

Senior Honors Project Proposal

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Exploring Diphosphene Synthesis with Trimethylsilicated and Imidazolidine Reductants

The following proposal is a description of the chemistry behind double bonded phosphorous atoms, or diphosphenes, as well as the research I conducted on them. My main area of interest was to create a diphosphene molecule using various methods of synthesis. I studied three different reactions using various reducing agents to try and create the molecule in question, however, none of them successful. I performed all of the research this past summer, 2013, at Case Western Reserve University with Dr. John Protasiewicz as the principal investigator.

Various reducing agents were tested to try and find a new way to synthesize the diphosphene $\text{DmpP}=\text{PDmp}$ (Dmp = 2,6-dimesitylphenyl).

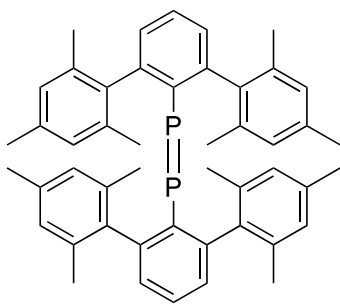


Figure 1: $\text{DmpP}=\text{PDmp}$

The reducing agents tested were an organosilicon-based compound, 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD), 3,6-

bis(trimethylsilyl)1,4-cyclohexadiene (BTCD), and 1,3,1',3'-tetraethyl-bis(2,2'-imidazolidine).

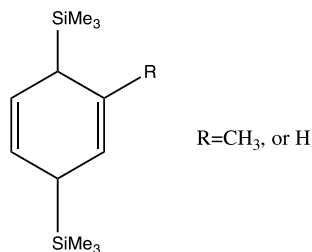


Figure 2: MBTCD, R= CH₃ and BTCD, R=H

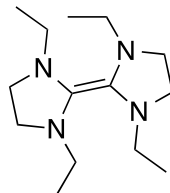


Figure 3: 1,3,1',3'-tetraethyl-bis(2,2'-imidazolidine).

Through the use of dimesitylphenyl phosphorous dichloride (DmpPCl₂), it is thought that the chemistry exhibited by these reducing agents on similar compounds could be applied to compounds with PCl₂ groups, such as DmpPCl₂, in the hopes of creating the diphosphene DmpP=PDmp.

Compounds with double bonds between phosphorous atoms, or diphosphenes, are molecules that have been of great interest as examples of compounds with multiple bonds between main group elements. These molecules have been studied extensively to further elucidate the complex chemistry with phosphorous and have been synthesized using various methods. Diphosphenes are unstable due to the small π -bond energy *ca.* 34 kcal mol⁻¹ compared to N-N π -bond energy of 94 kcal mol⁻¹.¹ As nitrogen and phosphorous are both Group 15 elements, it would be expected that they would have similar π -bonding properties. However, the lower bond energy makes for a less stable molecule, compared to those with

¹ Power, P. Homonuclear multiple bonding in heavier main group elements. *J. Chem. Soc. Dalton Trans.* **1998**, 2939-2951.

nitrogen double bonds. Despite the less stable π -bond, it has been shown that having a large protective bulky group can stabilize these low coordinated organophosphorous compounds.² The lower stability of the phosphorous π -bond is due to the large overlap of the orbitals compared to those seen in nitrogen. This overlap causes instability and in turn make is more energetically favorable for phosphorous atoms to make single bonds, as opposed to double bonds. The bond length between diphosphenes of 1.985\AA ³ is smaller compared to the bond length between single P-P bonds of 2.22\AA . This shorter bond length, due to π -bond formation as well as changes in the σ -hybridization,¹ is commonly seen between single and double bonds. It is unusual that this shorter π -bond between phosphorous atoms is less stable compared to the single bond between phosphorous atoms. As mentioned above, the large overlap in orbitals explains this strange occurrence and the sterically bulky groups are necessary to protect the double bond from degradation to a single bond.

Previous successful attempts at creating diphosphenes have been performed by reducing DmpPCl_2 . Dimesitylphenyl, as seen in Figure 4 below, has been the most successful sterically bulky group to produce diphosphenes, such as $\text{DmpP}=\text{PDmp}$.³

² Yoshifuji, M. Coordination chemistry of some low-coordinate organophosphorus compounds. *Pure Appl. Chem.* **1999**, 71, 503-512.

³ E. Urnezius, J.D. Protasiewicz. *Main Group Chem.*, 1 (1996)

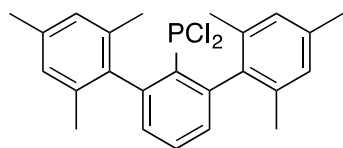


Figure 4: DmpPCl₂

The diphosphene DmpP=PDmp, was first successfully synthesized using activated magnesium as a way to reduce the DmpPCl₂ without creating phosphorous centered radicals in the process. Creating phosphorous centered radicals is one way to obtain diphosphenes, however, other side products also include cyclooligomers of phosphinidenes in Figure 5. As the cyclooligomers are not of interest, a method to produce diphosphenes without them is being sought. When reducing DmpPCl₂ with activated magnesium, the reaction occurs very rapidly, and the DmpP=PDmp was successfully created. There were, however, other cyclometallated species, shown in Figure 6, that formed as well. Where a double bond should have occurred within the molecule, a ring structure was observed. ⁴

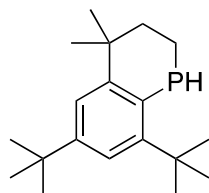


Figure 5: Cyclooligomer of Phosphinidene⁴

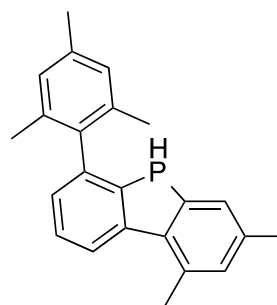


Figure 6: Cyclometallated Species⁴

⁴ Rhett C. Smith, Shashin Shah, John D. Protasiewicz. Journal of Organometallic Chemistry, 646, (2002) p. 255–261

Finding other ways to create $\text{DmpP}=\text{PDmp}$, without the side products that have been previously observed using different reducing agents, has been the main topic of this research.

The organosilicon-based reductant, 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD) and 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (BTCD) are shown in Figure 2 above. It was found by Arteaga-Müller et al.⁵ that both MBTCD and BTCD were successful in producing linear α -olefins through a catalytic system that involves the salt-free reduction of TaCl_5 with these two compounds in the presence of ethylene. This catalytic system produces 2 equivalents of Me_3SiCl , $\text{C}_6\text{H}_5\text{R}$, ($\text{R}=\text{CH}_3$ or H) and Ta(III) species active for ethylene trimerization. This is important as it shows that MBTCD and BTCD are able to successfully reduce chloride compounds and abstract the chloride atoms, as is the goal with the reduction of DmpPCl_2 . These two reducing agents were also shown to generate low-valent niobium species, Nb(III). This was done by reduction of NbCl_5 with BTCD in the presence of 3-hexyne. This reduction led to the formation of a 3-hexyne complex of $\text{NbCl}_3\text{-(3-hexyne)(DME)}$.⁵

It was also shown by Tsurugi et al, that MBTCD could successfully reduce TaCl_5 in the presence of α -diimine ligands to lower valent tantalum complexes having redox-active α -diimine ligands. The following tantalum complexes that were

⁵ Rocío Arteaga-Müller., New Tantalum Ligand-Free Catalyst System for Highly Selective Trimerization of Ethylene Affording 1-Hexene: New Evidence of a Metallacycle Mechanism. *JACS*. **2009**, 131, 5370-5371.

created using MBTCD as a reductant show that MBTCD is a useful reductant to abstract chloride atoms and create compounds with sterically bulky groups.⁶

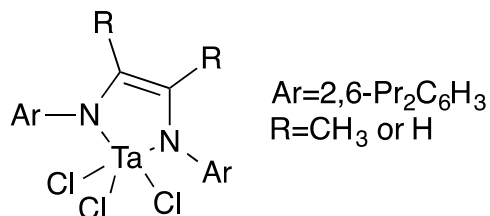


Figure 7: Tantalum complex formed from MBTCD⁶

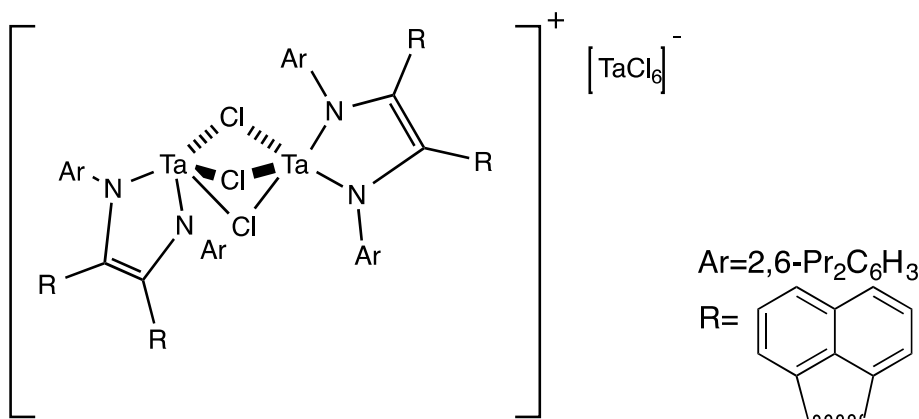


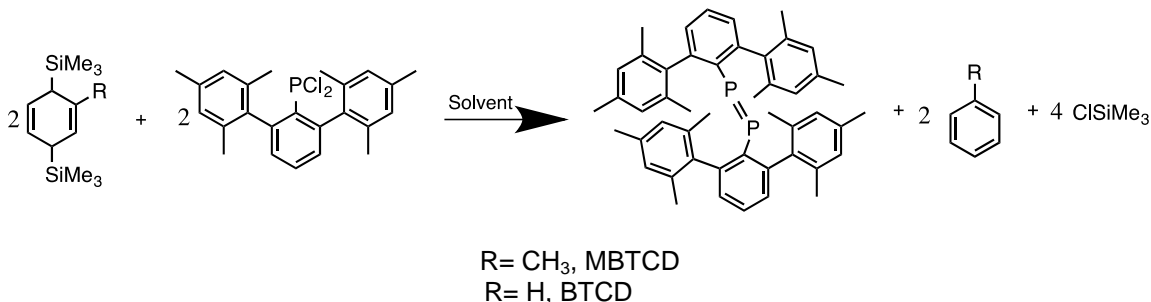
Figure 8: Second Tantalum complex formed from MBTCD⁶

Figures 7 and 8 show the five coordinate tantalum complexes that were formed with MBTCD. These complexes help show that MBTCD is a promising reagent to reduce phosphorous molecules containing sterically bulky groups with halides like DmpPCl_2 . MBTCD was also shown to successfully reduce WCl_6 in a salt free environment.⁷ MBTCD was again used to create large complexes but instead with a

⁶ Tsurugi, H., Carbon Radical Generation by d^0 Tantalum Complexes with α -Diimine Ligands through Ligand-Centered Redox Processes. *JACS*. **2011**, 133, 18673-18683.

⁷ Tsurugi, H, Tanahashi, H. Salt-Free Reducing Reagent of Bis(trimethylsilyl)cyclohexadiene mediates, Multielectron Reduction of Chloride Complexes of W (VI) and W(IV). 2013.

tungsten center. It was hoped that this could be applied to DmpPCl_2 in creating diphosphenes in the following way:

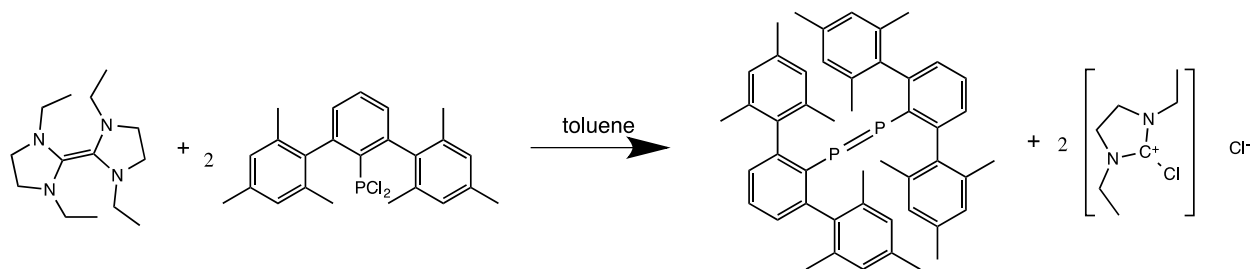


Scheme 1: Proposed reduction of DmpPCl_2 using trimethylsilylated cyclohexadienes

Scheme 1 depicts the proposed reaction for either MBTCD or BTCD with DmpPCl_2 . The other reducing agent shown above is BTCD, this compound is very similar to MBTCD except there is a hydrogen atom on the designated R instead of a methyl group (CH_3). This compound was explored as another potential reducing agent due to the similar properties that it shares with MBTCD.

A second reducing agent, 1,3,1'3'-Tetraethyl-bis(2,2'-imidazolidene), which is a mild homogenous reducer of P-Cl bonds was also of interest to create $\text{DmpP}=\text{PDmp}$. This mild reducing agent has been shown to successfully reduce P-Cl bonds in phosphonous or phosphinous chlorides to yield compounds that have phosphorous-phosphorous bonds. It was shown to successfully reduce

diarylphosphinous chlorides to tetra-aryldiphosphines faster than with metal reducing agents.⁸ The proposed reaction is as follows:



Scheme 2: Proposed reduction of DmpPCL₂ via bis-imidazolidine

I completed all of the necessary laboratory research this past summer at Case Western Reserve University with Dr. John Protasiewicz as the principal investigator on this project. During this semester I will continue with my research in a literature context. I will continue researching to determine the rationale as to why the proposed project was not successful. I plan on presenting a poster of my research at the Celebration of Scholarship in the spring and will finish a formal report of all of my findings through laboratory and literature research.

This research project has helped me realize that upon graduation from John Carroll University, I want to continue on to graduate school and obtain a doctorate in the field of chemistry. As far as what particular area of chemistry that will be in, I am not completely certain yet. However, organic synthesis and organo-metallic chemistry are two areas that I might want to pursue. This research project has given me insight on what typical research is like in graduate school. I was able to learn what other types of research are being actively pursued in various fields just

⁸ Goldwhite, H. Kaminski, J. et al. Phosphorous-phosphorous single or double bond formation from PCl_{3-n} R_n (n=1 or 2) and a bis-imidazolidine reducing agent. **1986**, 310, 21-25.

by being around other graduate students at Case. It was very insightful and helpful for me in deciding that graduate school is a path that I want to take.

Bibliography*

- Denk, Michael. Steric Stabilization of Nucleophilic Carbenes. *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2607-2608.
- Goldwhite, H. Kaminski, J. et al. Phosphorous-phosphorous single of double bond formation from $\text{PCl}_{3-n} \text{R}_n$ ($n=1$ or 2) and a bis-imidazolidine reducing agent. **1986**, 310, 21-25.
- Laguerre, Michael, Duogues, Jaques. Silylation D'Hydrocarbures mono-aromatiques mono-ou disubstitutes. *Journal of Organometallic Chemistry*, **1976**, 12, 49-59.
- Power, P. Homonuclear multiple bonding in heavier main group elements. *J. Chem. Soc. Dalton Trans.* **1998**, 2939-2951.
- Rhett C. Smith, Shashin Shah, John D. Protasiewicz. *Journal of Organometallic Chemistry*, 646, (2002) p. 255-261
- Rocío Arteaga-Müller., New Tantalum Ligand-Free Catalyst System for Highly Selective Trimerization of Ethylene Affording 1-Hexene: New Evidence of a Metallacycle Mechanism. *JACS.* **2009**, 131, 5370-5371.
- Tsurugi, Hayato. Saito, Teruhiko. Carbon Radical Generation by d^0 Tantalum Complexes with α -Diimine Ligands through Ligand-Centered Redox Processes. *JACS.* **2011**, 133, 18673-18683.
- Tsurugi, H, Tanahashi, H. Salt-Free Reducing Reagent of Bis(trimethylsilyl)cyclohexadiene mediates, Multielectron Reduction of Chloride Complexes of W (VI) and W(IV). 2013.
- E. Urnezis, J.D. Protasiewicz. *Main Group Chem.*, 1 (1996)
- Weyenberg, D. R. Toporcer, L, H. The Synthesis of 3-6-Disilyl-1,4-cyclohexadienes by the trapping of benzene anion-radicals. **1962**, 84, 2843-2844.
- Yoshifuji, M. Coordination chemistry of some low-coordinate organophosphorus compounds. *Pure Appl. Chem.* **1999**, 71, 503-512.

*Additional resources will be found through literature research

Proposed Time Line

Research Already Complete

Finish Proposal- Jan 27

First Draft of Paper- Feb 3

Meet With Advisor- Feb 5

Second Draft of Paper- Feb 10

Meet With Advisor- Feb 12

Third Draft of Paper- Feb 17

Meet With Advisor- Feb 15

Celebration of Scholarship-May 2014