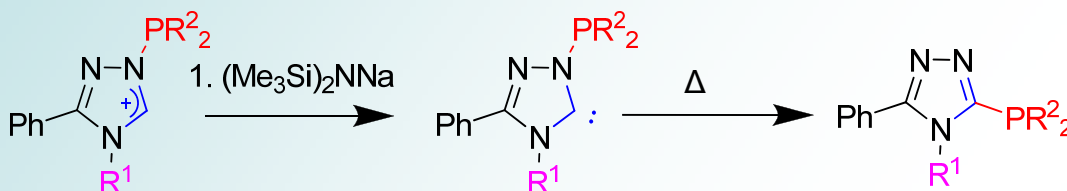




Stable N-phosphorylated triazol-5-ylidenes

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NHCs have established themselves as versatile and powerful ligands for homogeneous catalysis. Although carbenes based on the 1,2,4-triazole ring have received little attention, some promising results have been achieved. The most famous among triazol-ylidenes are 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (TPT) and 1,2,4-trimethyltriazole-3,5-diyldene, (ditz).

Considering versatility of NHCs as ligands it is of importance to develop new approaches to synthesis of NHCs and investigate them as the intermediates of reactions.

The "carbene" mechanism of the reaction of 1-alkylimidazoles with phosphorus (III) halides was experimentally proved by us earlier. It was found that unstable halides of N-phosphorylated imidazoles emerge in the beginning. Triflate analogs of such salts appeared to be stable and were isolated. Under treatment with strong base the latter give stable N-phosphorylated and N,N'-diphosphorylated imidazol-2-ylidenes, which were also isolated and characterized. Imidazol-2-ylidenes obtained rearrange to 2-phosphorylated imidazoles under heating.

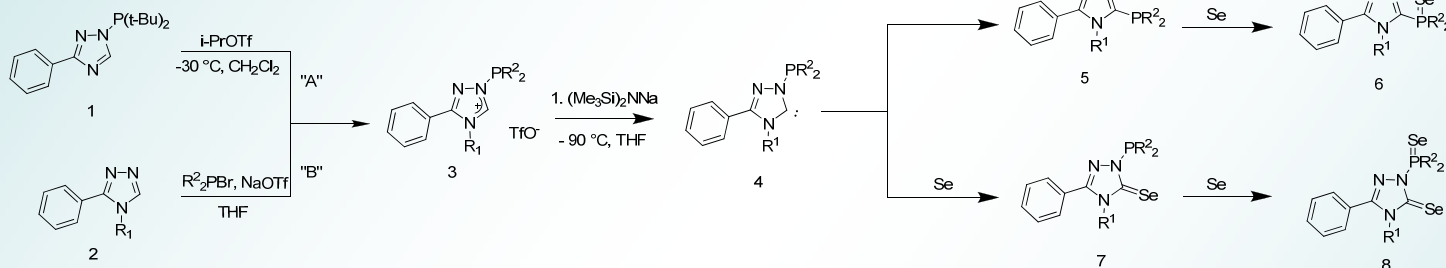
Considering probable generality of "carbene" mechanism for 1,3-azoles, investigation of intermediates of phosphorylation of 1,2,4-triazoles is of interest.

Continuing our study on mechanism of phosphorylation of nitrogen-containing heterocycles we report on our results of phosphorylation of trizoles and synthesis of new type of chelating ligands bearing two coordination sites – carbene and trivalent phosphorus.

The desired triazolium salts **3** were obtained by two routes – N-alkylation of N-phosphorylated triazole **1**, or phosphorylation of 4-alkyltriazoles **2**.

Salts **3** react with sodium bis(trimethylsilyl)amide in THF forming N-phosphorylated triazolylidenes **4**, which were isolated and characterized. They represent crystalline compounds sensitive to atmospheric air.

Compounds **4** do not show H5 signal at $\delta \sim 10$ ppm in the ¹H NMR spectra. In ¹³C NMR spectra highly deshielded signal, characteristic for carbene centre, emerges at $\delta \sim 220$ ppm. This peak appears in the range typical for non-phosphorylated (205 – 220 ppm) and N-phosphorylated (219 – 224 ppm) imidazol-2-ylidenes. However, carbene atoms of compounds **4** have the most downfield shift among known triazole-5-ylidenes (201 – 214 ppm).



A single crystal of representative carbene **4**, suitable for X-ray diffractational analysis, was grown from pentane. Triazole ring parameters are in the range typical for NHCs. Planes of C₂-phenyl and triazole rings make up angle of ca 60°, twice as large as in the case of known triazol-5-ylidenes (ca 30°). Steric hindrance causes *iso*-propyl and di-*tert*-butylphosphino groups to twist out as well.

As is already known, non-phosphorylated triazol-5-ylidenes often dimerize slowly at room temperature to give entetramines. However, such dimerization was not observed in case of carbenes **4** because of availability of more preferential path – rearrangement to 3-phosphorylated triazoles **5**. This rearrangement indirectly evidences for carbene-mediated mechanism of interaction of 1,2,4-triazoles with phosphorus (III) halides.

It is significant that N-phosphorylated triazole-5-ylidenes are less stable than corresponding N-phosphorylated imidazole-2-ylidenes.

3-Phosphorylated triazoles **5** were transformed to selenium derivatives **6**.

As in the case of most NHCs, compounds **4** add selenium to divalent carbon, forming selenones **7**. Oxidation of phosphorus atom with Se takes place under prolonged (15 – 120 h.) treatment of selenones **7** with Se.

Because of existence of two possible complexation sites per molecule of carbene of type **4**, it was of particular interest to us to study structure of complexes between carbenes **4** and transition metals. Such air-stable silver(I) complexes were obtained by reaction of silver oxide with 2 eq. of **4** in dichloromethane. After workup, complexes were isolated as highly thermally stable white crystals.

Molecular structure of representative complex was determined by means of single-crystal X-ray diffractational analysis. It represents dinuclear complex with angle C–Ag–P of ca. 168°. Ag–C and Ag–P bond lengths are in agreement with those of other silver(I) bis- or monocarbene and phosphine complexes previously reported. Triazole rings are planar, silver atoms and adjacent phosphorus atom all lay in the same plane.

In conclusion, synthetic routes to N-phosphorylated triazole triflates were developed. It was shown that obtained triazolium salts react with strong base forming N-phosphorylated triazol-5-ylidenes, which rearrange to C-phosphorylated triazoles under heating. Triazolium salts react with silver(I) oxide to give novel and highly stable dinuclear phosphinocarbene complexes.

