Hz); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 17.7$ (d, $^3J(C,P) = 13.3$ Hz; Me), 77.9 (d, $^1J(C,P) = 76.0$ Hz; P-*C*≡C), 108.1 (d, $^2J(C,P) = 13.8$ Hz, P-C≡*C*), 121.4 (s; *Ph*C≡C, C$_{ipso}$), 127.0 (d, $^1J(C,P) = 50.2$ Hz; CH-P), 152.1 (d, $^2J(C,P) = 12.2$ Hz; Me-*C*=), 196.2 (d, $^2J(C,P) = 7.5$ Hz; *cis*-CO), 199.5 (d, $^2J(C,P) = 18.5$ Hz; *trans*-CO); $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 2.19$ (s; Me), 6.36 (d, $^2J(H,P) = 38.1$ Hz; CH-P); MS ($^{184}$W): *m/z* (%): 536 (10) [$M^+$], 396 (100) [$M^+ - 5$CO]; elemental analysis (%) calcd for C$_{18}$H$_{13}$O$_5$PW: C 42.53, H 2.42; found: C 42.78; H, 2.46.

**4**: A solution of **3** (2.15 g, 5 mmol), dimethyl acetylenedicarboxylate (1.25 mL, 10 mmol) and diphenylacetylene (1.1 g, 6.25 mmol) in toluene (10 mL) was heated at 70–75 °C for 5 h. After evaporation of the solvent, the residue was purified by column chromatography eluting with hexane/

dichloromethane (10/1). Phosphirene complex **4** was isolated as yellow crystals (2 g, 66 %). $^{31}$P NMR (81 MHz, $CDCl_3$): $\delta = -201.0$ ($^1J$(P,W) = 294.9 Hz); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta = 89.3$ (d, $^1J$(C,P) = 18.8 Hz; P-*C*≡C), 93.9 (d, $^2J$(C,P) = 5.8 Hz; P-C≡*C*), 120.9 (s; C≡C-*Ph*, $C_{ipso}$), 195.9 (d, $^2J$(C,P) = 9.1 Hz; *cis*-CO), 198.4 (d, $^2J$(C,P) = 34.8 Hz; *trans*-CO); MS: *m/z* (%): 634 (6) [$M^+$], 494 (100) [$M^+ - 5$CO]; elemental analysis (%) calcd for $C_{27}H_{15}O_5PW$: C 51.10, H 2.36; found: C 51.48, H, 2.42.

**6**: Biphosphirene **6** was isolated as light yellow crystals by chromatography with hexane/dichloromethane (4/1). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta = 137.4$ (d, $^1J$(C,P) = 5.4 Hz; $C_{ipso}$, Ph-P), 143.2 (pseudo t, $^1J$(C,P) $\sim$ $^2J$(C,P) = 13.6 Hz; Ph-*C*(P)=C-P); MS: highest mass 785 [$M^+ - 10$CO $-$ H].

**7**: Biphosphirene **7** was isolated as a yellow powder by chromatography with hexane/dichloromethane (10/1). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta = 89.5$ (d, $^1J$(C,P) = 23.6 Hz; P-*C*≡C), 95.2 (d, $^2J$(C,P) = 6.5 Hz, P-C≡*C*), 120.5 (s; C≡C-*Ph*, $C_{ipso}$), 144.6 (pseudo t, $^1J$(C,P) $\sim$ $^2J$(C,P) = 15 Hz; Ph*C*(P)=C-P); MS: highest mass 632; elemental analysis (%) calcd for $C_{40}H_{20}O_{10}P_2W_2$: C 44.07, H 1.85; found: C 44.03, H 1.75.

**8**: Triphosphirene **8** was isolated as light yellow crystals by chromatography with hexane/dichloromethane (4/1); elemental analysis calcd (%) calcd for $C_{51}H_{25}O_{15}P_3W_3$: C 40.24, H 1.66; found: C 39.98, H 1.56.

Received: November 9, 2000 [Z16063]

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[8] X-ray structure data for **8a**: crystal dimensions 0.40 × 0.16 × 0.16, monoclinic, $P2_1/n$, $a = 12.467(5)$, b = 18.565(5), $c = 22.346(5)$ Å, $\beta = 91.220(5)^\circ$, $V = 5171(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.955$ g cm$^{-3}$, $\mu = 6.817$ cm$^{-1}$, $F(000) = 2872$, $\theta_{max} = 30.03^\circ$, *hkl* ranges: $-13$–17; $-21$–26; $-31$–25, 33543 data collected, 15050 unique data ($R_{int} = 0.0699$), 12185 data with $I > 2\sigma(I)$, 649 parameters refined, GOF($F^2$) = 1.008, final $R$ indices: $R1 = 0.0414$, $wR2 = 0.1095$; max/min residual electron density 2.082(.251)/$-3.219$(.251) e Å$^{-3}$. Data collection was with a Nonius Kappa CCD diffractometer, $\phi$ and $\omega$ scans, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 150$ K, structure solution with SIR97,refinement against F2 (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151986. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# Steam-Stable MSU-S Aluminosilicate Mesostructures Assembled from Zeolite ZSM-5 and Zeolite Beta Seeds**

Yu Liu, Wenzhong Zhang, and Thomas J. Pinnavaia*

The structural integrity of Al-MCM-41 and related mesoporous aluminosilicate molecular sieves has been significantly improved in recent years through direct assembly and post-synthesis treatment methods.[1] Nevertheless, the hydrothermal instability and mild acidity remain inferior to conventional zeolites and limit potential applications in petroleum refining and fine chemicals synthesis.[2] One might expect to improve both the stability and acidity of these materials if zeolite-like order could be introduced into the pore walls. One approach, first introduced by van Bekkum and co-workers,[3] is to transform the preassembled walls of Al-MCM-41 into zeolitic structures by post-assembly treatment with a microporous zeolite structure director, such as tetrapropylammonium cations. More recent studies have shown that the walls of the mesostructure can indeed be converted to a zeolitic product, but the microporous zeolite phase (ZSM-5) is segregated from the mesostructure, giving rise to ZSM-5/MCM-41 composites.[4] These composites exhibited an enhancement in acidity for hydrocarbon cracking in comparison to mechanical mixtures of ZSM-5 and MCM-41 and an improvement in steam stability for purely siliceous composites.[4c]

We recently reported an alternative approach to more acidic and hydrothermally stable mesostructures based on the direct assembly of nanoclustered aluminosilicate precursors that normally nucleate zeolite type Y crystallization.[5] These protozeolitic species, known as "zeolite seeds", promote zeolite nucleation by adopting $AlO_4$ and $SiO_4$ connectivities that resemble the secondary building units of a crystalline zeolite.[6] The assembly of the $Na^+$-nucleated zeolite type Y (faujasitic) seeds under hydrothermal conditions in the presence of cetyltrimethylammonium ions afforded hexagonal MSU-S mesostructures with Si/Al ratios in the range 1.6:1 to 10:1. The replacement of $Na^+$ by $NH_4^+$ ions in the as-made mesostructure, followed by calcination in the presence of the surfactant, afforded exceptionally acidic and steam-stable mesostructures. However, the steam stability was enhanced by structure-stabilizing occlusions of carbon that formed during the calcination process. That is, the steam stability at 800 °C was in part a consequence of the exceptional acidity of a framework that formed structure-stabilizing carbon, and not entirely a result of an intrinsically stable framework.

Here we also make use of protozeolitic nanoclusters to form exceptionally acidic and steam-stable aluminosilicate

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[**] The partial support of this research by the National Science Foundation through CRG grant 99-03706 is gratefully acknowledged.