

# 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.”<sup>[1]</sup> Yet while the all-phosphorus analogs of benzene and cyclobutadiene (the epitomes of aromaticity and anti-aromaticity) have been considered theoretically,<sup>[2-5]</sup> they remain elusive. What do exist are a few examples of reduced P<sub>6</sub> and P<sub>4</sub> ligands complexed to one or more metal centers.<sup>[6-9]</sup> Diphosphacyclobutadiene and valence isomers of triphosphabenzene have been accessed through metal-mediated oligomerization of phosphalkynes,<sup>[10-12]</sup> and two related reactions generate triphosphacyclobutadiene ligands  $\pi$ -complexed to reducing metal centers.<sup>[13, 14]</sup> There is also one example of a highly distorted P<sub>4</sub>(C<sup>t</sup>Bu)<sub>2</sub> ligand complexed between two Rh centers,<sup>[15]</sup> and a diradical valence isomer of a tetraphosphabenzene has been reported to contain multiple 1e<sup>-</sup> bonds.<sup>[16]</sup> Exploiting the chemistry of P<sub>2</sub>-derived *cyclo*-P<sub>3</sub> complexes,<sup>[17]</sup> we now describe neutral triphosphacyclobutadiene intermediates and isomers of tetraphosphabenzene that are stabilized only by mild W(CO)<sub>5</sub> substituents.<sup>[18]</sup>

Acylation of the W(CO)<sub>5</sub>-coordinated *cyclo*-P<sub>3</sub> complex [ $\{(OC)_5W\}_2P_3Nb(N[CH_2^tBu]Ar)_3\}^-$  with either pivaloyl chloride or 1-adamantanecarbonyl chloride affords the triphosphirene complexes [(OC)<sub>5</sub>W]<sub>2</sub>RC(O)P<sub>3</sub>Nb(N[CH<sub>2</sub><sup>t</sup>Bu]Ar)<sub>3</sub>, **1<sup>R</sup>** (Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R = 1-adamantyl, *tert*-butyl).<sup>[17]</sup> These complexes are thermally unstable toward deoxygenation of the acyl triphosphirene ligand to form ONb(N[CH<sub>2</sub><sup>t</sup>Bu]Ar)<sub>3</sub>, **2**, and red precipitate of empirical formula RCP<sub>3</sub>[W(CO)<sub>5</sub>]<sub>2</sub> (Scheme 1). As a monomer, the species RCP<sub>3</sub>[W(CO)<sub>5</sub>]<sub>2</sub>, **3<sup>R</sup>**, could possess an RCP<sub>3</sub> core with either tetrahedrane or butadiene-like structure: the latter structure would be one RC unit away from the elusive planar P<sub>4</sub>!

The poor solubility properties of the precipitate generated during the formation of **2** from **1<sup>Ad</sup>** proved a hindrance to identifying the phosphorus-containing products. However, the *tert*-butyl variant **1<sup>tBu</sup>** produces a coproduct with increased solubility in various solvents, allowing for a more thorough characterization. <sup>31</sup>P NMR data acquired on the crude reaction mixture formed by stirring **1<sup>tBu</sup>** 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 CH<sub>2</sub>Cl<sub>2</sub> solutions of the product mixture revealed three structurally distinct isomers, **4a-4c**.<sup>[19]</sup> All of these compounds were dimers of the <sup>t</sup>BuCP<sub>3</sub>[W(CO)<sub>5</sub>]<sub>2</sub> unit and their structures, depicted in Chart 1, can be compared to those known for phosphalkyne tetramers.<sup>[20, 21]</sup> One fraction was isolated in *ca.* 30% yield as a red powder that was insoluble in Et<sub>2</sub>O and showed sparing solubility in CH<sub>2</sub>Cl<sub>2</sub>, 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 <sup>31</sup>P NMR spectrum of the crude reaction mixture to that of isolated **4a** further confirmed this species as the major product. Additionally, the complex <sup>31</sup>P NMR splitting pattern was successfully simulated using the connectivity determined by X-ray diffraction (Figure S4, Supporting Information).<sup>[22]</sup> While the structural identity of the product originating from the fragmentation of **1<sup>Ad</sup>** could

not be definitively confirmed, based on the data available from  $\mathbf{1}^{tBu}$  it is assigned as one or more isomers of the dimer  $\{\text{AdCP}_3[\text{W}(\text{CO})_5]_2\}_2$ .

The structures of **4a-4c** suggest the intermediacy of the triphosphacyclobutadiene molecule  $\mathbf{3}^R$ , 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  $\mathbf{3}^{Ad}$  with suitable substrates. The platinum complex  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$  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  $\mathbf{3}^{Ad}$ .<sup>[23-27]</sup> Instead, a product incorporating the ethylene unit into the  $\text{CP}_3$  framework,  $(\text{Ph}_3\text{P})(\text{OC})\text{Pt}(\text{P}_3\text{C}(\text{C}_2\text{H}_4)\text{Ad})[\text{W}(\text{CO})_5]_2$ , **5**, was isolated in low yield and characterized by NMR spectroscopy and an X-ray crystal structure determination.<sup>[28]</sup>

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.<sup>[29-31]</sup> When  $\mathbf{1}^{Ad}$  was allowed to fragment in the presence of either 1,3-cyclohexadiene or 2,3-dimethylbutadiene, mixtures of products were observed by  $^{31}\text{P}$  NMR spectroscopy. Spiro[2.4]hepta-4,6-diene is known to be a particularly active Diels-Alder reagent,<sup>[32]</sup> and when **1** was allowed to fragment in the presence of this diene, one major product was observed by  $^{31}\text{P}$  NMR spectroscopy. This product,  $\text{C}_7\text{H}_8(\text{P}_3\text{CAd})[\text{W}(\text{CO})_5]_2$ , **6**, has resonances consistent with the desired trapping of the diphosphene functional group while the phosphalkene moiety ( $^{31}\text{P}$  NMR  $\delta = 295$  ppm) remains intact. Extracting away co-product **2** with *n*-pentane and recrystallization of the remaining fraction from toluene affords compound **6**.<sup>[33]</sup> 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  $\pi$ -bonds of the diene/alkene interact with the 4-membered ring while the sterically protruding spiro group aligns opposite the ring (Figure 2).<sup>[18]</sup> This product demonstrates clean diphosphene-like reactivity for the triphosphacyclobutadiene intermediate.

The dimerization reactions of triphosphacyclobutadiene  $\mathbf{3}^R$  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.<sup>[18, 34, 35]</sup> If this is the case then it should be possible to trap  $\mathbf{3}^R$  with a molecule containing a reactive  $\pi$ -bond. 1-Adamantylphosphaalkyne was employed in this role because of its potential to yield the Dewar isomer of tetraphosphabenzene as a trapping product.<sup>[12, 36]</sup> Gentle thermolysis of  $\mathbf{1}^{Ad}$  and AdCP for 4 h at 30 °C in benzene affords one major product as assayed by  $^{31}\text{P}$  NMR spectroscopy. This product exhibits two coupled resonances in the  $^{31}\text{P}$  NMR spectrum at 248 ppm and -13 ppm. These data are consistent with the  $C_2$ -symmetric tetraphosphadewarbenzene,  $(\text{AdC})_2\text{P}_4[\text{W}(\text{CO})_5]_2$ , **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 °C displays two broad  $^{31}\text{P}$  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  $\eta^2$ -coordinated to one  $\text{W}(\text{CO})_5$  unit and  $\eta^1$ -coordinated to the second  $\text{W}(\text{CO})_5$ , Figure 3c. The two broad signals in the  $^{31}\text{P}$  NMR spectrum of **8** can be attributed to a dynamic process in which the exchange of  $\text{W}(\text{CO})_5$  units between faces and termini of the diphosphene can equate pairs of P atoms. Upon cooling to -100 °C these two resonances resolve into four ( $\delta = 37$  (d), 10 (br), -21 (d), -232 (br) ppm) with a doublet pair displaying strong coupling ( $^1J_{\text{PP}} = 450$  Hz) that is consistent with P-P multiple bonding. This product can be seen as arising from intramolecular [2+2] cycloaddition of the phosphalkene moieties of **7** followed by radical rearrangements, and is consistent with the “rule of five.”<sup>[37]</sup> Such rearrangements have also been previously observed for monophosphadewarbenzenes.<sup>[38]</sup> The *Z*-diphosphene of **8** shows a short P-P distance of 2.1047(15) Å and acute angles of 96.93(14)° and 95.16(14)°. It is remarkable that such a species is stabilized by only one  $\pi$ -complexation and one  $\sigma$ -complexation from the relatively mild  $\text{W}(\text{CO})_5$ .<sup>[39, 40]</sup>

To investigate the mechanism by which **2** and  $\mathbf{3}^{Ad}$  are generated from  $\mathbf{1}^{Ad}$ , the kinetics of this reaction were monitored by both  $^1\text{H}$  and  $^{31}\text{P}$  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,  $\mathbf{1}'$ , displays three  $^{31}\text{P}$  environments and two  $^t\text{Bu}$  environments of the anilide ligands in its NMR spectra. The  $^{31}\text{P}$  resonances are a triplet ( $J_{\text{PP}} = 175$  Hz) at -4 ppm and two broad resonances at -28 and -37 ppm. By introducing a  $^{13}\text{C}$  label at the acyl carbon, C1, it was determined that in  $\mathbf{1}'$ , C1 is attached only to the one phosphorus with a chemical shift of -4 ppm ( $J_{\text{CP}} = 108$  Hz). Additionally, the  $^{13}\text{C}$  chemical shift for C1 in  $\mathbf{1}'$  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,<sup>[41]</sup> leading to the proposed structure for  $\mathbf{1}'$  that is shown in Scheme 2.

From  $\mathbf{1}'$  one can envision attack by one of the niobium bound phosphorus atoms on the Lewis acid-activated carbonyl to give  $\mathbf{1}''$  with a structure that is poised to eliminate the triphosphacyclobutadiene  $\mathbf{3}^{Ad}$  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 spiro[2.4]hepta-4,6-diene.

The decay of starting material **1<sup>Ad</sup>** follows first-order exponential behavior, but the ratios of species **1<sup>Ad</sup>**, **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  $4\pi$  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 tetraphosphabenzene. 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.<sup>[30, 42, 43]</sup>

## 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 in cif files available from the CCDC under deposition numbers 700883-700887.<sup>[44]</sup>

**6:** Solid red **1<sup>Ad</sup>** (195 mg, 0.125 mmol, 1 eq) was dissolved in 2 g of a 14 wt% THF solution of spiro[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 time 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). <sup>31</sup>P NMR ( $C_6D_6$ , 20 °C, 121.5 MHz):  $\delta$  = 295.4 (dd,  $^1J_{PP}$  = 125 Hz,  $^2J_{PP}$  = 28 Hz,  $J_{PW}$  = 240 Hz, C=P), 3.0 (dd,  $^1J_{PP}$  = 156 Hz,  $^2J_{PP}$  = 28 Hz, C=P-P-P), -24.9 (dd,  $^1J_{PP}$  = 156 Hz,  $^1J_{PP}$  = 125 Hz,  $J_{PW}$  = 210 Hz, C=P-P-P) ppm.

**7:** Solid red **1<sup>Ad</sup>** (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 time the orange mixture was filtered through Celite and evaporated to dryness. Niobium oxo **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). <sup>31</sup>P NMR ( $C_6D_6$ , 20 °C, 202.5 MHz):  $\delta$  = 248.3 (m, C=P, 2P), -13.3 (m, P-P, 2P) ppm.

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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<sup>R</sup>**. One of several possible linkage isomers of **3<sup>R</sup>** 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-P4 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<sup>Ad</sup>** proceeding through the observed intermediate **1'**.

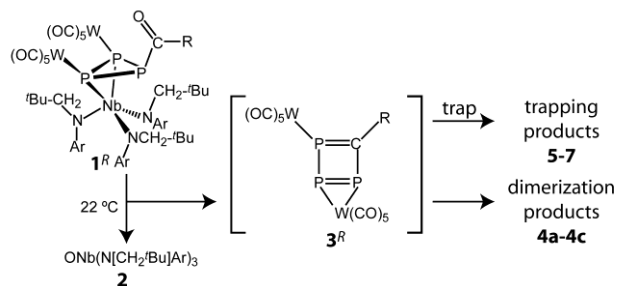
**Scheme 3.** Kinetic scheme (b) provides a better fit to the time-dependent concentrations of **1<sup>Ad</sup>**, **1'** and **2** than does the simpler model (a).

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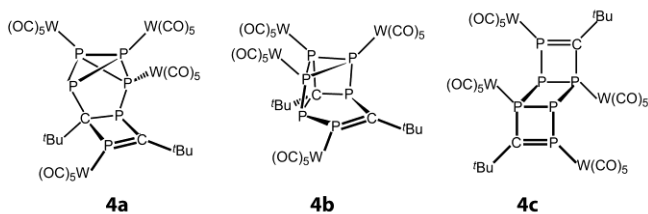
The O-atom of an acyl triphosphirene ligand is transferred to the Nb platform upon which it was constructed to liberate the putative triphosphacyclobutadiene intermediate  $RCP_3[W(CO)_5]_2$ . This reactive transient is shown to dimerize and engage in [2+4]-cycloaddition reactions with an organic diene and a phosphalkyne. 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

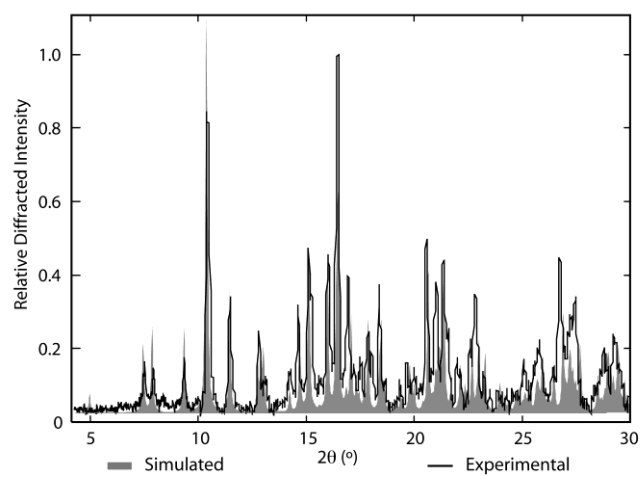
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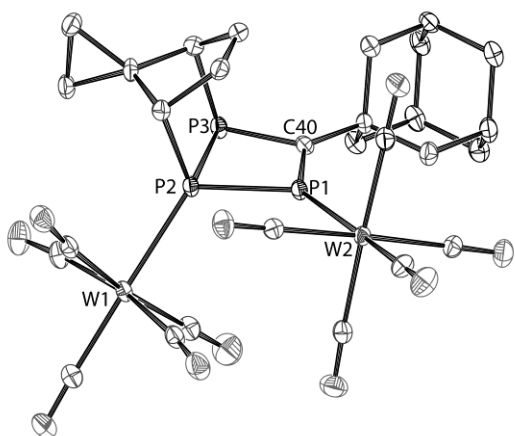
### Chart 1:



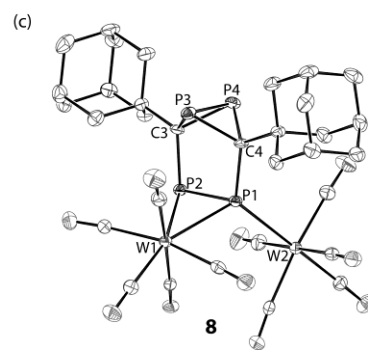
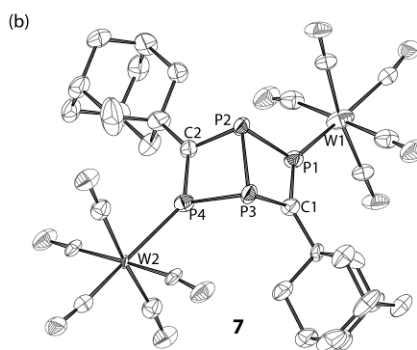
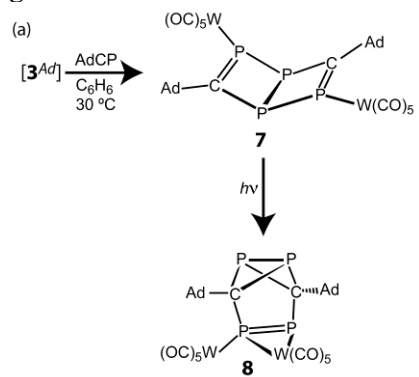
**Figure 1:**



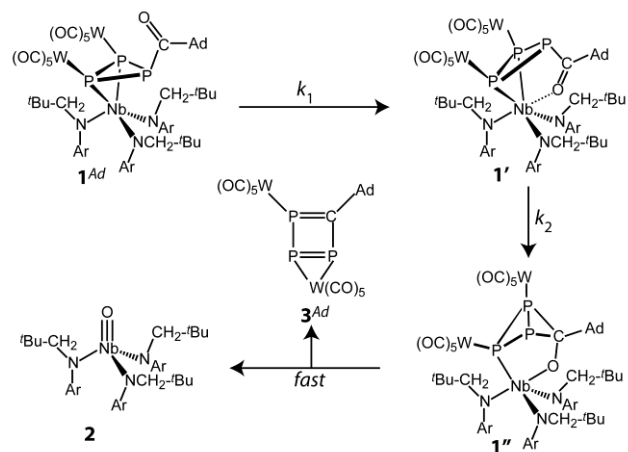
**Figure 2:**



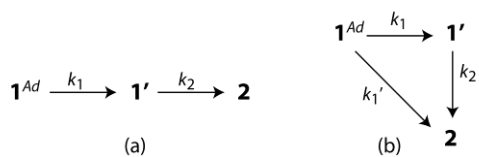
**Figure 3:**



### Scheme 2:



### Scheme 3:



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