

Cyclometallaphosphazenes: A New Family of Inorganic Heterocycles

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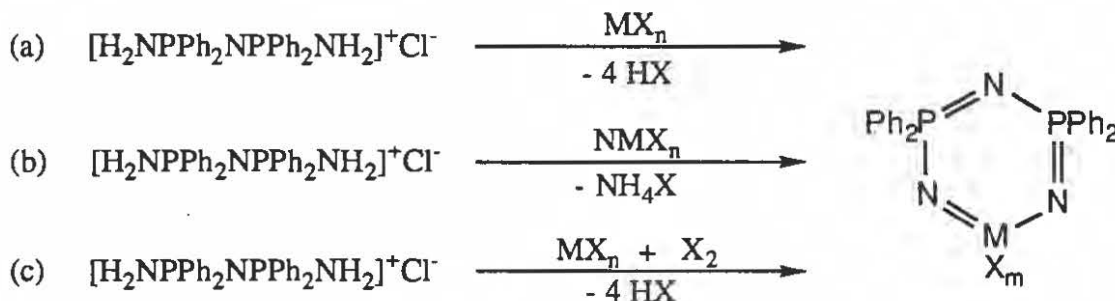
Phosphazene compounds were discovered in 1834 by Liebig and Wohler when they isolated a small amount of hexachlorotriphosphazene, $(\text{NPCl}_2)_3$, from the reaction of phosphorus pentachloride with ammonia [1]. Schenk and Romer improved this synthesis in 1924 [2] and, even today, their method remains the basis of commercial production of these materials [3]. The overall reaction scheme is



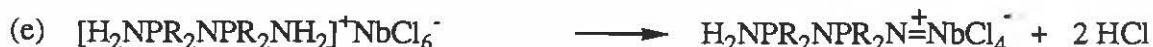
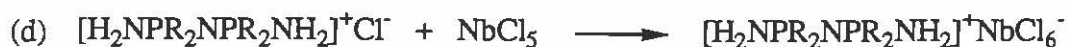
An important characteristic of the phosphazene polymer system is the ease with which the properties can be modified by the introduction of different substituent groups. Phosphazene polymers modified in this way have a number of unusual properties and show promise as plastics and sealants which remain flexible at very low temperatures, as outdoor surface and wire coatings which are highly resistant to visible and ultraviolet radiation, or as seals and gaskets in fuel delivery systems which demand materials resistant to chemical or solvent attack [3].

Although cyclic, trimeric phosphazenes have been known for over 150 years, only those derivatives with substituents on the ring, metal complexes of cyclophosphazenes, or phosphazene polymers have been synthesized [3,4]. The synthesis of cyclophosphazenes containing transition metals as part of the ring skeleton was unexplored until recently [5]. Aside from their novel structural chemistry, such cyclometallaphosphazenes are of interest as precursors to transition metal containing phosphazene polymers [5,6].

The most popular synthetic approach was inspired by the ring closure reactions of the linear phosphazene salt $[\text{H}_2\text{NPPh}_2\text{NPPh}_2\text{NH}_2]^+\text{Cl}^-$ with phosphorus (V) halides [7]. The synthesis of cyclometallaphosphazenes utilizes transition metal halides in place of phosphorus (V) halides. The reaction of the phosphazene salt with metal halides or metal nitride halides (methods a,b) works well for metal precursors in their highest oxidation state. For other metal halides, the reaction requires the introduction of the appropriate halogen into solutions containing lower metal halides (c) [5,6,8-10].



Evidence for the mechanism of cyclometallaphosphazene formation comes from the isolation of hexachlorometallates, and an acyclic unsymmetrically substituted intermediate (eqns. d,e) [6, 11]. Monitoring the reactions by $^{31}\text{P}\{^1\text{H}\}$ NMR shows the appearance of a pair of doublets, indicating unsymmetric acyclic compounds, disappearing with the growth of a singlet corresponding to the cyclic phosphazene (eqn. f) [6].



Other cyclometallaphosphazenes have been prepared by the reaction of an acyclic silylated phosphazene with a high valent metal [12-16]. A variety of metallaphosphazenes can be synthesized by this method, including a volatile vanadium-containing cyclophosphazene, homo- and heterobimetallic cyclophosphazenes, and cyclometallaphosphazenes with carbon incorporated into the ring.

Recently, Roesky et al. have succeeded in preparing the first polymetallaphosphazenes [17]. These polymers are obtained via the thermal ring opening reaction of $N_3(PPh_2)_2MCl_3$, ($M = Mo, W$). The THF-soluble portions of each polymer were fractionated by HPLC and the molecular weight distributions determined by comparison with polystyrene calibration standards. The viscosity average molecular weights, M_v , were determined from viscosity measurements to be 24,000 and 37,000, respectively. In contrast to their precursors, both polymers are virtually inert towards hydrolysis, even in boiling water, and they do not decompose below 300 °C [17].

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