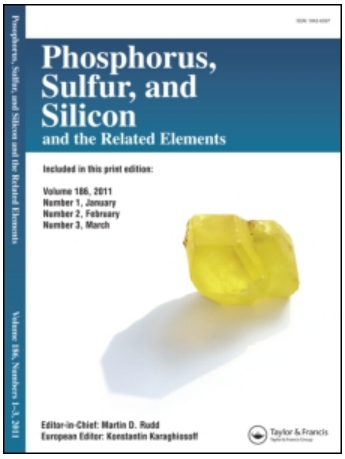

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Cyclometallaphosphazenes - Synthetic and Structural Investigation of a New Class of Heterocyclic Compounds

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CYCLOMETALLAPHOSPHAZENES - SYNTHETIC AND STRUCTURAL INVESTIGATION OF A NEW CLASS OF HETEROCYCLIC COMPOUNDS

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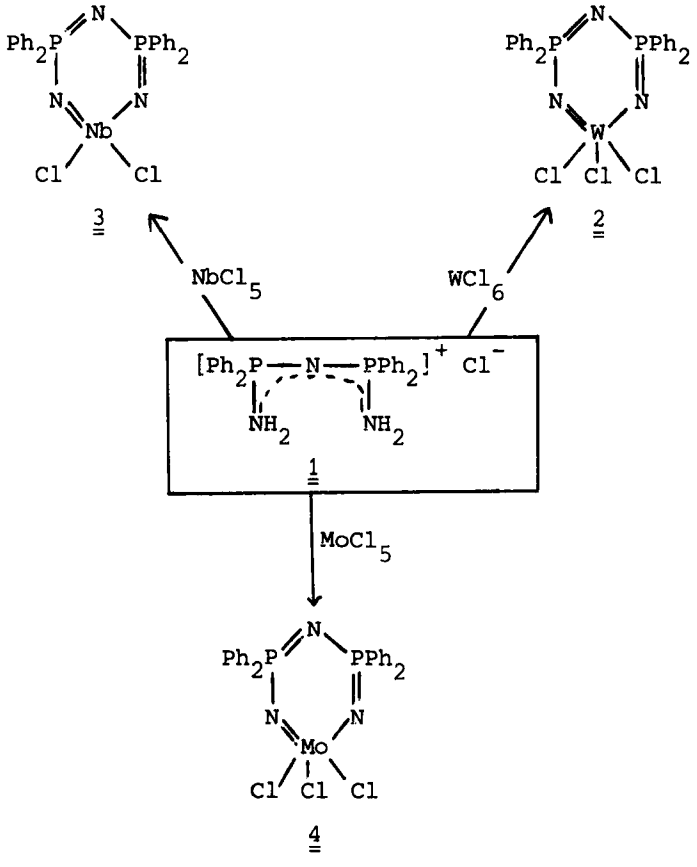
Abstract A new class of inorganic heterocyclic compounds, cyclometallaphosphazenes, has been prepared by treating the linear phosphazene salt, $[H_2NPPh_2NPPh_2NH_2]^+ Cl^-$, with transition metal halides. An alternative route to synthesise these cyclometallaphosphazenes has also been investigated, which involves the reaction of the linear phosphazene salt with metal nitride chloride. The compounds are characterized by NMR investigations and mass spectrometry. The structure of the cyclometallaphosphazenes containing W and Mo are confirmed by X-ray structure analysis.

Our investigations to be presented here have their origin from our detailed studies on sulfur-nitrogen ring compounds : The insertion of phosphorus in the S_4N_4 ring[1], the incorporation of W, V and Mo in the same ring system through oxidative addition reactions across the S-N bond.[2] With this success on the S-N ring compounds, we turned our attention to realize the incorporation of transition metals in the P-N ring compounds in general and, particularly, in phosphazene rings. Although, several classes of phosphazenes, including those that contain transition metal organometallic units in the side-chains are known[3], upto now there are no examples of compounds which contain transition metals directly in the phosphazene ring. We report here the synthesis and structure of the first phosphazene derivative containing transition metal in the ring.

Our synthetic approach was inspired by the ability of the Bezman salt, $[H_2NPPh_2NPPh_2NH_2]^+ Cl^-$, to produce different cyclophosphazene derivatives in its reactions with phosphorus halides.[4] We have treated this linear phosphazene salt with the halides of W, Mo

and Nb in chloroform to obtain the hitherto unknown cyclometallaphosphazenes as shown in scheme 1.[5]

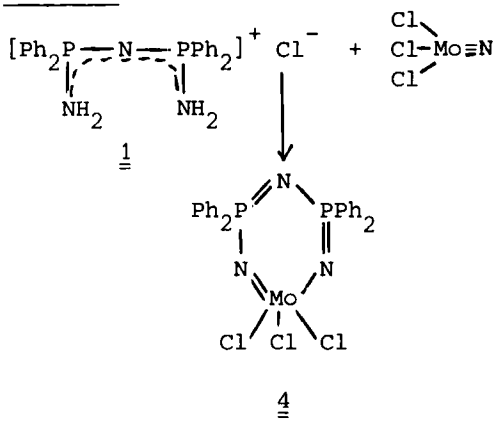
SCHEME 1



The reactions of WCl_6 and $NbCl_5$ produce good yields of the metal incorporated phosphazenes whereas $MoCl_5$ gives a mixture of products as evidenced by ^{31}P nmr spectroscopy. This is probably a consequence of prior dissociation of $MoCl_5$ to $MoCl_4^+$ and $MoCl_6^-$ followed by substitution.

We have developed an alternative elegant route to obtain compound 4 in good yields as shown in scheme 2.

SCHEME 2



All compounds have been characterized by nmr spectroscopy and mass spectrometry. The structures of compounds 2 and 4 have been confirmed by X-ray structure analysis.

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