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Tetraphosphabenzenes Obtained via a Triphosphacyclobutadiene Intermediate**

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The ability to replace “RC” units in organic motifs by the isolobal phosphorus atom has led to phosphorus being dubbed the “carbon copy.”[1] Yet while the all-phosphorus analogs of benzene and cyclobutadiene (the epitomes of aromaticity and anti-aromaticity) have been considered theoretically,[2-5] they remain elusive. What do exist are a few examples of reduced P₄ and P₂ ligands complexed to one or more metal centers.[6-8] Diphosphacyclobutadiene and valence isomers of triphosphabenzenes have been accessed through metal-mediated oligomerization of phosphaalkynes,[10-12] and two related reactions generate triphosphacyclobutadiene ligands π-complexed to reducing metal centers.[13, 14] There is also one example of a highly distorted P₄(CBu)₂ ligand complexed between two Rh centers,[15] and a diradical valence isomer of a tetraphosphabenzene has been reported to contain multiple 1e⁻ bonds.[16] Exploiting the chemistry of P₂-derived cyclo-P₃ complexes,[17] we now describe neutral triphosphacyclobutadiene intermediates and isomers of tetraphosphabenzenes that are stabilized only by mild W(CO)₅ substituents.[18]

Acylation of the W(CO)₅-coordinated cyclo-P₃ complex [(OC)₅W]₂P[Nb(N[CH₂Bu]Ar)₃] with either pivaloyl chloride or 1-adamantancarbonyl chloride affords the triphosphiren complexes [(OC)₅W]₂RC(O)P[Nb(N[CH₂Bu]Ar)₃], 1[R = 3,5-Me₂C₆H₃, R = 1-adamantyl, tert-butyl].[19] These complexes are thermally unstable toward deoxygenation of the acyl triphosphiren ligand to form ONb(N[CH₂Bu]Ar)₂, 2, and red precipitate of empirical formula RCP₃[W(CO)₅] (Scheme 1). As a monomer, the species RCP₃[W(CO)₅], 3[R], could possess an RCP₃ core with either tetraedrane or butadiene-like structure: the latter structure would be one RC unit away from the elusive planar P₄.

The poor solubility properties of the precipitate generated during the formation of 2 from 1[R] proved a hindrance to identifying the phosphorus-containing products. However, the tert-butyl variant 1[R]ₜₜₜ produces a coproduct with increased solubility in various solvents, allowing for a more thorough characterization. ³¹P NMR data acquired on the crude reaction mixture formed by stirring 1[R] for several hours at 22 °C indicated that a mixture of phosphorus-containing products had formed, though one major product was present. X-ray diffraction analyses performed on several small, red-orange crystals that were grown from CH₂Cl₂ solutions of the product mixture revealed three structurally distinct isomers, 4a-4c.[19] All of these compounds were dimers of the 'BuCP₃[W(CO)₅] unit and their structures, depicted in Chart 1, can be compared to those known for phosphaalkyne tetramers.[20, 21] One fraction was isolated in ca. 30% yield as a red powder that was insoluble in Et₂O and showed sparing solubility in CH₂Cl₂, and this red powder was subjected to an X-ray powder diffraction study. Powder diffraction patterns for 4a-4c were simulated based on the single-crystal data and these patterns were compared to the experimental patterns for the isolated compound. While two of the simulations showed a poor match to experiment, the simulated pattern for 4a was in very good agreement with the diffraction pattern of the isolated powder, and this match is shown in Figure 1 (see Figure S2 in Supporting Information for simulated patterns of 4b and 4c). Comparing the ³¹P NMR spectrum of the crude reaction mixture to that of isolated 4a further confirmed this species as the major product. Additionally, the complex ³¹P NMR splitting pattern was successfully simulated using the connectivity determined by X-ray diffraction (Figure S4, Supporting Information).[22] While the structural identity of the product originating from the fragmentation of 1[R]ₜₜₜ could
not be definitively confirmed, based on the data available from 1Bu it is assigned as one or more isomers of the dimer [AdCP,P[W(CO)3]2].

The structures of 4a-4c suggest the intermediacy of the triphosphacyclobutadiene molecule 3#, which is depicted as one of several possible linkage isomers in Scheme 1. To probe the chemistry of such an intermediate we attempted to trap the reactive species 3#d with suitable substrates. The platinum complex (Ph3P)2Pt(C6H5) has been used successfully to trap units of P-P unsaturation with simple displacement of the ethylene molecule, but this was not the case in its reaction with intermediate 3#d.[23-27] Instead, a product incorporating the ethylene unit into the Cp2 framework, (Ph3P)2OCPh2[P(C6H5)]W(CO)3, 5, was isolated in low yield and characterized by NMR spectroscopy and an X-ray crystal structure determination.[28]

Seeking to trap the putative triphosphacyclobutadiene intermediate in a simple one-to-one reaction, we employed organic dienes that are known to react via [4+2] cycloadditions with diphosphenes.[29-31] When 1Bu was allowed to fragment in the presence of either 1,3-cyclohexadiene or 2,3-dimethylbutadiene, mixtures of products were observed by 31P NMR spectroscopy. Spiro[2.4]hepta-4,6-diene is known to be a particularly active Diels-Alder reagent,[32] and when 1 was allowed to fragment in the presence of this diene, one major product was observed by 31P NMR spectroscopy. This product, C6H5(P,CAd)[W(CO)3]2, 6, has resonances consistent with the desired trapping of the diphosphene functional group while the phosphalkene moiety (31P NMR δ = 295 ppm) remains intact. Extracting away co-product 2 with n-pentane and recrystallization of the remaining fraction from toluene affords compound 6.[33] A single-crystal X-ray diffraction study revealed the stereochemistry of the product to be consistent with the prediction arrived at through consideration of steric and secondary orbital interactions: the π-bonds of the diene/alkene interact with the 4-membered ring while the sterically protruding spiro group aligns opposite the ring (Figure 2).[18] This product demonstrates clean diphosphene-like reactivity for the triphosphacyclobutadiene intermediate.

The dimerization reactions of triphosphacyclobutadiene 3# that are observed when no trap is present in solution suggest that this intermediate can participate as both a dieneophile and as a diene partner in [4+2] cycloaddition reactions, much as does cyclobutadiene itself.[18, 34, 35] If this is the case then it should be possible to trap 3# with a molecule containing a reactive π-bond. 1-Adamantylphosphaalkyne was employed in this role because of its potential to yield the Dewar isomer of tetraphosphabenzenes as a trapping product.[32, 36] Gentle thermolysis of 1Ad and AdCP for 4 h at 30 ºC in benzene affords one major product as assayed by 31P NMR spectroscopy. This product exhibits two coupled resonances in the 31P NMR spectrum at 248 ppm and −13 ppm. These data are consistent with the C2-symmetric tetraphosphadewarbenzene, (AdC)2P,[W(CO)3]2, 7, Figure 3a. This structure was confirmed by a single crystal X-ray diffraction study on an orange crystal of 7 grown from benzene solution and is depicted in Figure 3b.

Upon prolonged light-exposure of solutions of 7, isomerization takes place to provide 8, which at 20 ºC displays two broad 31P NMR resonances at +19 and −108 ppm. This conversion can be accelerated by photolysis of 7 in THF with high intensity broadband light (low-pressure Hg lamps) to afford 8 in less than 20 min. An X-ray diffraction study performed on a crystals grown from mixtures of 7 that had been exposed to ambient light revealed a benzvalene structure with a diphosphene moiety η4-coordinated to one W(CO)3 unit and η1-coordinated to the second W(CO)3, Figure 3c. The two broad signals in the 31P NMR spectrum of 8 can be attributed to a dynamic process in which the exchange of W(CO)3 units between faces and termini of the diphosphene can equate pairs of P atoms. Upon cooling to −100 ºC these two resonances resolve into four (δ = 37 (d), 10 (br), −21 (d), −232 (br) ppm) with a doublet pair displaying strong coupling (Jpp = 450 Hz) that is consistent with P-P multiple bonding. This product can be seen as arising from intramolecular [2+2] cycloaddition of the phosphahkaene moieties of 7 followed by radical rearrangements, and is consistent with the “rule of five.”[37] Such rearrangements have also been previously observed for monophosphadewarbenzenes.[38] The Z-diphosphene of 8 shows a short P-P distance of 2.1047(15) Å and acute angles of 96.93(14)º and 95.16(14)º. It is remarkable that such a species is stabilized by only one π-complexation and one σ-complexation from the relatively mild W(CO)3.[39, 40]

To investigate the mechanism by which 2 and 3#d are generated from 1#d, the kinetics of this reaction were monitored by both 1H and 31P NMR spectroscopy. The decay of starting material 1 was found to follow clean first-order kinetics, but the growth in of an intermediate was found to accompany production of 2. This intermediate, 1’, displays three 31P environments and two Bu3Sn ligands in its NMR spectra. The 31P resonances are a triplet (Jpp = 175 Hz) at −4 ppm and two broad resonances at −28 and −37 ppm. By introducing a 13C label at the acyl carbon, C1, it was determined that in 1’, C1 is attached only to the one phosphorus with a chemical shift of −4 ppm (JCP = 108 Hz). Additionally, the 13C chemical shift for C1 in 1’ was found to shift downfield by 46 ppm relative to the starting material (from 213 ppm to 259 ppm), consistent with Lewis acid activation of the carbonyl group,[41] leading to the proposed structure for 1’ that is shown in Scheme 2.

From 1’ one can envision attack by one of the niobium bound phosphorus atoms on the Lewis acid-activated carbonyl to give 1” with a structure that is poised to eliminate the triphosphacyclobutadiene 3#d upon formation of 2 via...
a 6e⁻ rearrangement with formation of the strong niobium-oxo bond. Importantly, the same intermediate 1’ was observed in the presence of either AdCP or spirollo[2.4]hepta-4,6-diene.

The decay of starting material 1’ follows first-order exponential behavior, but the ratios of species 1’², 1’, and 2 did not fit the simple kinetic model shown in Scheme 3a. Rather, the data were better suited by a model where there is a competitive process that proceeds without an observable intermediate with a rate constant \( k_1' \approx k_1 \), Scheme 3b (see Supporting Information for details). It is possible that the coordination sites of the two W(CO)₅ units coupled to subtle conformational differences leads to two rates of rearrangement from structures analogous to 1’.

Herein we have described the first reactivity of a triphosphacyclobutadiene intermediate. The reactions observed suggest that this species can dimerize or serve as either a reactive Z-diphosphene or as a 4π electron cycloaddition partner, depending on the added reagents present. Such reactivity has led to the synthesis of the most phosphorus-rich congeners of benzene isomers reported, the Dewar and benzvalene isomers of tetraphosphabenzenes. This chemistry was accessed by exploiting the thermodynamic driving force of strong niobium oxo bond formation to offset the energetic costs of high-energy small molecule transient generation.\(^{[30, 42, 43]}\)

**Experimental Section**

**General:** All manipulations were carried out under anhydrous and oxygen-free conditions. Full synthetic protocols and spectroscopic data for all compounds and kinetics experiments are presented in the Supporting Information. Details of the X-ray structure determinations are presented in the Supporting Information, Table 1S, and cif files available from the CCDC under deposition numbers 700883-700887.\(^{[46]}\)

6: Solid red 1’\(^{[46]}\) (195 mg, 0.125 mmol, 1 eq) was dissolved in 2 g of a 14 wt% THF solution of spirollo[2.4]hepta-4,6-diene (280 mg, 24 eq) and the solution was then diluted with THF to a total volume of 5 mL. The solution was stirred at 22 °C for 5 h, after which the solution was bright yellow in color. The mixture was filtered through Celite and the filtrate was concentrated to dryness under dynamic vacuum. The resulting residue was suspended in pentane (4 mL) and cooled to −35 °C for 24 h to precipitate the product as a bright yellow powder, which was collected atop a sintered glass frit and washed with cold pentane (65 mg, 53% yield). \(^{31}P\) NMR (CD₃CN, 20 °C, 121.5 MHz): \( \delta = 295.4 \) (dd, \( J_{PP} = 125 \) Hz, \( \gamma J_{PP} = 28 \) Hz, \( \delta J_{PP} = 240 \) Hz, \( \gamma C = P = \gamma P = \delta C = P = \delta P \)), 3.0 (dd, \( J_{PP} = 156 \) Hz, \( \gamma J_{PP} = 28 \) Hz, \( \delta C = P = \gamma P = \delta C = P = \delta P \)), −24.9 (dd, \( J_{PP} = 156 \) Hz, \( \gamma J_{PP} = 125 \) Hz, \( \delta J_{PP} = 210 \) Hz, \( \gamma C = P = \gamma P = \delta C = P = \delta P \)) ppm.

7: Solid red 1’\(^{[46]}\) (360 mg, 0.230 mmol, 1 eq) and solid colorless AdCP (83 mg, 0.46 mmol, 2 eq) were mixed and then dissolved in benzene (10 mL) to give a deep red solution. The solution was heated to 35 °C for 3.5 h, after which the orange mixture was filtered through Celite and evaporated to dryness. Niobium oxide 2 was extracted from the orange residue with ca. 10 mL of pentane and the remaining solid was collected on a frit and then washed with 3 mL of pentane and dried in vacuo to yield 7 as an orange powder (130 mg, 53% yield). \(^{31}P\) NMR (CD₃CN, 20 °C, 202.5 MHz): \( \delta = 248.3 \) (m, \( C = P, 2P \)), −13.3 (m, \( P-P, 2P \)) ppm.

**References**

It is noteworthy, however, that Lewis acids have been reported to effect the reaction mechanisms and product distributions of reactive diphosphacyclobutadiene intermediates and the two W(CO)₅ moieties may have similar effects: C. Fish, M. Green, R. J. Kilby, J. E. McGrady, D. A. Pantazis, C. A. Russell, *Dalton Trans.* 2008, 3753-3758.

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Legends

**Scheme 1.** O-atom transfer from an acyl triphosphirene ligand to the Nb center liberates the putative triphosphacyclobutadiene intermediate, 3°. One of several possible linkage isomers of 3° is drawn.

**Chart 1.** Structures of identified dimerization products 4a-4c.
Figure 1. X-ray powder diffraction of 4a confirmed its structural identity by comparison of simulated and experimental data.

Figure 2. Complex 6 is shown with 50% probability ellipsoids (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): P1-C40 1.690(3); P1-P2 2.1969(11); P2-P3 2.2173(11); P3-C40 1.843(3); P1-W2 2.4515(8); P2-W1 2.5044(8); C40-P1-P2 89.02(11); P1-P2-P3 79.82(4); C40-P3-P2 84.66(11); P1-C40-P3 106.48(17).

Figure 3. (a) Synthesis of two valence isomers of tetraphosphabenzene supported by 2 equiv of W(CO)5. (b) and (c) Structures of 7 and 8 with 50% probability thermal ellipsoids (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): 7: P1-C1 1.71(1); P1-P2 2.197(5); P2-P3 2.220(5); P3-C1 1.83(1); P4-P3-C1 101.4(5); P1-C1-P3 104.8(6); P2-P1-C1 90.0(5). 8: P1-P2 2.1047(15); P3-P4 2.1559(17); W(1)-P(1) 2.6269(11); W(1)-P(2) 2.6704(10); P1-W2 2.5807(11); C3-P3-C4 82.27(19); P3-C4-P2 70.15(15); C4-P1-P2 96.93(14); C3-P2-P1 95.16(14).

Scheme 2. Proposed mechanism for formation of transient triphosphacyclobutadiene 3\textsuperscript{2+4} proceeding through the observed intermediate 1'.

Scheme 3. Kinetic scheme (b) provides a better fit to the time-dependent concentrations of 1\textsuperscript{2+4}, 1' and 2 than does the simpler model (a).

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The O-atom of an acyl triphosphirene ligand is transferred to the Nb platform upon which it was constructed to liberate the putative triphosphacyclobutadiene intermediate RCP\textsubscript{3}[W(CO)\textsubscript{5}]\textsuperscript{2}. This reactive transient is shown to dimerize and engage in [2+4]-cycloaddition reactions with an organic diene and a phosphaalkyne. The latter reaction serves as a synthesis of the Dewar isomer of a tetraphosphabenzene, which can be converted to a tetraphosphabenzvalene containing a Z-diphosphene.

Keywords: niobium · phosphacyclobutadiene · phosphabenzene · phosphorus · triphosphirene

Scheme 1:

Chart 1:
Figure 1:

Figure 2:

Figure 3:
Scheme 2:

Scheme 3:

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